
D C I E C H A Ń S K A, Institute of Chemical Fibres, Poland
and P N O U S I A I N E N, Tampere University of
Technology, Finland

4.1 Introduction

In order to evaluate sustainability of products and processes, the life cycle assessment (LCA) concept is a method for industry to understand, manage and reduce the environmental, health and resource consumption impacts associated with processes, products and activities.^{1,2} Due to the well-known environmental impacts of cotton and its further chemical processing, LCA evaluations have been used to develop the sustainability of man-made fibres, as well.³ In the case of cellulosic fibres based on cellulose polymers produced by photosynthesis, biodegradability can be seen as a benefit to fit the criteria of sustainability.

Recently, biotechnological methods of wood and pulp processing, polymer synthesis, biodegradation and biological transformation have been widely introduced into industry.⁴ Mechanical and chemo-mechanical methods have been increasingly replaced by chemical sulphate (Kraft) and sulphite pulping methods for raw materials of paper and cardboard.⁵ Enzyme technology has been successfully applied in the pulp and paper industries: the production of dissolving pulp, bleaching de-inking, removal of slime, removal of pitch, removal of shives, debarking, and retting of flax fibres can be done with enzymes.⁶ This trend is justified by numerous benefits resulting from the application of biotechnology, such as mild conditions of technological processes, low energy consumption, high safety, low amounts of by-products, renewable raw materials, economic aspects and others. The further development of enzymes in bio-processing of new applications and improved characteristics is based increasingly on gene isolation and transplantation technology.^{7,8}

Nowadays, the biotechnological processing of pulps using selected types of enzymes seems to be a promising method for the production of the cellulosic products. For modification of pulps the cellulase and xylanase extracted by submerged fermentation from fungi strains such as *Aspergillus niger* and *Trichoderma reesei* have been applied.^{9,10} The modification of molecular, supermolecular and morphological structure occurring during enzymatic

reaction has definitely improved the cellulose properties, i.e. solubility in alkaline solutions up to 100% (Celsol process), solubility in organic solvents (NMMO process) and chemical reactivity towards reactants.¹¹

Methods of biological utilisation of polyester/cellulose textile blends are based exclusively on the application of cellulolytic enzymes, like cellulases, catalysing the hydrolytic degradation of cellulose to a sugar mixture like glucose or cellobiose. The recovered polyester components were tested to be recycled in the melt process.¹²

Microbial synthesis of cellulosic fibres affords the opportunity of obtaining products with unique properties suitable for practical application in medicine and the electronics industry. For synthesis of modified bacterial cellulose, the *Acetobacter subsp.* strains have been applied. The selection of suitable polyaminosaccharide modifiers allows the production of bacterial cellulose characterised by valuable mechanical, electro-acoustic and biological properties. Practical applications of this cellulosic composite material for manufacture of novel wound-healing dressings as well as diaphragms for loudspeakers have been tested.¹³

Enzyme treatments of textiles, typically cellulose materials such as cotton, viscose or lyocell fabrics, have widely been used in the textile industry since the 1980s. There are some of advantages resulting from the use of enzymes for finishing cellulosic fibres and fabrics, i.e. smooth surface, better appearance, anti-pilling properties, soft and delicate feel, improved watability and dyeability.¹⁴ Enzymatic treatment of cotton in denim washing or other biopolishing is standard technique in industry. Various cellulases, e.g. purified *T. reesei* types, have been studied and optimised in cotton bioscouring and finishing.¹⁵ Flax fibres and linen fabrics containing higher amounts of pectin lignin need synergistic mixtures of cellulases, pectinases and ligninases or special flax retting enzymes.¹⁶

4.2 Life cycle assessment (LCA)

4.2.1 General procedure

Wood processing, fibre, and textile industries are continuously facing the need to increase their knowledge of the environmental impacts associated with production of pulp, paper, fibres, and textiles. Presently, companies are more or less transferred from the prevention of local risks to environmental management strategies. In general these strategies can be understood as the companies' environmental attitudes and guidelines. The environmental strategies can be roughly divided into four levels:

1. Strategy based on environmental requirements and laws, where the company's strategy is based on observance of environmental laws and other requirements.

2. Strategy based on preventive actions, when the company is concentrating on the prevention of environmental hazards and risks.
3. Strategy based on ecological competitiveness, when the company is improving its competitiveness by an effective use of resources and by making use of the eco-marketing possibilities.
4. Strategy based on the principles of a sustainable development. The company's environmental strategy pays attention to the social justice and to the rights of the future generation in addition to an effective ecological policy.

The first LCA attempts were carried out in the USA in the late 1960s. These assessments were only about energy requirements from 'cradle to grave' concerning package production. Later in the 1990s the development of LCA and life cycle inventory (LCI) accelerated including throughout development work on LCA methodology and its standardisation, and were applied to other industries, as well.¹⁷ Studies for cotton fibre production, textile, and laundry industries were included more thoroughly in the late 1990s.³ The general applications of LCA methodologies are often used for eco-labelling, namely a company's environmental claims on manufacturing and production stages as follows:

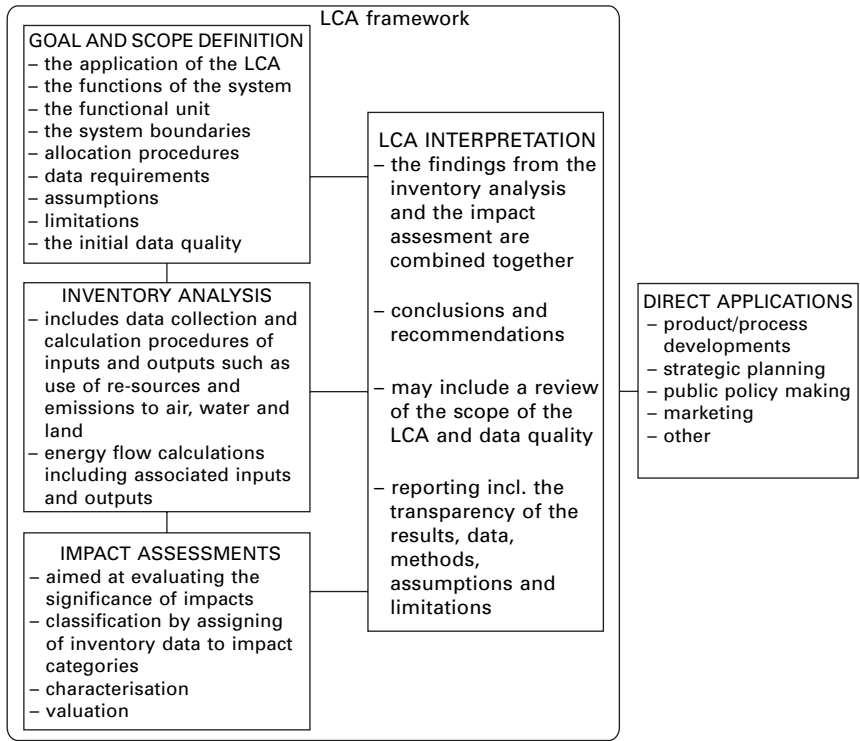
- identification of processes, ingredients and systems in order to minimise environmental impact;
- comparison of different options within product systems in order to minimise environmental impact;
- guidance in long-term strategic planning;
- evaluation of resource effects associated with particular products;
- training of product designers; and
- comparison of functionally equivalent products.

The overall scheme for LCA is presented in Fig. 4.1.

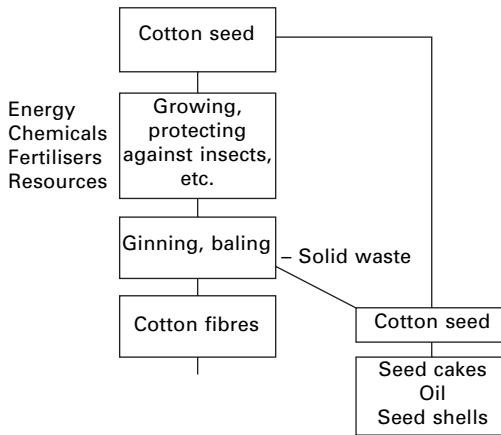
The Environmental Management and Audit Scheme (EMAS) has been standardised for the follow-up of environmental strategies, and as a tool in a company's commitment to continuous improvement of the achieved environmental status by using Best Available Technologies (BAT).

4.2.2 Life cycle assessment of cotton

The general life cycle scheme for cotton fibre is presented in Fig. 4.2. According to collected data of production for white terry sheets, the main negative impacts are related to consumption of water, use of fertilisers and pesticides, total nitrogen to waste water and, surprisingly, release of carbon dioxide during the whole life cycle.^{18,19} Because cotton is sensitive for attacks of various insects, such as boll weevil, pink ball worm, and many fungi, various pesticides and fungicides are used to improve its growth.²⁰ Thus, a high



4.1 The general overall scheme for LCA.



4.2 The life cycle scheme of cotton fibre.

share (25%) of pesticides and fungicides is used in cotton fields causing environmental problems in ground water and health problems for farmers. Gene transplantation technology is increasingly used to develop cotton species

resistant against biological attacks.²¹ However, a gene, e.g. of bacteria *Bacillus thuringiensis* controlling the production of pesticide-active protein, which is capable of destroying certain insects and some fungicides is still needed. Other methods for improving the sustainability of cotton include the organic cultivation of old species more resistant against insect attacks, lower use of fertilisers, and controlling the use of the irrigation water. The organic cultivation produces low yields of cotton and is presently not competitive with old or new types of non-organic methods.

4.2.3 Life cycle assessment of cellulosic and synthetic man-made fibres

Cellulosic fibres

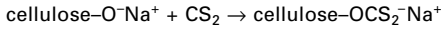
The production and manufacture of cellulosic fibres is based mainly on processing of dissolving pulp and cotton linters.^{22,23} This group of man-made fibres includes viscose, modal, cupro, lyocell and acetate as the main commercial products. Viscose has been produced by the xanthogenate method for more than 115 years. Other technologies applying the same chemical reactions of dissolving pulp with alkaline-activated carbon disulphide include modal, viscose, and polynosic fibre processing.²⁴ Compared with viscose, the modal and polynosic processes operate with cellulose of a higher alpha content (non-soluble in 18% NaOH) and degree of polymerisation (DP), lower cellulose concentration, a higher degree of filtration and chemical additives in the spinning bath, and a lower spinning speed.²⁵ Thus, the process for regular viscose fibres is more efficient regarding the consumption of raw materials. Solid waste production into water by unreacted hemicellulose and exhaust air by carbon disulphide are higher in the case of modal and polynosic, as well. All these processes have a high consumption of water due to the wet spinning, evaporating, and various fibre washing and finishing and drying stages.

The cupro and lyocell processes are based on the application of direct dissolution systems. The copper ammonia complex is prepared from copper sulphate and sodium carbonate with sodium and ammonium hydroxides, as presented in the equation in Fig. 4.3. The dissolution process is carried out for cuprammonium via weakening the intra/intermolecular hydrogen bonds and complex formation. Cupro and especially lyocell processes consume lower amounts of water, but a similar magnitude of energy.

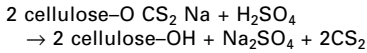
According to a novel method, enzymatic modification of cellulose by increasing the alkaline solubility enables the manufacturing of regenerated fibres without any derivative or organic solvent.²⁶ It has been proved that by using certain specific compositions of cellulolytic enzymes (a controlled ratio of endoglucanases to cellobiohydrolases) it is possible to obtain directly

A. Viscose process

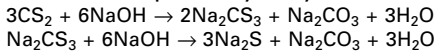
Xhantogenation



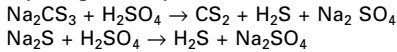
Regeneration



Carbon disulphide hydrolysis

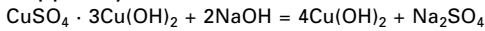


Hydrogen sulphide formation

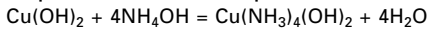


B. Cupro process

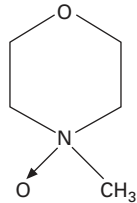
Copper hydroxide formation



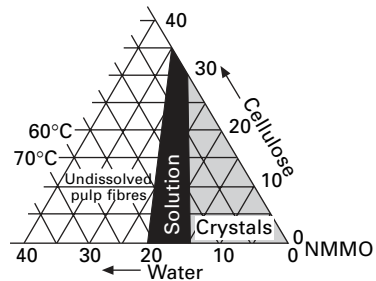
Cuprammonium complex formation



C. Lyocell process



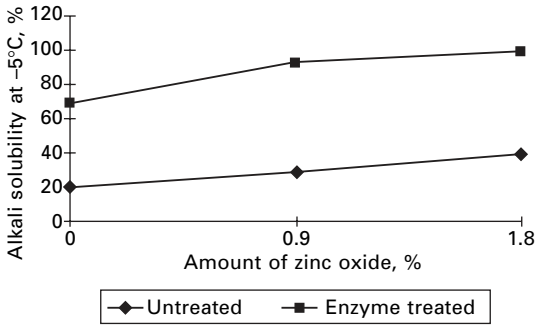
N-methylmorpholine oxide



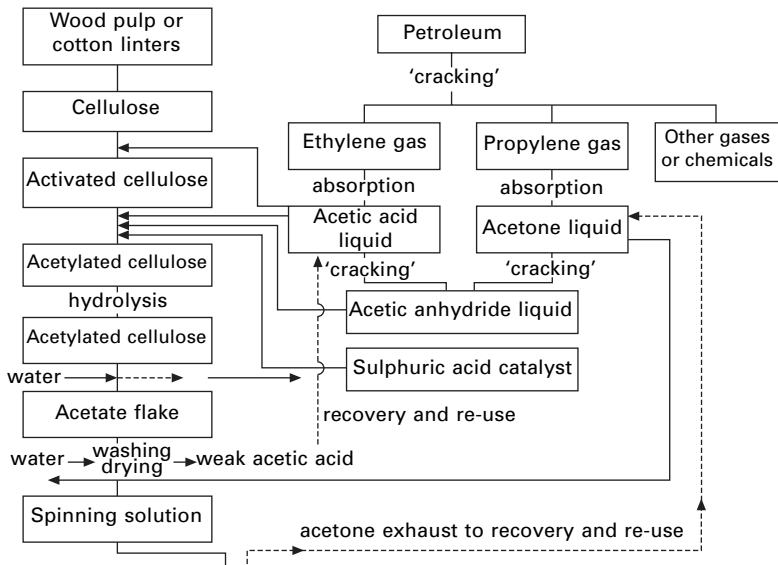
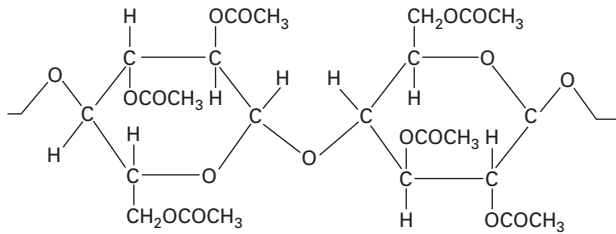
4.3 Main chemistry in viscose (A), cupro (B) and Lyocell (C) fibre processes.

alkali soluble cellulose and regenerated fibres without essential loss in DP, as shown in Fig. 4.4.²⁷ The method is further discussed in Section 4.5.1.

Cellulose secondary acetate fibres are manufactured from cotton linters by steeping in glacial acetic acid and sulphuric acid-catalysed reaction with acetic anhydride. The reaction is exothermic and the final product in a maximum of 20 hours is cellulose triacetate, which is converted to secondary acetate by adding sufficient water. The hydrolysis is stopped when 1/6 of the acetate groups have been randomly changed to hydroxyl groups. The precipitated polymer flakes are dissolved in acetone containing small amounts of water or alcohol. The chemical formula of cellulose triacetate and the diacetate fibre production chart are shown in Fig. 4.5.



4.4 The solubility of untreated and enzyme-treated pine sulphate paper grade pulps with the aid of zinc oxide.



4.5 The chemical formula of cellulose triacetate and scheme for production of cellulose diacetate.

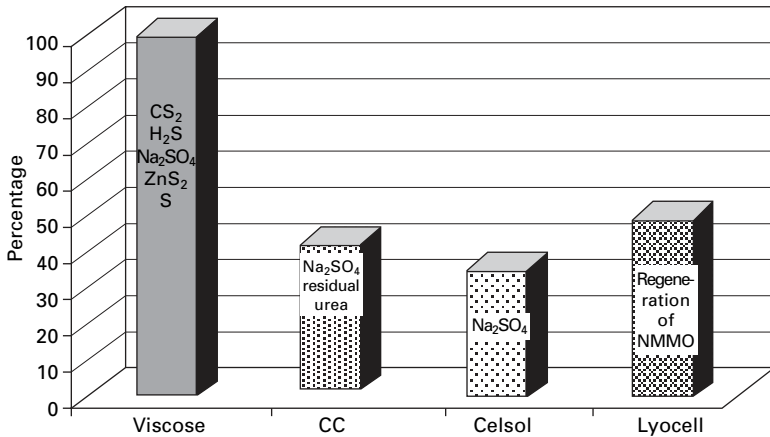
4.2.4 Properties and environmental costs of different processes of regenerated cellulosic fibres

According to a recent comparison of conventional and emerging processes, enzyme-based direct dissolving method (Celsol) and cellulose carbamate (CC) processes are capable for producing regular type regenerated cellulose fibres.²⁸ These methods, however, are either in semi-industrial stage (CC) or in pilot stage (Celsol), and further improvement of the fibre properties can be foreseen. This is evident when making comparisons with the development of viscose fibres during 100 years. Very strong fibres can be produced by the lyocell method; however, the well-known fibrillation tendency caused by highly oriented cellulose molecules demands special treatments to prevent any drawbacks in textile applications. The properties of selected regenerated cellulose fibres are presented in Table 4.1.

Table 4.1 The comparison of properties of different cellulosic fibres

Type of fibre	Titre (cN)	Tenacity (cN/tex)	Elongation (%)	WRV (%)
Viscose (regular)	1.7–3.3	15–25	15–27	50–80
CC	1.7–3.3	15–25	15–23	110–125
Celsol	1.7–3.3	~ 20	19–25	120–125
Lyocell	0.5–4.0	30–40	5–10	50–60

The life cycle assessment of regenerated cellulose fibres results in high water and energy consumption, as can be concluded from process descriptions. The recovery of regeneration cleavage products of viscose (CS₂, H₂S) and cellulose carbamate (*N*-compounds, urea) needs special units for the prevention of air and water pollution. Thus, the extra processing costs as ‘environmental costs’ are quite high, as presented in Fig. 4.6. The environmental protection processing cost distribution of the viscose process consists of active carbon recovery systems for CS₂ along the whole production line: wet spinning into sulphuric acid liquor, staple fibre web formation, alkaline sulphur removal, washing, and finishing. The formation of sodium sulphate is high due to the stoichiometry, and about 50–60% of the salt must be precipitated and purified. This is generally carried out in a separate factory, a ‘salt factory’, and sodium sulphate can be sold and utilised in the chemical industry as pulp, medicine, glass, and textile dyeing, etc. Additional conventional waste from cellulosic fibre production from dissolving pulp is the loss of 4–6% of hemicellulose based on starting pulp. Various attempts have been made in order to concentrate and separate hemicellulose (xylane) for xylitol and derived products. The processing costs are, however, too high for economic production and hemicellulose is increasingly removed in wastewater treatment plants.



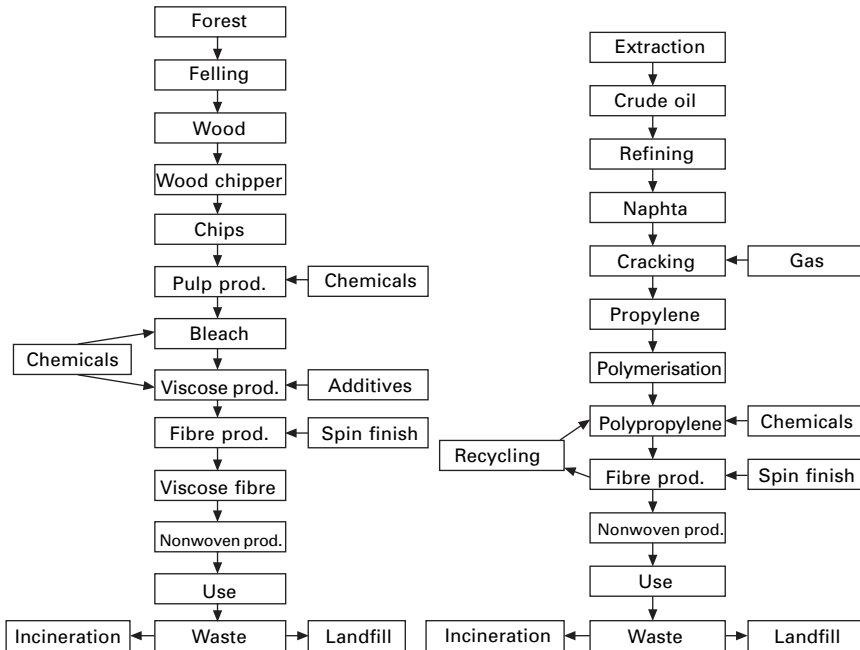
4.6 Environmental protection costs of selected processes for regenerated cellulose fibres.³²

The salt and hemicellulose formation are common in all systems based on neutralisation in viscose, modal, carbamate and Celsol processes, and to some extent in lyocell, as well. Wastewater treatment costs of hemicellulose are not included in calculations in Fig. 4.6.

4.2.5 Comparison of man-made fibres with cotton and cellulotics

The life cycle schemes of cellulose and polypropylene fibres, both representative of a polymer material based on a single monomer, are presented in Fig. 4.7. In both cases the actual fibre manufacturing process is only a part of the whole life cycle including raw material production and transportation, textile manufacture and use, and waste management by landfill (viscose) or incineration (polypropylene). The comparison of fibres gives advantages and drawbacks for both fibres, and it is very important to carry out the definition of goals and boundaries of the system to be considered, as presented in Fig. 4.8. The advantages for viscose are as follows: renewable raw material (through photosynthetic processes); good properties for clothing and hygienic purposes; and waste management. Furthermore, lyocell and cupro processes show lower environmental impacts, because of total recovery of solvents during processing. For polypropylene, in turn, advantages, such as the simplicity of the spinning process, low air and water emissions, low energy demand in drying, light weight, and the possibility for recycled products can be observed. General environmental profiles of cellulosic fibres depend on actual processes and parameters applied.

The life cycle inventory analysis of cotton, organic cotton and polyester



4.7 Life cycles of viscose and polypropylene as single-monomer fibre materials.

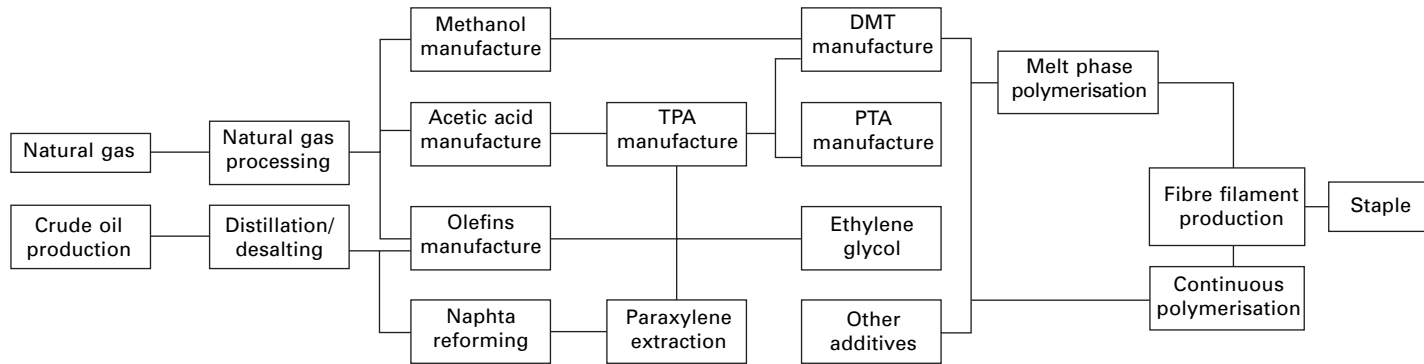
has been compared in a study on hotel textile production and services.²⁹ The detailed calculation, presented in Table 4.2, is divided into five important impact parameters:

- energy consumption;
- non-renewable resources;
- water consumption;
- emissions to air;
- emissions to water.

From the comparison in Table 4.2 it can be concluded that advantages of cotton are lower energy consumption, renewable resources, and possible (if known) lower emissions to water. Disadvantages are the high consumption of water, consumption of fertilisers and pesticides, and high emissions to air (particularly CO₂). Organic cotton shows slightly lower energy consumption, renewable resources, and slightly lower emissions to air.

4.3 The mechanisms of enzymatic reactions on wood and cellulose

The structure of enzymes is usually described in terms of molecular mass, isoelectric point, amount of amino acid residues, and structural organisation,



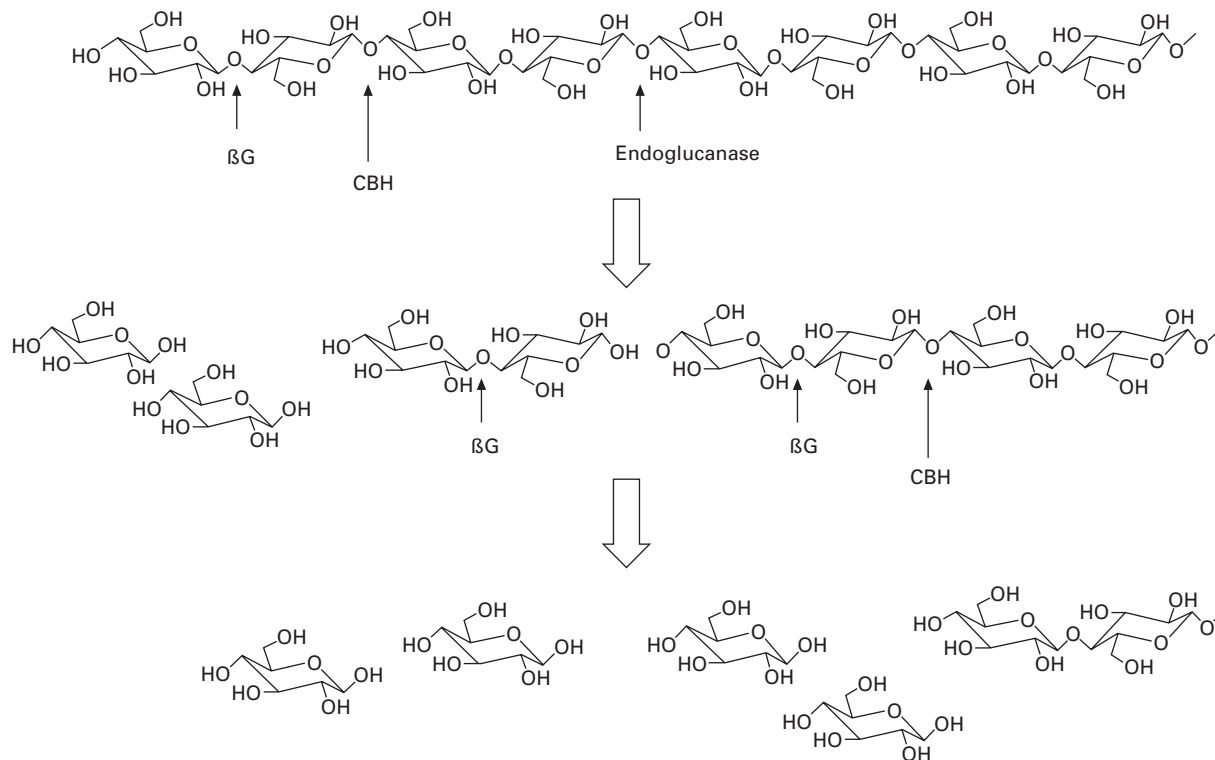
4.8 Life cycle scheme of polyester (PET) fibre materials as polymer based on two monomers' polycondensation.

Table 4.2 Life cycle inventory analysis of cotton, organic cotton and polyester (PET) fibres

Parameter	Unit/kg	Polyester	Cotton	Organic co. (Greenco)
Energy consumption	MJ	97.4	59.8	53.6
Electricity	MJ	15.2	12.1	13
Fossil fuel	MJ	82.2	47.7	40.6
Other energy type	MJ			
Renewable fuel	MJ			
Inherent energy	MJ			
Non-renewable resources	KG	2.4	1.4	1.3
Natural gas (r)	g	360	354	140
Natural gas, feedstock (r)*	g	287		
Crude oil (r)	g	410	527	567
Crude oil, feedstock (r)*	g	867		
Coal (r)	g	141	524	564
Coal, feedstock (r)*	g	373		
LP gas (r)	g		32	34.6
Hydro power (MJel) (r)	MJ	0.41	1	1.1
Natural uranium (r)	mg		14	15.1
Fertilisers	g		457	
Pesticides	g		16	
Other non-renewable resources (r)				
Water (r)	KG	17.2	22200	24000
Emissions to air:				
CO ₂	g	2310	4265	3913
CH ₄	g	0.1	7.6	6.1
SO ₂	g	0.2	4	4.2
NOx	g	19.4	22.7	22.7
CH	g	39.5	5	5.3
CO	g	18.2	16.1	17.2
Emissions to water:				
COD	g	3.2		
BOD	g	1		
Tot-P	g			
Tot-N	g			

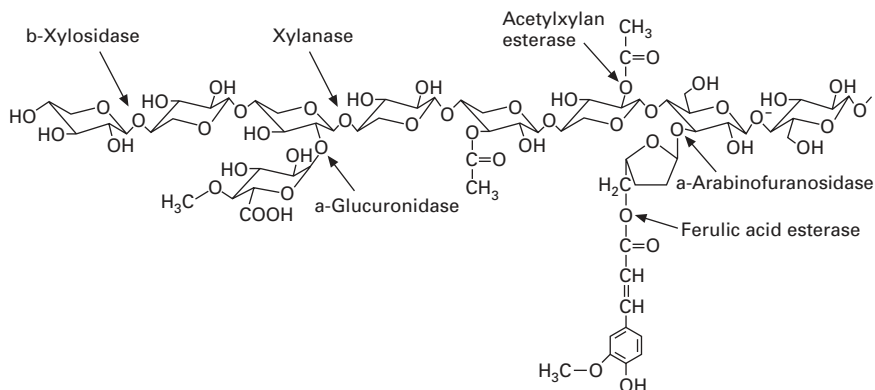
*feedstock values included to energy consumption.

as schematically presented in Fig. 4.9. The enzyme molecule comprises, normally, a binding domain (CBD), linker protein chain and the main active catalytic domain for hydrolysis of the specific substrate, as presented in Fig. 4.10.³⁰ The hydrolysis of wood fibres with enzymes comprises the action of a group of enzymes which hydrolyse by the specific catalytic action the different components present in the wood: cellulose, hemicelluloses and



4.11 The enzymatic hydrolysis of cellulose.

Hemicelluloses present in a wood fibre are exposed to the cellulolytic complex of enzymes by the action of different xylanases, which catalyse the hydrolysis of the xylose backbone of heteroxyylan chains layered on the heteroxyylan microfibrills. The xylanases act at random locations on the heteroxyylan chains that have themselves become exposed by the action of the action of the various debranching enzymes, as presented in Fig. 4.12.

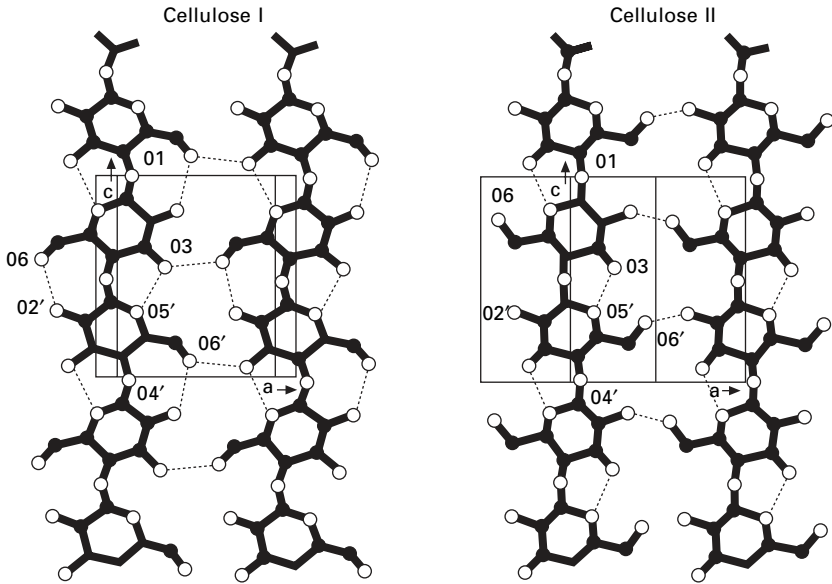


4.12 Enzymes involved in the hydrolysis of a hypothetical heteroxyylan.

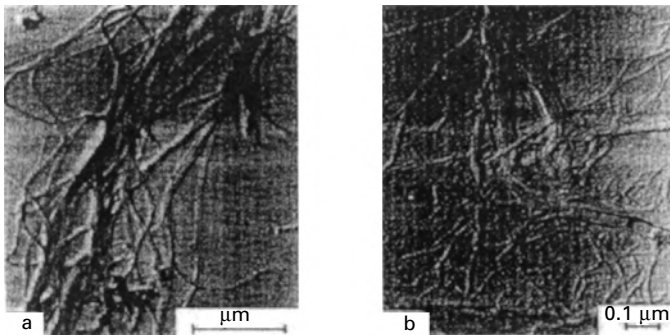
The supermolecular structure of cellulose consists of crystalline ordered regions formed by certain arrangement of hydrogen bonds between and inside the cellulose molecular chain. Due to the large number of hydroxyl and ether bonds of the chain, there are several possibilities for crystal formation, the main types classified as cellulose I and cellulose II, as schematically shown in Fig. 4.13. The formation of cellulose I is normally as the result of the bisynthesis process in nature, whereas cellulose II results in chemical swelling action of sodium hydroxide. There are also other types of crystalline cellulose, e.g. cellulose III generated during swelling with gaseous ammonia. The structure of isolated cellulose microfibrills of different origin (cotton linters and spruce sulphite pulp) is shown in Fig. 4.14.

The practical application of cellulose pulps for different processes is connected with the selection of different methods for modifying this valuable raw material in order to improve its reactivity and solubility. The cellulose modification process can be conducted by chemical (alkalination),^{32,33} physical (irradiation)^{34,35} or biochemical (enzymatic transformation)^{36,37} methods. Two major modified strains of *Aspergillus niger*³⁸ and *Trichoderma reesei*³⁹ have been selected as being the best producers of enzymes suitable for biotransformation of softwood- and hardwood-originated pulps.

The enzymatic transformation of cellulose occurs in a heterogenic system.



4.13 Hydrogen bond patterns of cellulose amorphs.

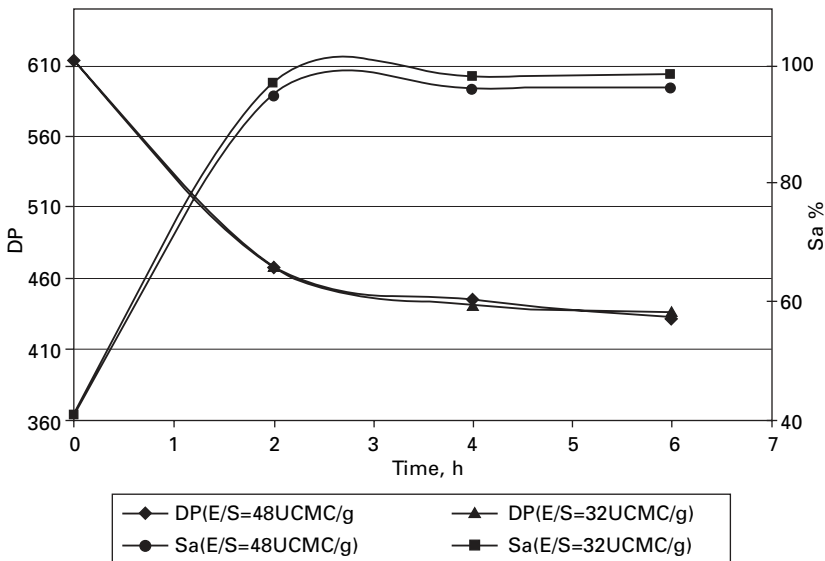


4.14 The structure of isolated cellulose microfibrills of different origin: (a) cotton linters, (b) spruce sulphite pulp.

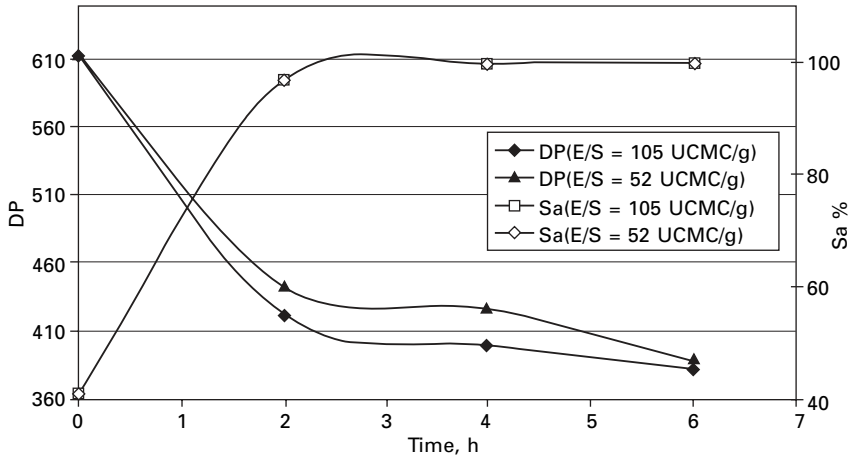
The course of biotransformation and the final product properties depend both on the type and composition of the enzyme complex and on the cellulose structure such as the average polymerisation degree and its distribution, crystallinity, capillary system and swelling behaviour as well as the physical–chemical parameters of processes such as ratio enzyme activity to cellulose content, time and temperature reactions. The increased susceptibility of cellulose chains is a result of the modified structure and developed intrinsic surface of cellulose obtained by using suitable pre-treatment methods, particularly mechanical processing.^{37,38}

It is well known that direct contact between the enzymes and the substrate is a prerequisite to hydrolysis. Since cellulose is an insoluble and structurally complex substrate, this contact can be achieved by diffusion of the enzymes into the cellulose matrix. Any structural feature that limits the accessibility of cellulose to enzymes will diminish the susceptibility of cellulose to hydrolysis.^{40,41} After pulping, the softwood has a more porous structure than the hardwood because the lignin is removed during this process. The softwood pulp seems to be accessible enough to enzymes after mechanical pre-treatment, whereas the hardwood pulp is less affected and needed additional treatment. The main effect of mechanical shredding is to subdivide cellulosic material into fine particles which are highly susceptible to acid or enzymatic hydrolysis. The smaller particles have a larger surface-to-volume ratio, thus rendering the cellulose more accessible to hydrolysis. In the case of acid pre-hydrolysis of hardwood pulp the creation of micropores by removal of hemicelluloses, a change in crystallinity and reduction of DP have been discovered.⁴²

The significant correlation between the decrease of an average polymerisation degree and increase of cellulose solubility degree in aqueous sodium hydroxide solution has been investigated. The effects of cellulase treatment on average polymerisation degree (DP) and solubility degree (Sa) of cellulose treated by cellulolytic complexes from *Aspergillus* and *Trichoderma* strains are presented in Figs 4.15 and 4.16.⁴³

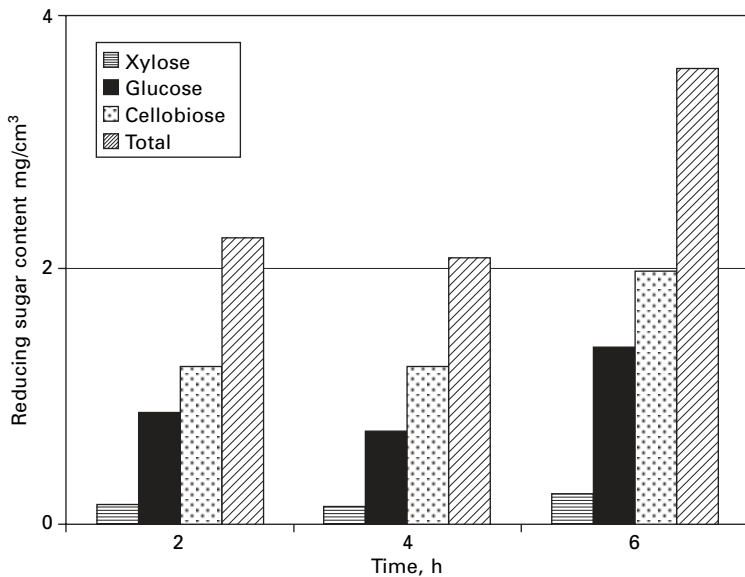


4.15 Changes of average polymerisation degree $\bar{D}P$ and solubility degree Sa vs time of biotransformation process (for cellulase from *Aspergillus niger*).



4.16 Changes of average polymerisation degree $\bar{D}P$ and solubility degree Sa vs time of biotransformation process (for cellulase from *Trichoderma reesei*).

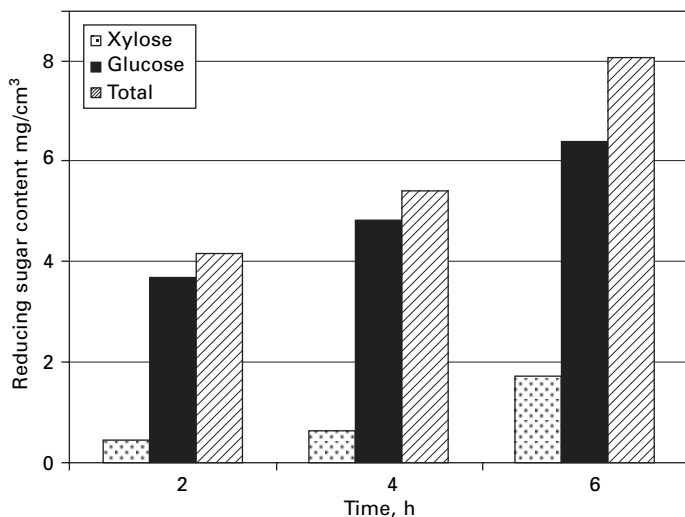
The quality and quantity of reducing sugars generated during cellulose biotransformation differ depending on the process parameters, i.e. mainly type of enzyme (mechanism of enzyme action) and time of reaction. The effect of the time of reaction on the amount of reducing sugars realised during the biotransformation process of cellulose using cellulolytic complexes from *Trichoderma reesei* and *Aspergillus niger* is demonstrated in Figs 4.17



4.17 Changes of soluble sugars content vs time of biotransformation process (for cellulase from *Trichoderma reesei*).

and 4.18. The reducing sugars found in enzyme solutions after biotransformation with cellulolytic complex were as follows:

- for enzymes from *Aspergillus niger*: glucose (3.68–6.39 mg cm⁻³), xylose (0.45–1.68 mg cm⁻³), cellobiose (lack) and total amount (4.15–8.01 mg cm⁻³);
- for *Trichoderma reesei*: glucose (0.87–1.38 mg cm⁻³), xylose (0.15–0.68 mg cm⁻³), cellobiose (1.23–1.98 mg cm⁻³) and total amount (2.25–3.59 mg cm⁻³).



4.18 Changes of soluble sugars content vs time of biotransformation process (for cellulase from *Aspergillus niger*).

The sugar content and composition of solubilised carbohydrates of cellulose treated by purified cellulases from *Trichoderma reesei* have been estimated (see Table 4.3).⁴²

When the cellulases were compared at the same protein dosages, both endoglucanases (EGI and EGII) were able to hydrolyse pulp more efficiently than the cellobiohydrolases (CBHI and CBHII). With an enzyme dosage of 2.5 mg g⁻¹ the hydrolysis yields of EGI and EGII were 1.6% and 1.4% of pulp, corresponding to 1.36% and 1.47% of initial cellulose solubilised, respectively (based on the original carbohydrate composition of the pulp). CBHI and CBHII solubilised 0.49% and 0.81% of pulp, respectively, with the same dosage (see Table 4.3).

Neither overall degradation nor saccharification of cellulose is a required phenomenon in the biotransformation process of pulps. The controlled

Table 4.3 Composition of solubilised carbohydrates of the reference and enzyme-treated cellulose

Enzyme	Dosage (mg g ⁻¹)	Solubilised sugars (% of dry weight)	Sugar composition of solubilised carbohydrates (% of dry weight)	
			Glucose	Xylose
EGI	0.1	0.19	0.12	0.07
	0.5	0.70	0.54	0.16
	2.5	1.60	1.33	0.27
EGII	0.1	0.22	0.16	0.06
	0.5	0.65	0.62	0.03
	2.5	1.44	1.44	0.00
CBHI	0.1	0.15	0.13	0.02
	2.5	0.49	0.49	0.00
	5.0	0.89	0.89	0.00
CBHII	0.1	0.21	0.16	0.05
	2.5	0.81	0.77	0.04
	5.0	1.28	1.28	0.00
Control	0.0	0.11	0.03	0.08

degradation of cellulose chain (reducing DP to below 400) and changes in supermolecular and morphological structure allow preparation of directly alkali-soluble cellulose applied in the Celsol process.⁴¹ Structural characteristics of biotransformed cellulose are presented in Tables 4.4 and 4.5.

Table 4.4 Molecular weight distribution of enzyme-transformed pulp

Type of pulp	Mn (kDa)	Mw (kDa)	DPw	Pd	Percentage content of DP fraction		
					< 200	200–550	>550
Initial softwood pulp	47	119	740	2.6	17	39	44
Biotransformed pulp	25	64	395	2.5	40	42	18

The biotransformation of pulp causes, in comparison to the initial pulp, several changes as follows: decrease in the average polymerisation degree and crystalline degree, reduction of hydrogen bonds, increase in intrinsic surface and increase in the solubility in aqueous sodium hydroxide.

Table 4.5 Characteristic of supermolecular and morphological structure of enzyme-transformed pulp

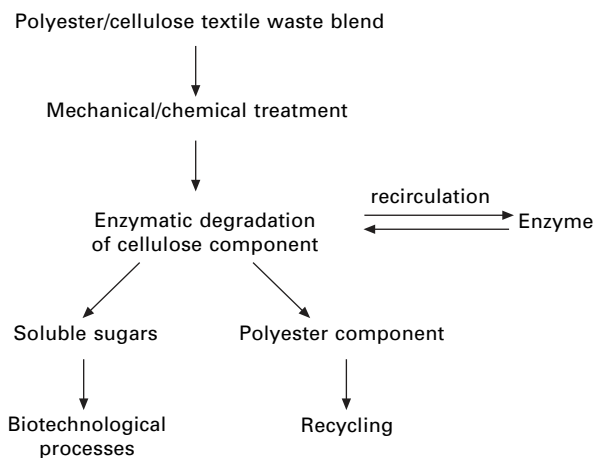
Type of pulp	Crystalline degree	Energy of hydrogen bond E_H (kJ mol^{-1})	Total volume of pores ($\text{mm}^3 \text{g}^{-1}$)	Total porosity (%)	Intrinsic surface ($\text{m}^2 \text{mm}^{-3}$)	Solubility degree in 9% NaOH (%)
Initial softwood pulp	0.52	20.0–22.0	253.8	6.09	4.9	17.0
Biotransformed pulp	0.48	12.9–15.1	316.4	9.17	9.6	99.5

4.4 Biodegradability of cellulose fibres in textile blends

Large quantities of textile wastes consisting of blended polyester and cellulose fibres such as cotton and viscose fibres are produced in the textile industry. Most of such waste is discarded or converted into wiping cloths of very little commercial value. On one hand, due to the storage of textile fibres the recycling and conversion of such wastes into useful products has become a very important problem. On the other hand, the reuse of such blends composed of polyester and cellulose fibres is a particularly difficult problem due to the unique properties of these two types of fibres. During recent years there has been a growing interest in the problem of textile waste utilisation involving polymeric blends, in particular of recycling and conversion of such wastes into useful products.^{44–46} Various studies performed in this field have been dictated, by ecological considerations, which are one of the most important technological problems in contemporary industry. Well-known methods of utilisation of textile wastes including polyester–cellulose blends such as chemical processing, storage in waste dumps, or burning are characterised by large hazards to the natural environment due to toxic gas emission or sewage seepage into the water table.⁴⁷ The alternative method for utilisation of such wastes is a biotechnological method based on application of cellulolytic enzymes, catalysing the hydrolytic degradation of cellulose to mixture of mono and oligosaccharides.⁴⁸ In the saccharification cellulose process, the cellulolytic complex originating from *Trichoderma reesei* fungi is especially advantageous. Because of the high specificity of the enzyme, it is possible to obtain a well-defined final product of decomposition of a natural polymer in the form of low-molecular products (glucose, cellobiose, oligosaccharides).^{49,50} These products could be applied in some chemical processes such as production of ethyl and methyl alcohol or methane.^{51,52}

The rate of enzymatic hydrolysis depends on the structural features of cellulose, as well as on the composition of the cellulolytic complex. Structural features such as crystallinity and accessible surface area determine the

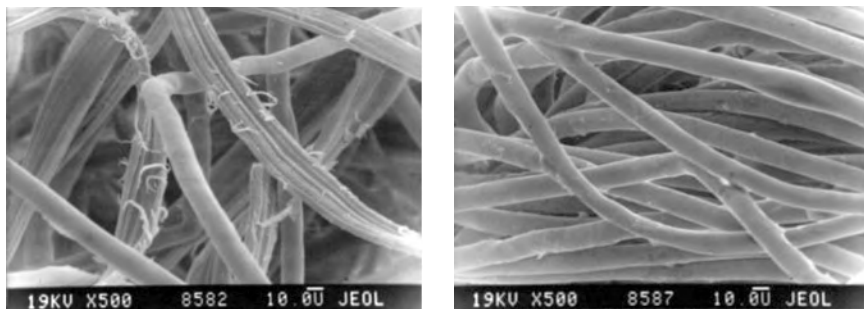
susceptibility of cellulose to enzymatic degradation. Macromolecules of cellulose of low-ordered regions are hydrolysed easier than those of high-ordered regions. As should be expected, the key to success in increasing the rate and yield of the biodegradation process is the breakdown of the crystalline structure of cellulose or surface displaying, making it accessible to enzyme action. It has been found that mechanical pre-treatment affects the increasing absorption ability of enzymes on the cellulose surface.⁵³ An increase in accessibility is a result of the opening up of the cellulose structure and its internal surface enlargement. Although many chemical pre-treatments for enhancing biodegradation of cellulose are based on treatment with Cadoxen, sulphuric acid, phosphoric acid, sodium hydroxide^{54,55} or hydrogen peroxide⁵⁶ generate partial recrystallisation of cellulose and influence an increase in efficiency of the enzymatic cellulose hydrolysis, these processes involve the application of harmful reagents and the necessity of by-product inactivation. Utilisation of textile blends is performed according to the scheme presented in Fig. 4.19.⁵⁷



4.19 Scheme of bioutilisation of textile waste blends composed of cellulose and polyester fibres.¹⁴

Application of scanning electron microscopy (SEM) allows the observation of appearance of fibres and their changes during the enzymatic degradation (see Fig. 4.20). As a result of the enzymatic degradation process for the polyester–cellulose fibrous blends, the degree of saccharification of cellulose fraction was achieved at a level up to 99 wt.%.

The final product resulting from the biodegradation process was composed mainly of the polyester fibres with a relatively low content of residual cellulose fibres. The mechanical properties of the polyester fibres isolated from the blend after enzymatic treatment are comparable to the standard PET fibres



4.20 Scanning electron microscopic image of the polyester–cellulose blend: (a) initial blend, (b) after biodegradation of cellulose fibres.

(see Table 4.6). The results of experiments indicated that the cellulose biodegradation process did not essentially affect the properties of polyester fibres.⁵⁸

Table 4.6 Some properties of isolated polyester fibres¹⁵

Parameter	Unit	PET fibres standard	Residual PET fibres
Average molecular weight	g mol^{-1}	16 900	16 100
Linear density	dtex	3.65	3.50
Breaking force	cN	13.4	12.9
Tenacity	cN/tex	36.7	36.9
Elongation	%	54.8	62.5
Coefficient of variation of breaking force	%	14.4	13.4

After separating the natural component from the blend, the remaining polyester may be garnered to obtain staple fibre products, for the manufacture of nonwoven products, or may be recycled in the melt spinning method. Formation of filament or films occurs without problems when the product of degradation is used as an addition to the standard polyester material.⁵⁸

4.5 Biotechnology for manufacture and modification of cellulosic fibres

4.5.1 Bioprocessing of cellulose for new chemical fibres

An increasing interest in the protection of the natural environment was manifested at the close of the twentieth century and continues in the early twenty-first century. Many different industrial technologies are characterised by the emission of highly dangerous substances, e.g. carbon disulfide and hydrogen sulphide, which continue to poison the environment.

Due to the environmental risk caused by the use of carbon disulphide in the viscose process, attempts have been made to develop new types of processes for fibre production from cellulose, such as pulp directly dissolved in organic solvents, e.g. *N*-methylmorpholine-*N*-oxide (NMMO)⁵⁹ application of cellulose derivatives such as cellulose carbamate⁶⁰ and dissolving pulp in aqueous sodium hydroxide (biotransformed pulp).⁶¹

Currently the cellulose dissolving methods, which are used on an industrial scale, are cuprammonium, viscose and NMMO methods. In the two first methods, a certain cellulose derivative has to be formed prior to dissolution. Accordingly, regeneration is necessary for converting this cellulose derivative to the so-called regenerated cellulose. Both processes are energy intensive, which to a large extent cancels out the potential savings obtainable from the use of cellulose as a renewable raw material. Further, both the cuprammonium process and the viscose process produce effluent streams containing significant amounts of toxic materials, which must be removed before the effluent can be disposed of. In the NMMO process, cellulose is dissolved directly in *N*-methylmorpholine-*N*-oxide at high temperature and the fibres are formed by extruding the solution into an aqueous solution of NMMO. The solvent is almost completely recycled making the process more ecological than the cuprammonium and viscose processes. However, the solvent is expensive and the plant requires high founding costs. Many cellulose-dissolving methods, which are not utilised industrially, have been discovered including the use of different metal complexes or organic solvents. However, these methods are not superior to the industrial methods because of the use of toxic components such as heavy metals and amines or complicated multi-component solvent systems, which are very expensive and from which the solvents are difficult to recover. Thus, these methods are disadvantageous from an environmental and economical viewpoint.

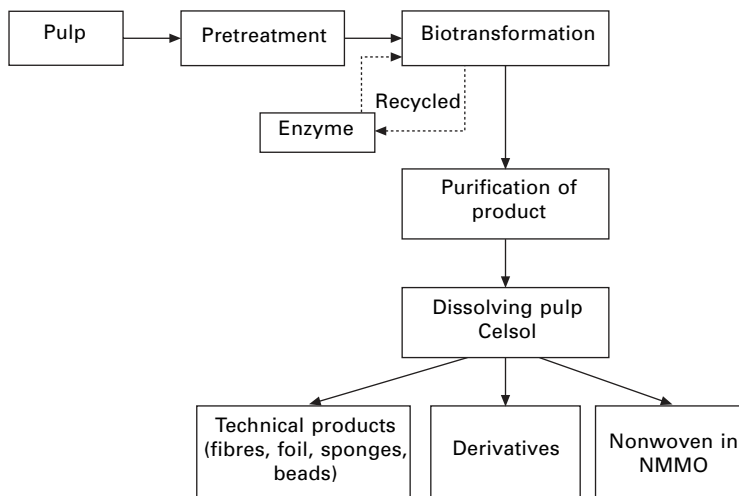
Apparently, it is extremely difficult to dissolve cellulose safely in a simple and cheap solvent and accordingly, there exists a need for a process capable of manufacturing cellulosic products economically and in an environmentally acceptable manner. This is especially important for improving sustainability and for reducing environmental and health impacts of the industry producing shaped cellulosic articles.

The benefits of biotransformed cellulose pulp (discussed in Section 4.3) in connection with its technological simplicity and economical effectiveness promote this biotechnological method as the most useful way of processing pulp into fibres. The modification of cellulose structure during biotransformation has definitely improved the main properties of cellulose pulp such as solubility in aqueous sodium hydroxide and chemical reactivity leading towards obtaining:

- direct soluble pulps (Celsol), with solubility in an aqueous sodium hydroxide; solution up to 99.5 wt %, ⁶²⁻⁶⁴

- highly soluble pulps, with improved solubility in NMMO;^{65,66}
- highly reactive pulps with improved reactivity toward reactants such as acetic anhydride.⁶⁷

There are great opportunities to obtain the most reactive biotransformed cellulose, which can be utilised for preparation of cellulosic products such as fibres, films, derivatives, sponges, etc. The enzymatic transformation of pulps into direct soluble cellulose (Celsol) is shown schematically in Fig. 4.21.



4.21 Scheme of biotransformation process.

From the samples of biotransformed cellulose characterised by a dissolution degree of cellulose in the aqueous sodium hydroxide of over 99%, alkali spinning solutions have been prepared. The characteristics of performed alkali solutions are presented in Table 4.7.⁶⁸

Table 4.7 Some properties of alkaline solution of biotransformed pulp

Parameter	Biotransformed pulp
α -cellulose content (wt%)	5–7
Alkali content (wt%)	7–8
Viscosity (s)	40–100
Ripeness degree ($^{\circ}$ H)	8–10
Stability of solution at 5 $^{\circ}$ C (h)	48

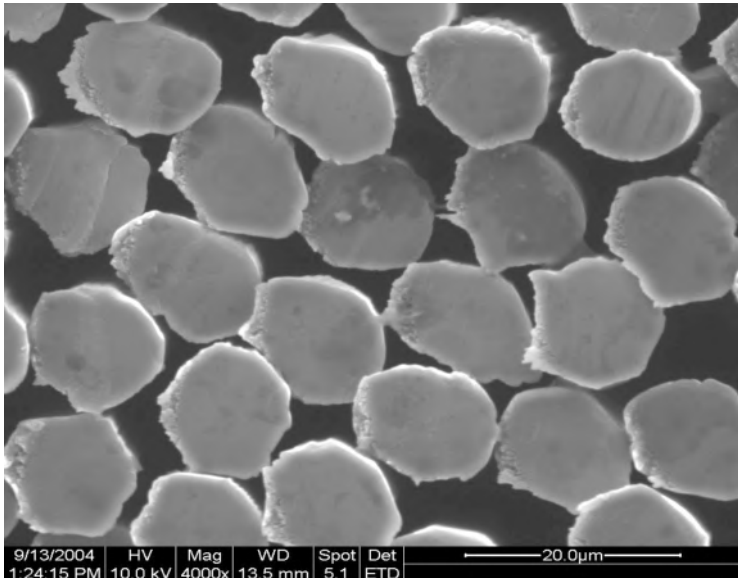
The spinning of regenerated cellulose fibres (Celsol)⁶⁹ using an alkaline solution of biotransformed pulp and acidic regeneration bath, to produce the

fibres with high purity and sorption capacity, produces fibres with a tenacity value of 19 cN/tex. The affectivity of fibre and film production using a biotransformation process is generally on a level of 93–95% to the weight of initial pulp. Some properties of regenerated cellulose fibres spun from alkali solutions of biotransformed pulp are presented in Table 4.8. The SEM photo of the fibre's cross-section is shown in Fig. 4.22. The fibres are characterised by an oval cross-section with little developed boundary line; they are regular and show no sticking.

There are great opportunities to improve this property during the development stage of the discussed method. It is well known that several parameters including spin additives, coagulation time and temperature, spin bath chemicals, spinneret type, jet draw, finishing and stretch have significant effect on the fibre properties. These parameters have not been developed sufficiently yet.

Table 4.8 Some physical–mechanical properties of Celsol fibres

Parameter	Celsol fibres
Titre (dtex)	2.55
Breaking force (cN)	4.95
Tenacity (cN/tex)	19.4
Elongation at break (%)	13.0



4.22 SEM photos of Celsol fibres – cross-section.

4.5.2 Microbial synthesis of cellulosic fibres

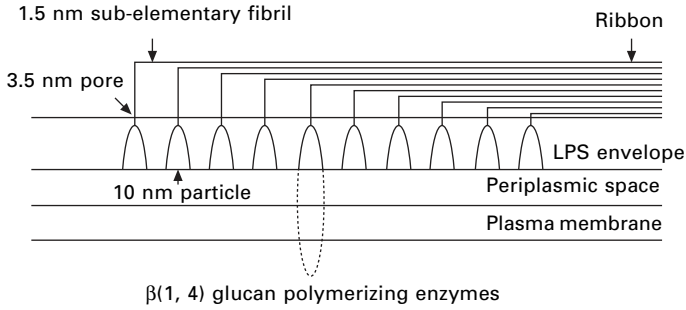
The bacteria belonging to the genera of *Acetobacter*, *Agrobacterium*, *Rhizobium*, *Pseudomonas* or *Alcaligenes* show ability for cellulose biosynthesis (see Table 4.9).^{70–74} The synthesis of cellulose in *Acetobacter xylinum* – the best producer, occurs between the outer membrane and cytoplasmic membrane by a cellulose-synthesising complex, which is in association with pores at the surface of the bacterium (see Fig. 4.23).⁷⁵ The cellulose synthase is considered to be the most important enzyme in this process. A biochemical pathway from glucose to cellulose is presented in Fig. 4.24.⁷⁶ The cellulose is produced in the form of microfibrils synthesised at the bacterial surface at sites external to the cell membrane. The microfibrils released outside the bacterial cells are joined together by strong hydrogen bonds and form a gelatinous film on the surface of the nutrient medium in the static method and an unwoven fabric in the dynamic method. The microfibrils of bacterial cellulose are composed of pure cellulose, which is devoid of lignin, hemicellulose, and other substances.

Table 4.9 Bacterial cellulose producers⁷⁵

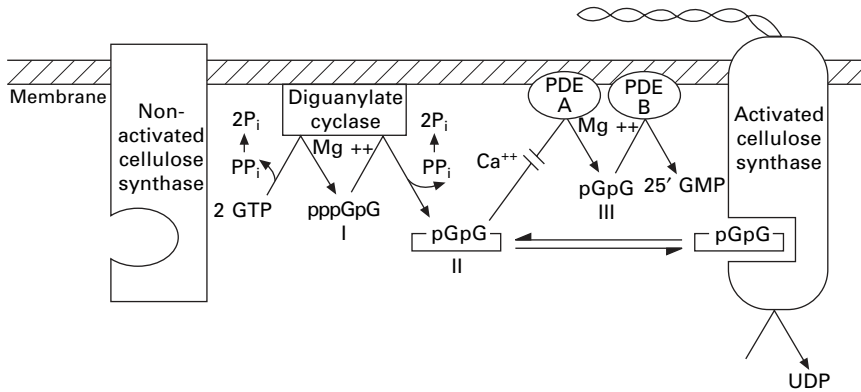
Organisms (genus)	Cellulose produced	Biological role	Ref. in 75
<i>Acetobacter</i>	Extracellular pellicle Cellulose ribbons	To keep in aerobic environment	(1, 2, 8)
<i>Achromobacter</i>	Cellulose fibrils	Flocculation in wastewater	(1–3)
<i>Aerobacter</i>	Cellulose fibrils	Flocculation in wastewater	(2, 3, 8)
<i>Agrobacterium</i>	Short fibrils	Attach to plant tissues	(2, 3, 8)
<i>Alcaligenes</i>	Cellulose fibrils	Flocculation in wastewater	(1–3)
<i>Pseudomonas</i>	No distinct fibrils	Flocculation in wastewater	(1–3, 8)
<i>Rhizobium</i>	Short fibrils	Attached to most plants	(1, 8)
<i>Sarcina</i>	Amorphous	Unknown	(5, 8)
<i>Zoogloea</i>	Not well defined	Flocculation in wastewater	(2, 3)

Source: reprinted from *Polymer Degradation and Stability*, vol. 59, Rainer Jonas and Luiz F. Farah, 'Production and application of microbial cellulose', 101–106, copyright (1998), with permission from Elsevier

Two types of production methods are used at present: static, where the cellulose net is growing on a surface of nutrient solution, and dynamic, being under intensive studies. The method used for preparation of bacterial cellulose



4.23 Scheme for the formation of bacterial cellulose⁷⁵ (reprinted from *Polymer Degradation and Stability*, vol. 59, Rainer Jonas and Luiz F. Farah, 'Production and application of microbial cellulose', 101–106, copyright (1998), with permission from Elsevier).



4.24 Model for regulation of cellulose biosynthesis in *A. xylinum*⁷⁶ (reprinted from *Polymer Degradation and Stability*, vol. 59, E.J. Vandamme, S. De Baets, A. Vanbaelen, K. Joris and P. De Wulf, 'Improved production of bacterial cellulose and its application potential', 93–99, copyright (1998), with permission from Elsevier).

(BC) depends on the strain type. Generally, the *Acetobacter* strains are most suitable for static (emers) cellulose biosynthesis. However, this method is not effective with respect to the yield of the final product. Therefore, the dynamic (submers fermentation) method has to be considered. The most important question of this method is to have stable bacteria strains because an unstable strain produces spontaneously inactive bacteria (Cel^-). Therefore, the preparation of highly effective bacteria strains by mutagenisation and genetic manipulation improves the dynamic production of BC. The best pilot-scale world producer of BC is Weyerhaeuser Co., Tacoma, WA, USA in cooperation with Cetus Corp., Emerville, California, USA.

The main benefits for BC, generally different from a native plant-produced

cellulose pulp, are connected with its extraordinary properties and behaviour summarised in the following: high purity and crystallinity, high sorption capacity and porosity, high intrinsic surface and adhesivity, as well as high tenacity and Young's modulus. Mechanical properties of bacterial cellulose pellicle can exceed by far those of usual synthetic polymers and of regenerated cellulosic (cellophane) films.⁷⁷

Based upon these special properties, BC is proposed to be used for several applications in papermaking, textile, food, electronic industries as well as medicine. Taking advantage of the high modulus, Sony Co. is using bacterial cellulose for manufacture of sound membranes. BC having non-allergic behaviour can be used as wound healing dressings or artificial skin. The highly developed intrinsic surface and sorption ability of BC allows the application of this material for special paper preparations or as a carrier in biotechnology. A list of potential applications of bacterial cellulose (most of them are patented) is presented in Table 4.10.^{75,78–92}

Table 4.10 Application of bacterial cellulose⁷⁵

Material	Application	Reference
Temporary artificial skin Biofill [®] , Bioprocess [®] , Gengiflex [®]	Therapy of burns, ulcers, dental implants	(54, 55)
Nonwoven paper or fabric	Improvement of latex or other binders	(56)
	Repairs of old documents	(57)
Sensitive diaphragms	Stereo headphones	(8)
Cellulose	Immobilisation of proteins, chromatographic techniques	(51, 58–60)
Edible cellulose	Addition to food	(61–63,67)
Cellulose	Stabiliser of emulsions in cosmetics, food	(64, 65)
Cellulose	Coating compositions	(66)

Source: reprinted from *Polymer Degradation and Stability*, vol. 59, Rainer Jonas and Luiz F. Farah, 'Production and application of microbial cellulose', 101–106, copyright (1998), with permission from Elsevier

In recent years, many different theories about cellulose biosynthesis can be observed and it has been found that cellulose is produced from a wide range of substrates, e.g. glucose, fructose, mono and disaccharides, starch hydrolysates, molasses, and others. The capacity for biosynthesis as well as the properties of biopolymers produced is strongly dependent on strain productivity, medium composition, and culture conditions. The biosynthesis of modified cellulose is carried out using culture media composed of

different substrates and other additives, i.e. natural and synthetic polymers and fibres.

Blends of BC and chitosan and/or derivatives thereof have been studied quite intensively under various aspects, including determination of mechanical properties as well as swelling and water retention, development of pharmaceuticals and drug release formulations, design of biodegradable plastics, non-woven fabrics, fibres and membranes, for use in speciality paper manufacture and for applications in biotechnology.

The novel bacterial cellulose with new functions (especially with chitinous properties) and higher susceptibility for chitinolytic enzymes is produced on the surface of a liquid medium by *Acetobacter* bacteria adapted to a medium containing oligo- and poly-aminosaccharides. The modification of bacterial cellulose consists in introducing the glucosamine monomeric unit into the cellulose chain, in consequence of the degradation of oligo- and poly-aminosaccharides which appears in the culture medium, as well as in the association of these mentioned agents with the cellulose fibres.^{93,94} Comparing the FTIR spectra (see Fig. 4.25), the peaks for chitosan-modified bacterial cellulose at 1650 cm^{-1} (amide I) and 1560 cm^{-1} (amide II), attributed to amide groups characteristic for chitosan, have been found. SEM photographs of chitosan-modified bacterial cellulose are shown in Fig. 4.26.

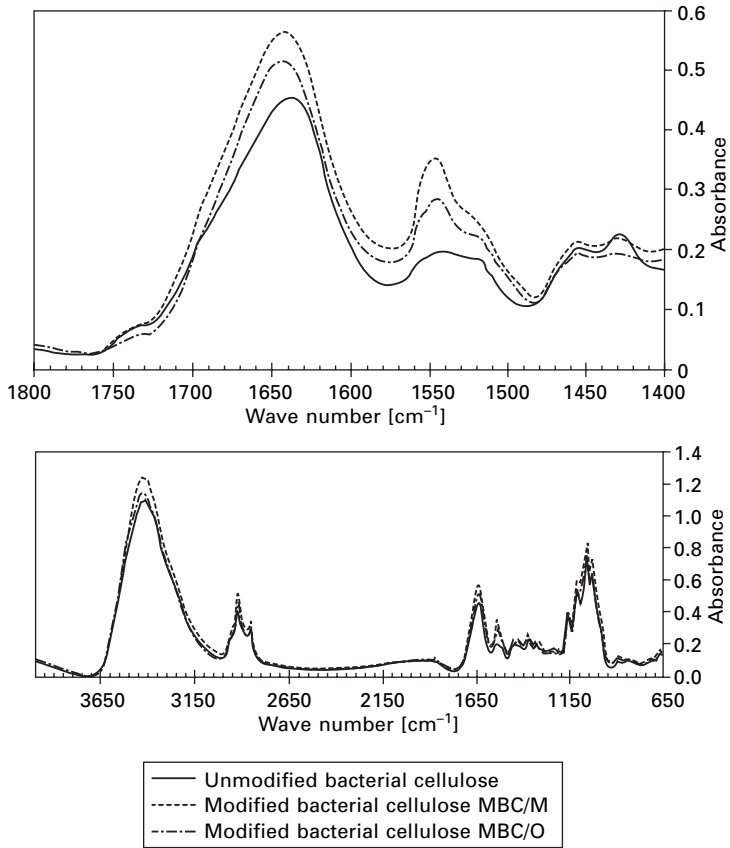
The chitosan-modified bacterial cellulose, characterised by unique properties, i.e. bioactivity, biodegradability, biocompatibility, no toxicity and non-allergic action, connected with good mechanical tenacity, has been found to be a great material for biomedical applications such as dressings for wound healing.⁹⁵

The application of chitosan-modified bacterial cellulose for manufacturing of acoustic diaphragms allows the manufacture of new loudspeaker constructions with special, unique parameters, including: the mid-tweeter with a very wide sound transmission range (from 580 Hz up to 22 kHz), which replaces mid-range and tweeter loudspeakers. Practically, membranes made from chitosan-modified bacterial cellulose can be used in all types of electro-acoustic transducers, i.e. earphones, hearing aids, microphones, alarm buzzers, etc.⁹⁶

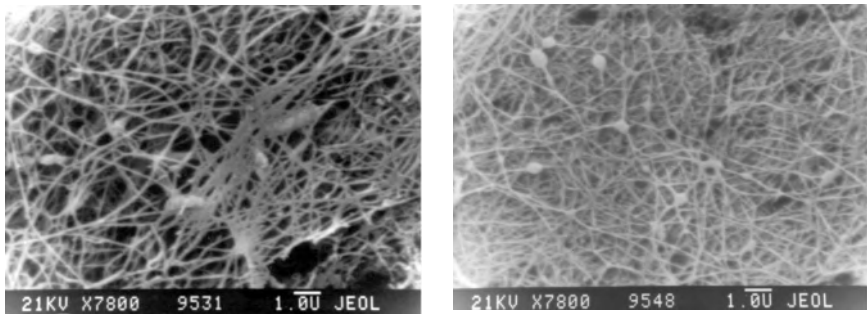
4.6 Enzyme applications in fabric and dyestuff processing

4.6.1 Cellulose fibres

Cellulases are increasingly being used in the textile industry. Their most successful application is in producing the stone-washed look of denim garments.^{97–102} Other processes that improve fabric appearance by removing fuzz fibres and pills or deliver softening benefits have also been introduced.



4.25 FTIR spectra of unmodified and modified bacterial cellulose (static culture).



4.26 SEM photographs of modified bacterial cellulose: (a) sample MBC/O and (b) sample MBC/M.

Increased use is also being made of cellulases in domestic fabric washing products where they are claimed to aid detergency and to clean fibre surfaces, improving appearance and colour brightness. Nowadays, these finishing and washing effects represent the largest market for cellulase enzymes worldwide.

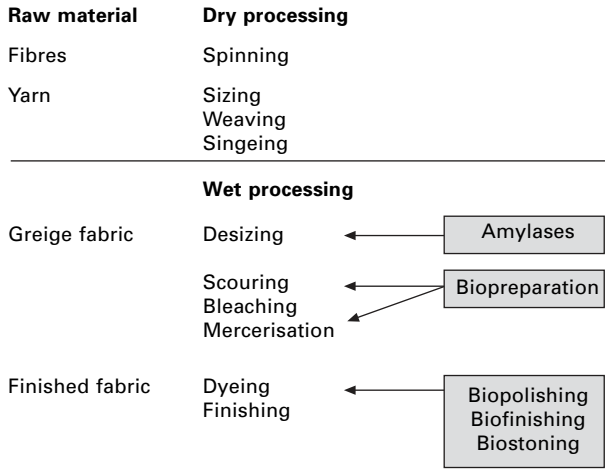
Scouring and bleaching of cotton fabrics are also attractive targets for enzyme-based processes, due to the severe environmental impact of these processes. These processes are also very energy demanding. Raw cotton contains about 10% of impurities. Pectins, waxes and coloured components can all be partially removed from raw cotton by enzymatic treatments but the residual seed coating remains a problem.

Cellulase treatment of cellulose materials, such as cotton, viscose, lyocell, cupro or polynosic fabrics and their blends, has gained increasing interest with growing consumer and industrial concern about environmental issues. The best known applications of cellulases are in denim, garment washing, biostoning, as an alternative to stone washing and in surface modification of cotton fabrics, biofinishing, to improve the surface properties. Cellulase enzymes can replace the pumice stones and result in less damage to the cloths, machinery and environment. In biofinishing cellulases remove fuzz from the surface of cellulose fibres, which eliminates pilling, making the fabric smoother and cleaner-looking. This technique is particularly promising for the new generation of solvent spun cellulose fibres such as Tencel and lyocell. The exploitation of novel cellulase processes for the textile industry has been enabled by the development of molecular engineering techniques.

Enzymatic treatment with amylases has replaced the harsh processes since the beginning of the twentieth century, and is still used as a BAT in desizing.¹⁰³ The process characteristics are suitable for existing machinery and production speeds; however, research for the improvement of economics and consistency of the process including use of heat stable enzymes is continuously carried out. The greatest number of enzymatic treatments has been applied to industrial processing of cellulosic fibres for obtaining new finishing effects or to replace harsh chemicals used in conventional cotton processing.

Conventional industrial processing of cotton may include several chemical steps during wet processes, which can be partly replaced by enzymatic processes, as shown in Fig. 4.27. The main categories additional to desizing include biopreparation, biopolishing, biofinishing, and biostoning of cotton and other natural cellulosic fibres. These processes are resulting in smoother, glossier or shaded appearances of the fabric. The loss of mechanical properties of fabrics can be reduced by using purified, special enzymes.¹⁰⁴

Cotton processing provides several possibilities for enzyme applications. The removal of cotton impurities is essential for fabric manufacture and is generally carried out by scouring with alkali. However, environmentally harsh scouring can be replaced with an enzymatic treatment, in which cotton impurities, such as protein, wax, pectin and ash, can be efficiently removed



4.27 Stages of cotton processing.

prior to further processing.¹⁰⁵ Cotton fibres have been treated with different pectinases, proteases, laccases and lipases whereafter the effect of the enzymatic action was analysed using HPLC, GC, ESCA, titration, watability and metal content measurements. The bioscouring process using the most potential enzyme mixture has been compared to the traditional alkaline scouring with respect to yarn or fabric processability, brightness and strength. Enzymatic and simple buffer treatments in the presence of a non-ionic surfactant improve water watability of fabrics to a level equal to alkaline scouring.¹⁰⁶

Most fibres made from regenerated cellulose such as viscose, lyocell, and Celsol are characterised by stiffness as well as a fuzzy and uneven surface that makes fabrics susceptible to pilling, even over a short period of use. In order to modify the surface properties of cellulosic fibres and fabrics and to improve their quality biotechnological approaches based on specialised enzymes are widely used. Finishing processes, employing cellulases and xylanases, can replace a number of mechanical and chemical operations, which have been applied until now to improve comfort and quality of fibres and textiles. The principle of enzyme action in the finishing process is controlled hydrolysis of cellulose, in which impurities and fuzz are removed from the surface of fibres, without decreasing their mechanical tenacity or the elasticity of the fabric.

Biofinishing of cellulosic fabrics is limited on controlled removal of fibre hairiness, pilling or other non-desired properties after dyeing. Enzymes – at present – are not capable for modifying or chemically cross-linking of cellulose polymers. Some effects on improvements on dimensional stability, however, have been observed. An overview of patents and research on the treatment of cotton with modified or purified cellulases is presented in Table 4.11. The

Table 4.11 An overview of the patents and research on denim with modified or purified cellulases¹⁵

Enzymes used	Analyses	Results
<i>Trichoderma longibranchiatum</i> free of CBH type components	Evaluating stone washing appearance	Reduced backstaining
<i>T. reesei</i> TC* + EGI, EGII, CBHI and CBHII	Weight loss, tensile strength, lightness units, blueness units and colour difference of denim fabrics	Elevated EGII contents increased stone washing effect
<i>T. reesei</i> , TC*, <i>Humicola insolens</i> , EGV, EGV-core <i>Cellulomonas fimi</i> , CenA-core	Staining levels, effect of mechanical action	Cellulases without CBDs and mechanical action caused less backstaining
α -amylase, EG V and EG III from e.g. <i>Scytalidium</i> (f. <i>Humicola</i>), <i>Fusarium</i> , <i>Myceliophthora</i> , <i>Trichoderma</i>	Evaluating streaks and stone-washing appearance	A one-step process for combined desizing and stone washing

*TC: total crude cellulase

biostoning process of denim can be carried out with some alternative enzyme preparations achieving reduced backstaining, increased effect, and combined effect of desizing and stone-washing, as presented in Table 4.12.

Results of biofinishing and biopolishing are dependent on enzymes and process conditions applied. The effects of different dosages of various enzymes on cotton interlock knitting are shown in Table 4.12. The dosage and type of enzyme are important in treatments and effect on desired properties, such as lowering the pilling tendency, as seen in Table 4.13. The pilling value improvement of a cotton knitted fabric can be raised from 2–3 to 5. At the same time, however, weight and strength loss should be minimised. Purified cellulase EG II has been showing lowest damaging effect and highest improvement of the pilling value.

4.7 Hygienic and medical fibres

4.7.1 Cellulosic fibres for medical and health-care products

Viscose fibres are increasingly used for hygienic and medical applications. In Europe the share of hygienic and medical applications among nonwovens

Table 4.12 An overview of enzymatic textile applications investigated and their commercial status¹⁵

Substrate	Microorganism	Enzymes	Aim of the study	Properties measured
Fibres	<i>T. reesei</i>	CBHI, CBHII, EGI	Effects on spinnability	Microscopic analysis, spinnability
Yarns		CBHI, EGII	Evaluate fabric properties	Yarn evenness, tenacity hairiness, pilling
Poplin fabric	<i>Humicola insolens</i> <i>Cellulomonas fimi</i>	EGV + core CenA + core	Effect of agitation, binding	Adsorption/desorption, weight loss
Fabric	<i>Cellulomonas fimi</i>	CBD	Binding	Dye affinity, washing fastness, migration, strength loss, reducing ends
Fabric	<i>Trichoderma longibrachiatum</i>	Cellulase mixture free of CBHI	Provide an improved cellulase composition; decrease strength loss	Strength loss, hand, appearance colour enhancement, softness, stone-washed appearance
Fabric	<i>Fungal cellulase</i>	CBH1-enriched	Provide an improved cellulase composition; decrease strength loss	Strength loss, hand, appearance colour enhancement, softness stone-washed appearance
Fabric	<i>Humicola insolens</i>	Monocomponent, 43 kD endoglucanase	Improved pilling	Pilling, weight loss

Table 4.12 Continued

Substrate	Microorganism	Enzymes	Aim of the study	Properties measured
Fibres, linters	<i>T. reesei</i>	CBHI, CBHII, Endo-2	Synergistic action	Reducing sugars, DP, thin-layer chromatography, electron microscopy
	<i>Irpex lacteus</i> <i>Aspergillus niger</i>	EX-1, En-1 Exo-A, EG-1		
Fabric	<i>T. reesei</i>	TC*, CBH-rich, EG-rich	Adsorption	Cellulase activity, adsorption
Fabric Indigo dyed	<i>T. reesei</i>	TC*	Influence of cellulases on indigo backstaining	Staining levels, effect of mechanical action
	<i>Humicola insolens</i> <i>Cellulomonas fimi</i>	EGV, EGV-core CenA-core		
Fabric, woven and knitted	<i>T. reesei</i>	Over-producing strains (CBH II rich or EG II rich) + purified EGI, EGII, CBHI and CBHII	Provide an improved cellulase composition for treating cellulose containing textiles	Pilling, weight loss, tensile strength, visual appearance, colour
Fabric, woven and knitted	<i>T. reesei</i>	TC*, EG-rich	Optimising the use of cellulases in finishing cellulosic fabrics	Pilling, weight loss, tensile strength, drapeability
Fabric knitted	<i>Aspergillus</i>	TC*, endoenriched, monocomponent acid endoglucanases	Optimisation of bio-polishing	Pilling, weight loss, strength loss

Table 4.12 Continued

Substrate	Microorganism	Enzymes	Aim of the study	Properties measured
Fabric woven	<i>T. reesei</i>	TC*, CBH-rich, EG-rich	Effects of agitation on the adsorption-desorption behaviour	Weight loss, strength loss, softness, shear and bending hysteresis, bound protein, reducing sugars
Fabric, woven and knitted	<i>T. reesei</i>	TC*, CBH-rich, EG-rich, genetically modified strains	Improve dimensional stability of fabrics	Weight loss, strength loss, dimensional stability

Table 4.13 Effect of dosage of various cellulases on cotton interlock properties

Sample	Dosage mg/g	Weight loss %	DNS % of d.w.	Strength loss %	Pilling value
EGII	5	1.9 (+/-0)	0.27	13.7	5
	2.5	1.4 (+/-0.1)	0.20	5.4	5
	1.0	1.0(+/-0)	0.17	6.4	5
	0.5	0.7 (+/-0)	0.13	1.4	5
	0.25	0.5 (+/-0.1)	0.10	4.6	4
	0.1	0.4 (+/-0)	0.07	2.4	4
	0.01	0.4 (+/-0.1)	0.04	1.8	3-4
Biotouch L	5	2.9 (+/-0.2)	1.53	8.9	5
	1.0	1.1 (+/-0.1)	0.71	8.2	4
	0.5	0.9 (+/-0)	0.47	5.5	4
	0.25	0.6 (+/-0.1)	0.28	4.0	3-4
	0.1	0.6 (+/-0.1)	0.19	4.3	3-4
	0.01	0.4 (+/-0.1)	0.05	3.7	2-3
Cellulase E	1.0	1.4 (+/-0.3)	0.44	6.2	5
	0.5	1.2 (+/-0.3)	0.32	7.5	5
	0.25	0.7 (+/-o)	0.22	7.9	4-5
	0.1	0.6 (+/-0.1)	0.14	7.2	3-4
	0.01	0.5 (+/-0.1)	0.04	3.3	2-3
Cellulase F	1.0	(+/-0.1)	0.68	5.9	5
	0.5	0.7 (+/-0.1)	0.47	4.9	5
	0.25	0.6 (+/-0)	0.30	10.3	4
	0.1	0.4 (+/-0.1)	0.16	7.2	3-4
	0.01	0.3 (+/-0.1)	0.04	0.6	2-3
Ref.	-	0.2 (+/-0.1)	0.04	-	2-3

is around 39%.¹⁰⁷ Main products need to show high water absorbency properties and safety when used in contact with skin. Thus, the main materials are viscose for water absorbency and polypropylene for bonding and reinforcing. Biodegradability and easy composting/incineration possibilities for waste handling offer further advantages for viscose and regenerated cellulose fibres. Main application areas can be classified as follows:

- Hygiene products: baby nappies, bandages, sanitary napkins, tampons, incontinence products, cleaning waddings, cleaning wipes:
- Medical products: absorbents, wound dressings, cleaning wipes.

Microbial synthesis of cellulosic fibres affords the opportunities to create products with unique properties suitable for practical application in human and veterinary medicine. Due to its high water absorption capacity, high mechanical strength in the wet state, substantial permeability for liquids and gases, wet cellulose can be used as a temporary artificial skin to treat severe skin burns.

Bacterial cellulose somehow seems to enhance the growth of human skin

cells. Biofill[®] and Gengiflex[®] are products of bacterial cellulose that now have wide applications in surgery and dental implants and realities in the human health-care sector.^{75,108} The authors documented the following advantages for Biofill in more than 300 treatments: immediate pain relief, close adhesion to the wound bed, diminished post-surgery discomfort, reduced infection rate, easiness of wound inspection (transparency), faster healing, improved exudates retention, spontaneous detachment reepithelisation, and reduced treatment time and costs. The disadvantage was limited elasticity in areas of great mobility. Gengiflex[®] was developed to recover periodontal tissues.^{109,110} The application of bacterial cellulose (Cellumed) in veterinary medicine to treat recent, large surface wounds on horses has been investigated.¹¹¹ In experiments with dogs biosynthetic cellulose was also successfully applied to substitute the dura matter in the brain.¹¹²

Novel biological hydrogel wound healing dressings made from chitosan-modified bacterial cellulose has been performed.^{113,114} Bacterial cellulose modified with chitosan combines the beneficial, from a medical point of view, properties of the two biopolymers providing an excellent dressing material. Poly-aminosaccharides including chitosan and its derivatives have excellent biostimulating properties which ease the recovery of infected tissue and prevent the formation of large scars. A specific feature of chitosan, essential for its medical application, is biological activity resulting from the susceptibility to degradation influenced by lysozyme, an enzyme present in tissue fluids. Mono- and oligo-aminosaccharides, being the products of enzymatic chitosan degradation, stimulate tissue granulation which, in turn, accelerates the wound healing. The dressings from modified bacterial cellulose have an advantage over similar products mainly in the antibacterial activity of protecting the wound against secondary infections. In addition to the bacterial cellulose method, a hydro-thermal method for manufacture of cellulose micro- and nano-scale fibres (fibrils) has been developed.^{115,116} This process is competitive with commercially applied processes for its simplicity and ecological advantage.

4.7.2 Tissue engineering

The worldwide market for biomaterials is estimated to be €25 billion, growing approximately 10 to 15% per annum.¹¹⁷ The application areas of biomaterials consist of low-tech biomaterial-based prosthetic devices used in the fields of orthopedics, dental, drug delivery, cardiovascular and ophthalmology and high-tech biomaterials with applications in tissue and bone regeneration, wound healing, bio-adhesives, radio-therapeutics and cosmetic surgery fields. The growth of cardiovascular biomaterial business has shown a positive tendency of 12–14% p.a., and the tissue engineering business has even higher growth figures of 10–25%.

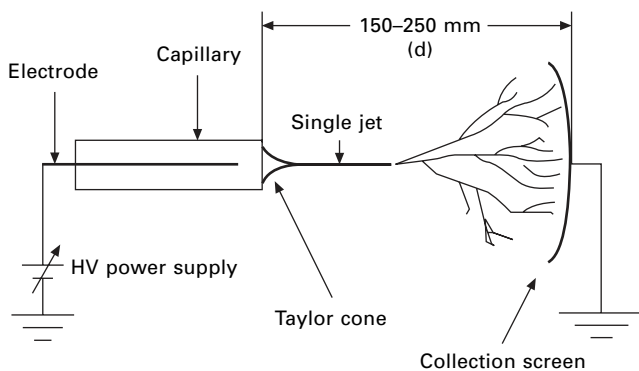
The main present applications of biomaterials within tissue engineering are:

- Tissue regeneration:
 - bio-engineered tendons/nerves;
 - artificial skin.
- Wound management:
 - absorbents/wound dressings;
 - bio-films/membranes/barriers;
 - tissue regeneration agents;
 - artificial skin;
 - hemostatic agents.

Instead of cellulose, collagens have many inherent properties that make these proteins ideally suited as a biomaterial for tissue engineering. In living organisms, cellulose as a high molecular weight fibril acts as a reinforcing material; however, in human tissues this is normally carried out by collagen fibrils. To date, only collagen type I has been used in tissue engineering applications. This is because it is the only collagen available in sufficient quantity and human material, as well as the rarer types of collagen, has been essentially unavailable. A recombinant collagen technology has been developed which allows, for the first time, use of the appropriate collagen for the tissues undergoing repair. Materials usually applied in tissue engineering are organic hydrogels of poly(*N*-isopropylacrylamide), poly(*N*-*p*-vinylbenzyl-*O*- β -D-galactopyranosyl-D-gluconamide), poly(glucosyloxyethyl methacrylate), collagens, gelatin, chitosans, and alginate.¹¹⁸ For the implantation applications of cellulose a high molecular weight fibrous materials are not possible due to be low biodegradability. However, some cellulose derivatives, nano-fibres, and biodegradable fibres of low molecular weight could possibly be used in composite 3-D structures for tissue engineering of skin, cartilage and bone with poly(lactic acid) (PLA), poly(glycolic acid) (PGA), collagen and inorganic additives.^{119,120} Some anti-inflammatory or anti-thrombogenic surface treatment with heparin or chitosan for various structures is often needed. Electrospinning is a technique for obtaining nano-scale fibres from various polymer solutions, including PLGA, poly(lactide-b-ethylene glycol) (PLA-b-PEG) diblock copolymer and PLA.^{121,122} Cellulose solutions are needed for manufacture of nano-scale structures and coatings on films or on fibrous materials enables the application of double-level structures for tissue engineering, as presented in Fig. 4.28.

4.8 Future trends

Due to the widespread availability of natural raw materials, and the present limitations of cotton cultivation, there is a high demand for simple, ecological



4.28 The principle of electrospinning and structure of nonwoven by SEM photographs: thick fibres viscose and nanofibres (150–200 nm) PVA.

and economic processes for production of cotton-type man-made cellulose fibres with similar or better properties. The production of synthetic fibres, especially polyesters and olefines, has reached a share of two-thirds of a total consumption of 100–120 million metric tons of textile fibres within 40 years. The petrochemical industry, however, has to reduce the consumption of crude oil for fuels in order to keep sufficient raw material reserves for chemicals and fibres. When managing it successfully, and taking into account a slight increase in cotton production, a demand of 10–15 million tons of cellulose fibres remains in order to produce all varieties of clothing textiles. It is very important to apply new technology and biotechnology for developing feasible processes for future cellulose fibres although the technology may yet return to its basic principles developed in the nineteenth century.

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