Lenzinger Berichte, 85 (2006) 1-5

Vorwort LENZINGER BERICHTE

Thomas Fahnemann

Vorstandsvorsitzender, Lenzing AG, Austria

“Was bleibt, ist die Veränderung; was sich verändert, bleibt.”[1]

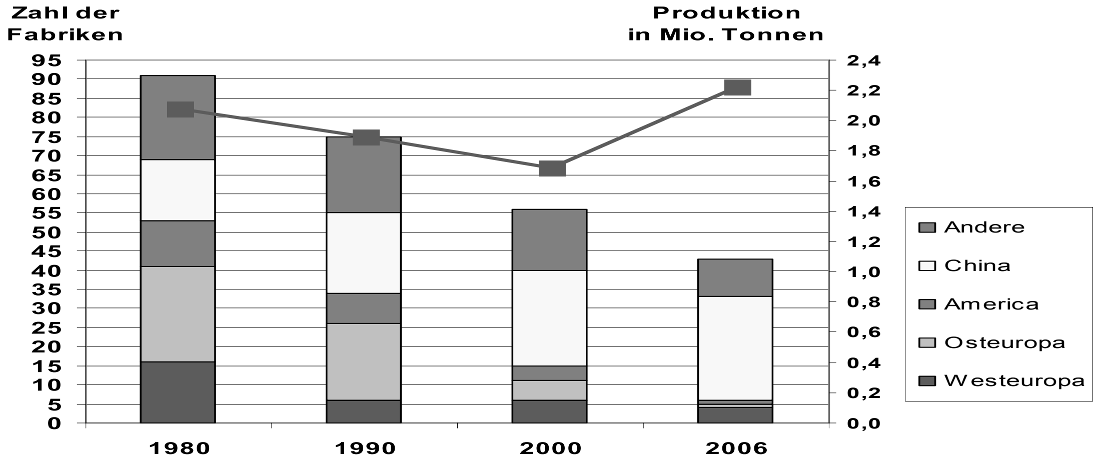
Die Fähigkeit, sich auf Veränderung einstellen zu können, ist für die Wirtschaft der Erfolgsfaktor der Zukunft geworden. Die Zukunft ist zwar ungewiss, aber nicht so ungewiss, dass man sich nicht auf sie vorbereiten kann. Das Stichwort dazu: Innovation auf allen Ebenen, von der technologischen Seite bis hin zum Markt und Veränderung auch beim Unternehmen als Organisation.

Der Prozess der laufenden Anpassung auch komplexester Unternehmensstrukturen an die Herausforderungen des Marktes wird entscheidend dafür sein, ob wir in Europa in 20 Jahren noch eine Region des Wohlstandes sein werden, in der industrielle Wertschöpfung den Takt bestimmt, oder ob uns nur mehr die nostalgische Rückschau auf die „gute, alte Zeit“ bleibt, in der wir die Dinge noch in der Hand hatten.

Hier liegt auch eine große sozialpolitische Verantwortung der Manager, denn wenn der ökonomische Unterbau einer Gesellschaft nicht international wettbewerbsfähig ist, können selbst die besten Politiker mit den besten Ideen nichts bewirken.

Dramatischer Strukturwandel

Vor rund 50 Jahren, zu Zeiten des Wiederaufbaues nach dem zweiten Weltkrieg gab es in Westeuropa rund 50 Industrieunternehmen, die Viscosefasern herstellten. Heute sind nicht mehr als vier Unternehmen dieser doch bedeutenden Industrie übrig geblieben. Ein noch dramatischeres Bild bietet sich bei einem Blick in die Länder Osteuropas und Russlands. Dort wurden vor dem Fall des eisernen Vorhanges noch rund 800.000 Tonnen Viscose-Stapelfasern p.a. produziert, fast ein Viertel der Weltproduktion. Heute stehen wir bei rd. fünf Prozent der früheren Produktionsmenge.



Grafik 1.Viscosestapelfaser: Weltweit weniger Produzenten → steigende Mengen

---

[1] Michael Richter (*1952), deutscher Zeithistoriker

Für diesen dramatischen Strukturwandel war nicht zuletzt der der Erdölboom in den 60er Jahren verantwortlich, der zu einem Siegeszug von Textilfasern auf Basis von Erdöl-Polymeren wie Polyester, Acryl und anderen Produkten führte. Die Viscosefaser auf Basis des natürlichen Rohstoffes Holz schien veraltet und wurde als Kunstfaser verdrängt. Diese Verdrängung ist ein Klassiker der Industrie – denn Polyesterfasern sind relativ einfach herzustellen, die Eintrittsbarrieren sind niedrig und der Anwendungsbereich im Massenwarengeschäft ist sehr breit. Ein weiterer wichtiger Grund war natürlich auch die Tatsache, dass Polyester zu Zeiten der unlimitierten Rohölversorgung vor allem auch billig war. Die Herstellung von Viscosefasern dagegen ist ein aufwändiger, komplexer chemischer Prozess, der auch erhebliche Umweltinvestitionen erfordert – und Umweltthemen waren es auch, die letztlich vielen unsauberen Produktionen, auch in den CEE-Staaten, ein Ende bereitet haben.

Stetig steigendes Tempo der Veränderung

Diese durchaus beeindruckende Entwicklung vollzog sich in einem Zeitraum von Jahrzehnten. Die Geschwindigkeit der Veränderung hat sich in den letzten Jahren aber nochmals enorm beschleunigt. Bestes Beispiel dafür war das Jahr 2005 – für unsere Industrie ein Wendejahr: Die vollständige Liberalisierung der Textilimportquoten aus Asien, die mit 1. Jänner 2005 eingeführt wurde, führte binnen weniger Monate zu einer derart dramatischen Veränderung der europäischen Textilindustrie-Landschaft, dass schätzungsweise über eine Million Arbeitsplätze in Westeuropa de facto mit einem Schlag wegfielen. Ein Veränderungsprozess, der in der europäischen Wirtschaftsgeschichte mit dieser Geschwindigkeit seinesgleichen sucht.

An solche Veränderungsgeschwindigkeiten werden wir uns aber gewöhnen müssen. Wir können gerade aus den jüngsten Erfahrungen dieser ständigen Beschleunigung der wirtschaftlichen Rahmenbedingungen einen Schluss ziehen:

“Was bleibt, ist die Veränderung; was sich verändert, bleibt.”

Die wesentlichen Gründe, warum erfolgreiche Unternehmen diese Herausforderungen besser meistern als die nicht erfolgreichen sind:

- Produktinnovationen stat austauschbarer Produkte
- Kostenoptimierung durch hohe Kapazitätsauslastungsquoten und laufende
- Prozessoptimierung
- Hohe Flexibilität und Anpassungsgeschwindigkeit, mit denen auf Markttrends reagiert wird
- Internationalisierung der Absatzmärkte
- Soziale/ umweltmäßige Akzeptanz durch rechtzeitige Umweltinvestitionen

Diese Veränderungen und laufenden Anpassungen sind auch die einzige Möglichkeit, den positiven Erhaltungszustand eines Unternehmens auf Dauer zu garantieren. Die Herausforderung für das Management bei der Initiierung und Steuerung von Veränderungsprozessen ist entsprechend groß. So kann man etwa die Frage stellen, warum in Großbritannien, dem Heimatland der „British Craftsmanship“ von einer zweistelligen Anzahl von Herstellern toller Autos in den 50er Jahren kein einziges britisches Unternehmen eigenständig überlebt hat, während gleichzeitig Großbritannien für Honda oder BMW ein attraktiver Produktionsstandort ist? Man könnte auch darüber philosophieren, warum etwa in ein und demselben Konzern, ja sogar in ein und demselben Land das eine Konzernunternehmen von Rekord zu Rekord eilt, das andere Unternehmen aber von einer Krise in die nächste schlittert – ich meine im Konkreten die höchst unterschiedliche Entwicklung von Volkswagen und Audi.

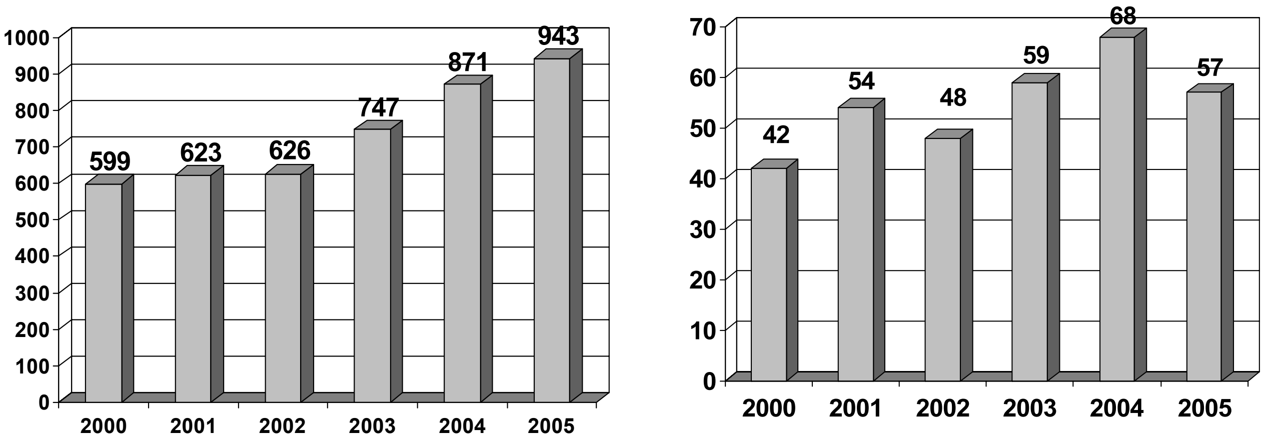
Alle diese Analysen münden letztlich in einer Basiserkenntnis – nämlich dass unternehmerischer Erfolg eine direkte Funktion des Veränderungswillens und der Veränderungsgeschwindigkeit von Unternehmen ist.

Dies lässt sich am Beispiel der Lenzing AG sehr gut zeigen:

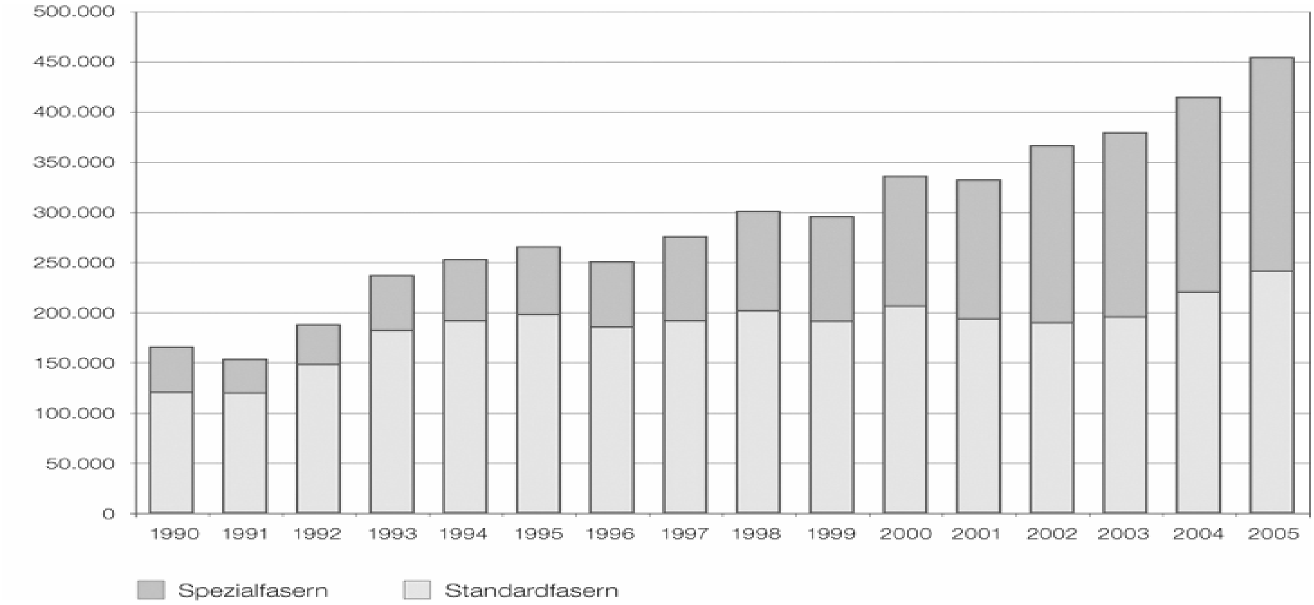
Die Lenzing Gruppe ist Weltmarktführer, eben weil Lenzing rechtzeitig und sehr konsequent den Weg des Wandels gegangen ist. Lenzing hat sich vor allem von einem europäischen Massenprodukthersteller zu einem Nischenplayer entwickelt. Wir stellen heute hochwertige Faserspezialitäten für jeweils ganz spezielle Einsatzgebiete her – Produkte, die schwer austauschbar sind und eine Prämie am Markt gegenüber Commodities erzielen. Zudem haben wir durch unsere Größe und eine attraktive und abgesicherte Rohstoffbasis genügend hohe freie Cashflows erzielt, um sehr konsequent zu internationalisieren. Wir sind heute auf allen Textilfasermärkten präsent, teilweise auch mit eigenen Produktionen. Und Lenzing hat bereits in den 70er Jahren den Trend erkannt, dass die Musik in unserer Industrie künftig in Asien spielen wird. Vielleicht war es auch für Lenzing wichtig, seit den 50er Jahren des vergangenen Jahrhunderts zum Export „verdammt“ gewesen zu sein, da die Produktionskapazität des Stammwerkes Lenzing für die Abdeckung der österreichischen Binnennachfrage schon immer viel zu groß war. Zudem hatte Lenzing rechtzeitig hohe Summen in Umweltschutz investiert und dadurch seine soziale Akzeptanz als führendes österreichisches Industrieunternehmen abgesichert.

Lenzing war in den letzten Jahren äußerst erfolgreich – trotzdem gab es aber die klare Notwendigkeit zu einer weiteren Veränderung. Obwohl Lenzing ein seit Jahrzehnten extrem exportorientiertes Unternehmen war, fehlte Lenzing doch eine konsequente internationale Ausrichtung. Im Kern fühlte sich Lenzing als oberösterreichisches Unternehmen – trotz der starken internationalen Marktpräsenz. Die Organisation war funktional und dezentral. Einzelne Standorte standen am Markt quasi im Wettbewerb gegeneinander. Eine Drehung der Organisation um 90° hin zum Markt wurde eingeleitet. Die konsequent Internationalisierung wurde durch die Akquisition des Konkurrenten Tencel weiter geführt. Mit Tencel erwarb Lenzing nicht bloß zwei Fabriken und die vorhandene Hardware, sondern auch und in erster Linie soft skills wie Marketing Know-how, Marktanteile und mit TENCEL® auch einen wertvollen Brand für die Lyocellfaser. Auch auf der Mitarbeiterebene wurden durch die Änderung des Bonussystems, ABC Analyse und Mitarbeiter-Beurteilung neue Akzente gesetzt.

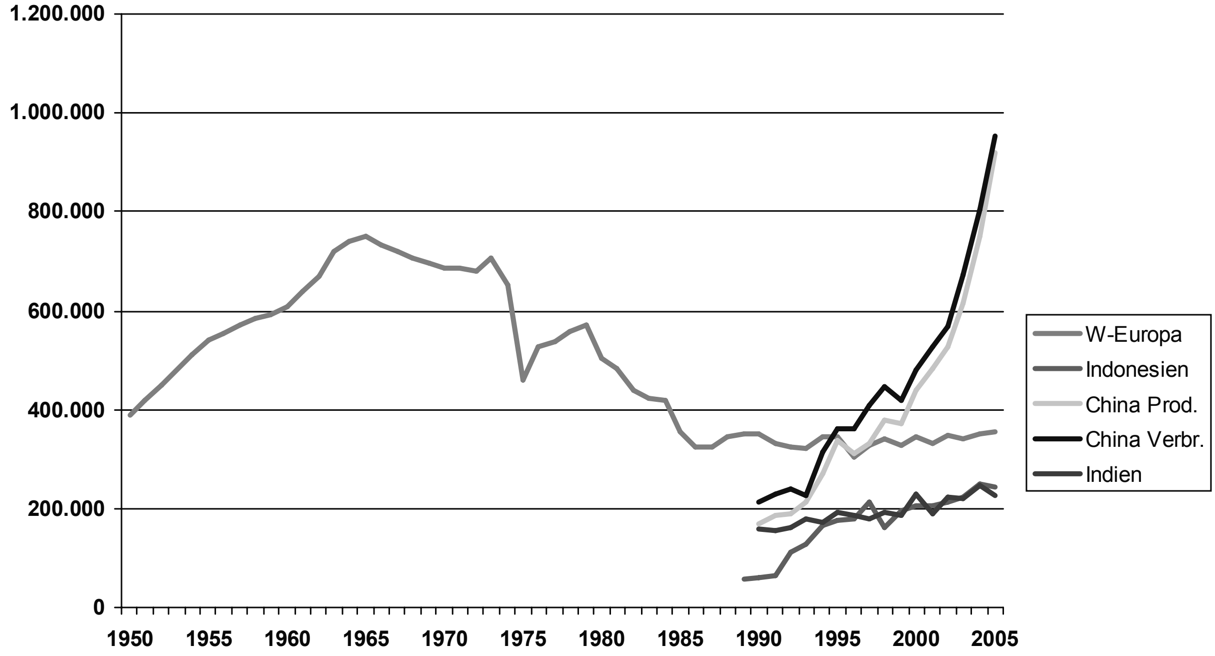
Mit diesen Maßnahmen ist es in den letzen Jahren gelungen, die Lenzing Gruppe in einem äußerst herausforderndem Umfeld zu einem globalen Unternehmen mit einer exzellenten Wettbewerbssituation weiter zu entwickeln.



Grafik 2. Lenzing Gruppe – World Leader in Cellulose Fiber technology / 6 Produktionsstandorte in Europa, USA und Asien / Weltweite Marktpräasenz / Innovationsführer – Technologieführer - Kostenführer



Grafik 3. Lenzing Gruppe Produktionsentwicklung



Grafik 4. Chinas Wachstum stellt alles bisher Dagewesene in den Schatten

Die Entwicklung der weltweiten-Viscosefaserproduktion zeigt, dass das Wachstum Chinas – nicht nur in der Textilindustrie – alles bisher Dagewesene in den Schatten stellt.

Lenzing hat bereits die Weichen gestellt, sich auch dieser neuen Herausforderung erfolgreich zu stellen. Bereits im ersten Quartal 2007 wird eine eigene Viscosefaserproduktion in Nanjing, China mit 60.000 Tonnen erste Mengen für den chinesischen Markt erzeugen.

Als Weltmarktführer und Technologieführer mit einem einzigartigen Kompetenzzentrum für Innovation in Österreich ist die Lenzing Gruppe der einzige global agierende Cellulosefaserproduzent mit Produktionsstätten in allen wichtigen Regionen der Welt. Lenzing vereint als einziges Unternehmen weltweit alle Generationen von Cellulosefasern (Viscose, Modal, Lyocell) unter einem Dach. Lenzing erwartet mittel- bis langfristig einen weltweit steigenden Bedarf an Cellulosefasern, die im oberen Qualitätssegment einen festen Platz innerhalb der Textilfaserwelt erobert haben. Hoher Tragekomfort im textilen Bereich, herausragende technische Eigenschaften im Nonwovensbereich, stete Verfügbarkeit bei gleich bleibender Qualität machen Cellulosefasern zu einem unverzichtbaren Baustein für die Textil- und Nonwovensindustrie. Der wachsende Wohlstand in den Emerging Markets und immer neue Anwendungen im Nonwovens Sektor (Megatrend Gesundheit und Wellness) sind die Wachstumstreiber für unsere Industrie. Das starke Wachstum in den Synthesefasern erzeugt auch für Viscose ein Potenzial als Mischungsfaser. Die Push-Strategie bei den Spezialfasern, die von Lenzing verfolgt wird, wird durch die sinkenden Margen in der Commodity Produktion (Baumwolle, Polyester) unterstützt, das z. T. ausgereizte Innovationspotenzial bei Baumwolle bereitet den Weg für neue Fasern mit Potenzial wie z. B. TENCEL®. Die Textilproduzenten zeigen erhöhte Bereitschaft zur Kooperation, weil sie zur Differenzierung am Markt zusätzliche Verkaufsargumente suchen.

Als großer Player in einer – weltweit gesehen – kleinen Nische ist die permanente Interaktion zwischen den Faserarten (Substitutionspotenzial) Chance und Risiko zugleich. Lenzing wird jedenfalls in Zukunft sehr konsequent den Weg gehen, Chancen aufzuspüren und erfolgreich zu nützen - Getreu dem Motto “Was bleibt, ist die Veränderung; was sich verändert, bleibt.”

Lenzinger Berichte, 85 (2006) 6-8

TEXTILE VISCOSE FILAMENT TECHNOLOGY FROM WESTERN EUROPE:

High Quality - Fine Denier - Specialities

Dr. Moritz Gimpel

ENKA GmbH & Co. KG, Kasinostr. 19-21, GER-42103 Wuppertal, Germany
phone +49 202 322409, fax +49 202 322417, www.enka.de, moritz.gimpel@enka.de

Summary

Four basic technology concepts are applied today to produce the majority of all Viscose Filament Yarn (VFY) worldwide.

Technological developments focus more and more on either “low cost ↔ mass products” or on “high value ↔ demanding quality”.

ENKA’s proprietary production technology satisfies the ever growing market demand for fine deniers with utmost regularity.

Drivers for Viscose Filament Yarn (VFY) Technology

Viscose Filament Yarns for textile applications have been produced for more than 80 years and still display the best available properties in moisture adsorption, colour brilliance, comfort and drape. Future developments of the VFY technologies are driven by two market trends:

- low cost ↔ high volume
- high value ↔ demanding quality.

Those market trends will also lead to differentiated technological concepts. Mass production for **low cost ↔ high volume** has predominantly a focus on the cost drivers:

- Investment & running costs
- Large volume products
- Yield

without neglecting quality and service. Engineering companies are offering complete investment concepts at competitive costs because there is an economy of scale when one machine concept can be offered to numerous companies.

Producers in high wage countries like ENKA are forced to excel on **high value ↔ demanding quality** and consequently developed their proprietary technologies. Key factors for success are highest quality and new products:

- Fluff level
- Evenness of dye affinity
- Fine denier
- Fine denier per filament
- Specialities (e.g. triangular shape)

without neglecting costs, production volumes and yield.

Sensitive Points for VFY Technologies

Filament formation is done in a chemical process in approx. 0.1 second. During this brief moment a multitude of chemical and physical parameters in and around the fibre are determining the optical and mechanical properties. Decisive factors range from chain lengths of the cellulose over dope-viscosity to the concentrations of numerous chemicals.

Equally important are the temperature of the chemicals, the reaction time and the design of the spinning devices [1-2].
Optical properties such as light reflection, dye uptake and brilliance depend on the morphology of the yarn (porosity, skin-core-ratio), which in turn are determined by the chemical parameters during spinning.
Tenacity and elongation are partially a result of the chemical parameters during spinning and also strongly influenced by the stretch ratio between spinneret and winding.

The number of fluffs and breakages of the yarn are decisive for the mechanical processability in weaving, knitting and twisting. This depends on the number of physical defects in individual capillaries which can be introduced during spinning (e.g. by impurities) or during textile after-treatment (abrasive yarn-machine-contacts).

The practical challenge for VFY production is the constancy of all those parameters over time, as this is the precondition for consistent yarn properties within one spool (outer versus inner part of a spool) and from spool to spool.

Basic Technologies Available Today

The processes applied today on large scale can be divided into the following basic technologies [3]:

- Centrifugal or Pot (batch)
- Nelson (continuous)

} Readily available technologies

- Spool (batch)
- Warp Type or CHEV (continuous)

} Proprietary ENKA technologies

The Centrifugal (or Pot) and the ENKA Spool technologies are both discontinuous processes. For all process steps (spinning, washing, drying and winding) optimal processing speed and parameters can be chosen. Disadvantages are the high labour intensity and long processing times.

Centrifugal is the standard batch technology for VFY spinning used all over the world. The limits of the centrifugal technology (control over yarn speed and stretching conditions) can be overcome with the ENKA Spool technology. As a result, coagulation, stretching and the yarn morphology are fully controlled, allowing the manufacturing of fine denier yarns and yarns with superior dye uniformity.

The Nelson and the Warp Type (ENKA CHEV) technologies are both continuous processes with very short cycle times. The Nelson process is very compact needing low space requirements. This results in comparatively low investment costs. But variances of physical and chemical parameters within one machine and between machines are creating variances in physical and dyeing properties of the yarn.

The technically more sophisticated ENKA CHEV process has a parallel yarn treatment. Nearly 500 yarn strands are spun at the same moment, in one machine, under the same physical and chemical conditions, therefore displaying identical yarn to yarn properties.

High Quality

The superiority of the ENKA Spool and Warp Type (ENKA CHEV) technology over standard designs can be demonstrated with the following examples:

Fluff level determines the efficiency during weaving, knitting and twisting, especially when using automated and high speed equipment.

Evenness of dye affinity was always highly esteemed by lining weavers and is now increasingly demanded by circular knitters as it supports just-in-time production.

The practical data of a mass production (2,300 tons of 75 den) at ENKA show the high and constant quality level with respect to fluff level and evenness of dye affinity.

Fine Deniers – Market Driven Solutions

While standard technologies are concentrating on the titer range between 75 and 500 denier, ENKA´s fine denier range covers next to 75 den also 60 den and now even 40 and 30 den. The latter presently marks ENKA´s limit for the large scale production of a flawless yarn (30 den Spool spinning).
Utmost regularity in finest cross sections is the prerequisite for this achievement and only made possible by the advanced spinning technologies of ENKA. It leaves the traditional product range of VFY far behind and penetrates the markets for silk and silk-like products.

The next challenge is the commercial break-through to real micro yarns with denier per filament (dpf) below 1. ENKA actually started deliveries of 75 den f 90 (ENKA CHEV spinning) to customers applying this product in lining fabrics. First reactions are very promising.

Fine dpf such as 75 den f 90 already have quite a history in ENKA. In 2000, ENKA successfully started commercial deliveries in 75 den f 60, followed by first deliveries of 100 den f 90 in 2001.
Fine dpf gives high softness and exclusive touch to garments. Cupro-like fabrics (weaving) and light-weight knitted fabrics are the main applications showing the exquisite touch and luster of this sophisticated yarn.

Steady Growth and Market Success

The steady growth and market success of ENKA’s fine denier and fine dpf products gives testimony to the fact that ENKA’s spinning technology sets the standard for “high value ↔ demanding quality” in the VFY industry.

The World of Specialities in VFY

ENKA actually observes technological trends (e.g. Triangular Yarns) as well as market trends (e.g. Yarn-dyed). But the biggest challenge is posed by the ever increasing demand for fine deniers in VFY displaying the same quality characteristics as the standard yarns.

More than 80 years since its invention, VFY is one of the oldest man made fibres. Despite that respectable history, further progress in spinning technology is to be expected. Main focus will be either on “low cost ↔ high volume” or on “high value ↔ demanding quality” standards. ENKA as the leading European producer for VFY will further push technological barriers of its proprietary technologies to offer new and exciting products.

References

[1] Ullmann´s Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A 5 (1986) 402 – 412.

[2] Nevell, T.P.; Zeronian, S.H. (Editors) *Cellulose Chemistry and its Applications*, Halsted Press, New York, (1985) 20 – 28.

[3] Gimpel, M.; Progress in Viscose filament Yarn Technology, *Presentation on the China MMF Conference* (2004).

Lenzinger Berichte, 85 (2006) 9-16

PRODUKTAUSZEICHNUNG "TRAGEKOMFORT" AM POINT OF SALE

Prof. Dr. K.H. Umbach

Hohensteiner Institute, D- 74357 Bönnigheim, Deutschland
Tel.: +49-(0)7143-27166; Fax: +49-(0)7143-27175; e-mail: kh.umbach@hohenstein.de

Tragekomfort als Verkaufsargument

Im heutigen "High-Tech"- und "Smart Clothes"-Zeitalter stellt der Kunde zahlreiche Anforderungen an Bekleidung und insbesondere an Sportbekleidung. Für die Entscheidung zum Kauf spielen längst nicht mehr nur Modeaspekte oder Kriterien der Haltbarkeit eine Rolle, sondern immer mehr die Funktion, insbesondere die physiologische Funktion, die häufig als "Tragekomfort" bezeichnet wird. Dies ist der Branche bekannt: In einer repräsentativen Umfrage der Fachzeitschrift "TextilWirtschaft" gaben 93 % der Einzelhändler der Sparten Damen-, Herren- und Kinderbekleidung, Wäsche und Sportbekleidung an, daß Funktion ein gutes Verkaufsargument liefert. Besonders die Klimaregulierung und der Feuchtigkeitstransport (= Tragekomfort) wurden von 81 % der befragten Einzelhändler als wichtige Hilfen beim Verkauf eingestuft; 75 % waren der Meinung, daß mit Funktion höhere Preise realisiert werden können.

Indessen kann Tragekomfort weder vom Verkäufer definiert noch vom Kunden durch bloße Anprobe des Kleidungsstücks im Laden beurteilt werden. Insbesondere Sportbekleidung beweist ihre wahre physiologische Qualität erst beim praktischen Benutzen/Tragen bei spezifischer sportlicher Aktivität oder bei extremen Klimabedingungen. Deshalb müssen Händler sowie Textil- und Bekleidungshersteller folgende Fragen stellen:

Wie kann "Tragekomfort" von Bekleidung objektiv ermittelt werden?

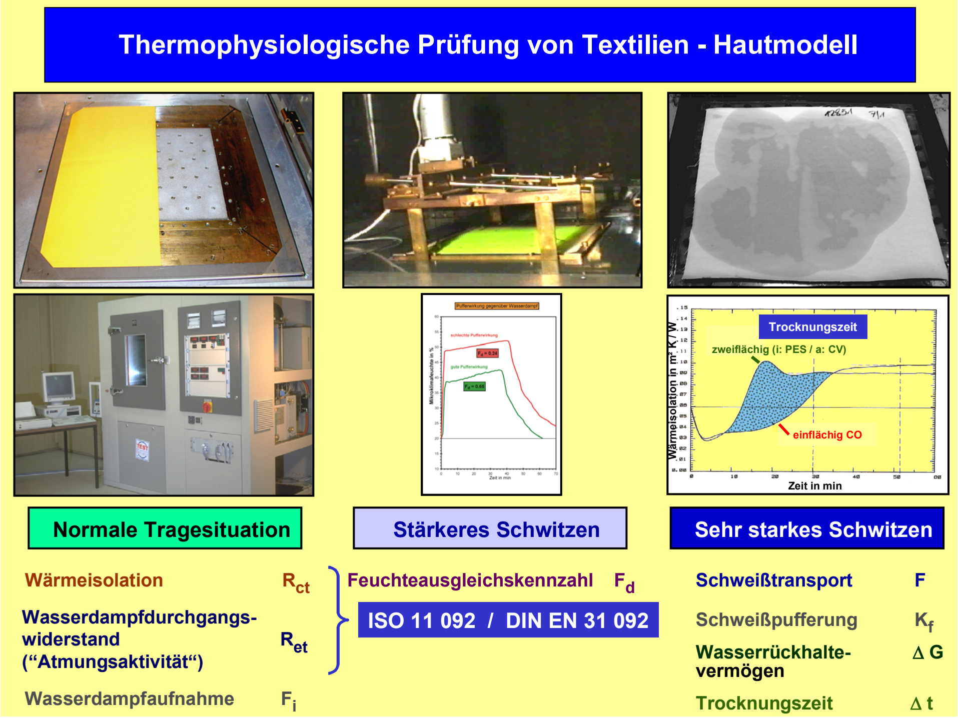
Wie kann "guter Tragekomfort" von Bekleidung den Kunden am Point of Sale (POS) bewiesen werden?

Quantitative Messung des Tragekomforts

Heute kann Tragekomfort deshalb gemessen werden, weil er nicht eine rein individuelle und somit überwiegend undefinierbare Empfindung ist, sondern die quantifizierbare Folge der Interaktion Körper-Klima-Kleidung. Was eine Person als "Tragekomfort" registriert, wird zum einen durch die thermophysiologische Funktion der Kleidung oder des Textils bestimmt, d.h. von deren Wärme- und Feuchtigkeitstransport. Zum anderen spielen sensorische Empfindungen eine Rolle, die vom mechanischen Kontakt des Textils mit der Haut hervorgerufen werden.

Der **thermophysiologische Tragekomfort** von Textilien wird mit dem Thermoregulationsmodell der menschlichen Haut (Hautmodell) ermittelt. Es besteht aus einer elektrisch beheizten, porösen Metallplatte, der Wasser zugeführt wird und die in einen Klimaschrank mit variierbarer Temperatur, Luftfeuchtigkeit und Luftbewegung eingebaut ist (s. Abbildung 1). Das Hautmodell simuliert die Wärme- und Feuchteabgabe der Haut. Letztere kann differenziert werden zwischen "normalen" Tragesituationen mit wenig Schwitzen und Situationen mit erhöhtem bzw. sehr starkem Schwitzen. Für jede dieser 3 Situationen liefert das Hautmodell (internationaler Standard ISO 11 092 und EN 31 092) spezifische Kenngrößen, z.B. Wärmeisolation, Wasserdampfdurch-gangswiderstand als Maß für die "Atmungsaktivität", Schweißtransport und Schweißpufferung, Trocknungszeit etc.

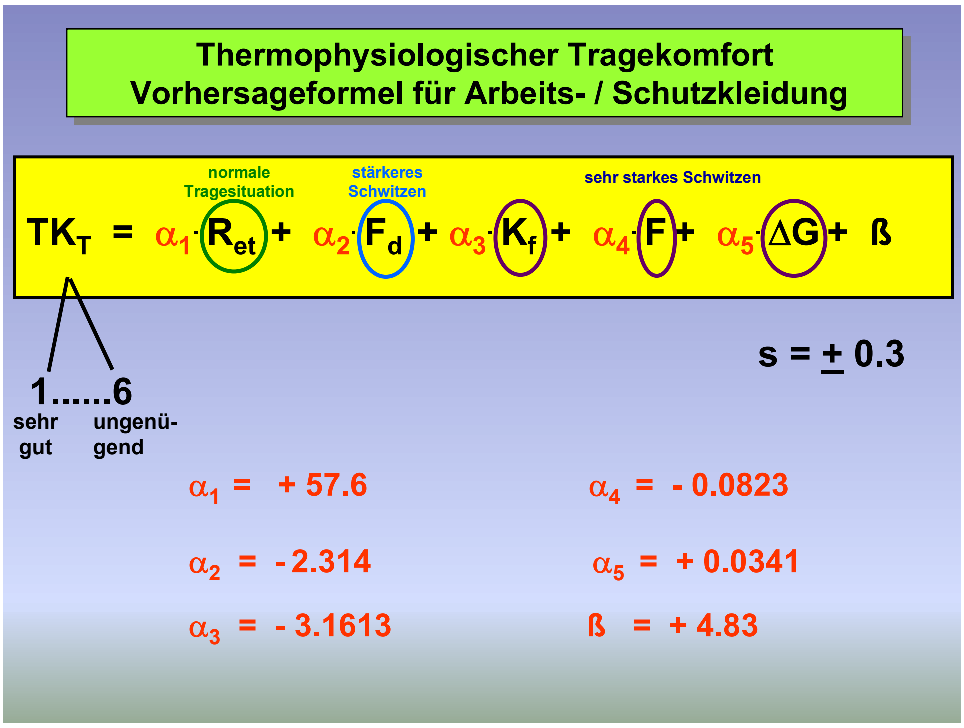
Diese Kenngrößen charakterisieren die thermophysiologische Qualität der Textilien. Als Ergebnis langjähriger grundlegender Forschung können sie in eine thermophysiologische Tragekomfortnote TK_T umgerechnet werden, die zwischen 1 "sehr gut" und 6 "ungenügend" liegen kann (s. Abbildung 2).



Thermophysiologische Prüfung von Textilien - Hautmodell

Normale Tragesituation		Stärkeres Schwitzen		Sehr starkes Schwitzen	
Wärmeisolation	R_{ct}	Feuchteausgleichskennzahl	F_d	Schweißtransport	F
Wasserdampfdurchgangswiderstand (“Atmungsaktivität“)	R_{et}	ISO 11 092 / DIN EN 31 092		Schweißpufferung	K_f
				Wasserrückhaltevermögen	Δ G
Wasserdampfaufnahme	F_i			Trocknungszeit	Δ t

Abbildung 1



Thermophysiologischer Tragekomfort
Vorhersageformel für Arbeits- / Schutzkleidung

normale Tragesituation — stärkeres Schwitzen — sehr starkes Schwitzen

$$TK_T = \alpha_1 \cdot R_{et} + \alpha_2 \cdot F_d + \alpha_3 \cdot K_f + \alpha_4 \cdot F + \alpha_5 \cdot \Delta G + ß$$

1......6
sehr gut — ungenügend

s = ± 0.3

α_1 = + 57.6
α_2 = - 2.314
α_3 = - 3.1613
α_4 = - 0.0823
α_5 = + 0.0341
ß = + 4.83

Abbildung 2

Der **hautsensorische Tragekomfort** von Textilien wird hauptsächlich durch deren Oberflächen-struktur bestimmt. Dafür werden relevante Kenngrößen mit speziellen Meßgeräten gemessen, u.a. der Klebekraftapparatur (s. Abbildung 3). Hier simuliert eine poröse gesinterte Glasplatte, der Wasser mittels einer Motorbürette zugeführt wird, die schwitzende Haut. Die Textilprobe, befestigt an einem Zylinder, wird über die Platte gezogen, und die dafür notwendige Zugkraft wird gemessen. Sie ergibt den "Klebeindex". Damit kann beurteilt werden, ob das Textil beim Schwitzen unangenehm an der Haut kleben wird.

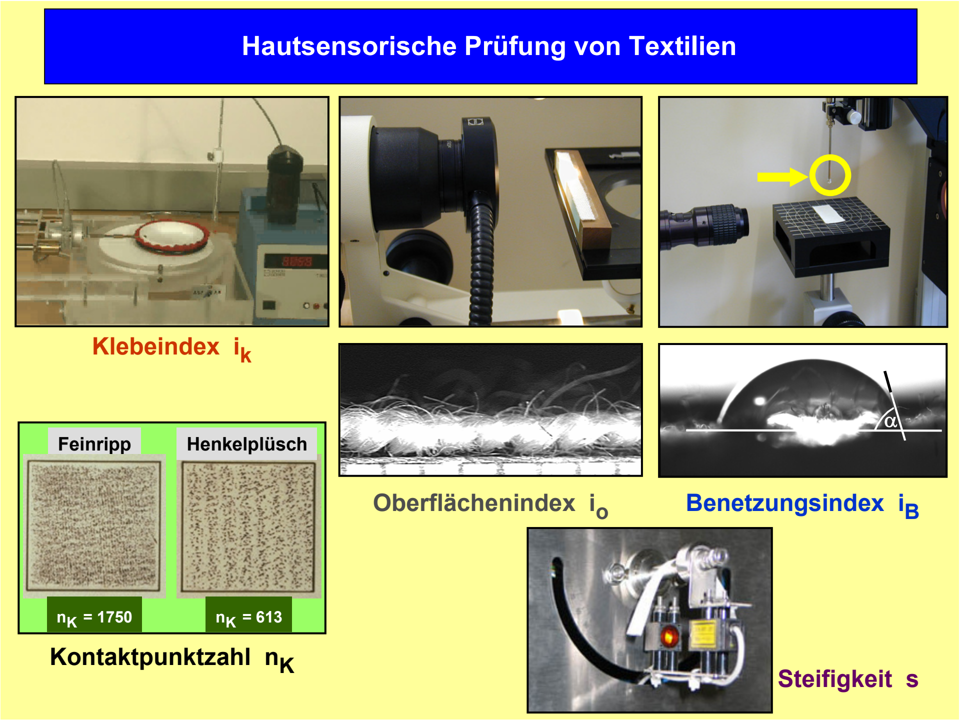
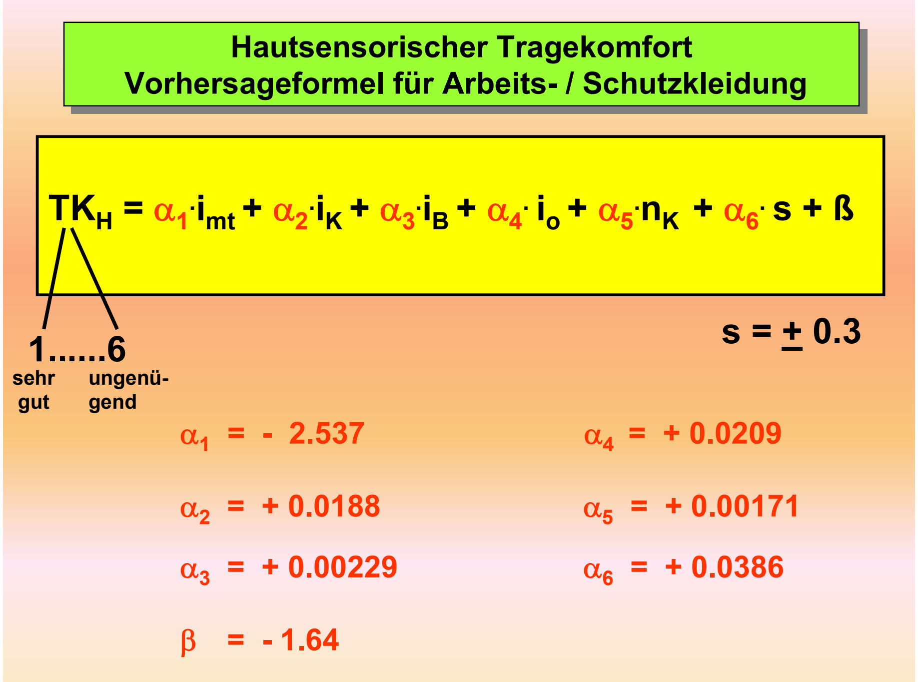


Abbildung 3

An einen Oberflächenscanner bzw. ein Mikroskop angekoppelte Bildanalysesysteme zeigen für die Textilien die "Kontaktpunktzahl" sowie einen "Oberflächenindex" als Maß für die Kontaktfläche mit der Haut bzw. die Haarigkeit der Oberfläche. Des weiteres wird die Steifigkeit des Stoffes aus dem Biegewinkel eines auf einem Pin plazierten Probestreifens abgeleitet, der von einem Laserstrahl abgetastet wird.

Weil die Sensibilität der Haut für mechanische Irritationen mit zunehmender Feuchtigkeit größer wird, ist es für den sensorischen Tragekomfort von Vorteil, wenn das Textil den Schweiß möglichst rasch von der Haut abtransportiert. Diese Eigenschaft wird durch einen "Sorptionsindex" quantifiziert, d.h. die Geschwindigkeit, mit der ein auf das Textil auftreffender Wassertropfen von diesem absorbiert wird.

Diese charakteristischen Kenngrößen werden in einer Vorhersageformel in eine sensorische Komfortnote TK_H umgesetzt (s. Abbildung 4). Zusammen mit der vorstehend erläuterten thermo-physiologischen Note kann damit eine umfassende Tragekomfortnote TK angegeben werden, die das insgesamte subjektive Komfortempfinden des Trägers ausdrückt. Dies ist möglich, da Forschungsarbeiten gezeigt haben, daß die Tragekomfortempfindung zu ca. 66 % durch die thermophysiologischen und zu ca. 34 % durch die hautsensorischen Eigenschaften der Textilien verursacht wird.



Hautsensorischer Tragekomfort
Vorhersageformel für Arbeits- / Schutzkleidung

$$TK_H = \alpha_1 \cdot i_{mt} + \alpha_2 \cdot i_K + \alpha_3 \cdot i_B + \alpha_4 \cdot i_o + \alpha_5 \cdot n_K + \alpha_6 \cdot s + \text{ß}$$

1……6
sehr gut … ungenügend

$s = \pm 0.3$

$\alpha_1 = -\ 2.537$

$\alpha_2 = +\ 0.0188$

$\alpha_3 = +\ 0.00229$

$\beta = -\ 1.64$

$\alpha_4 = +\ 0.0209$

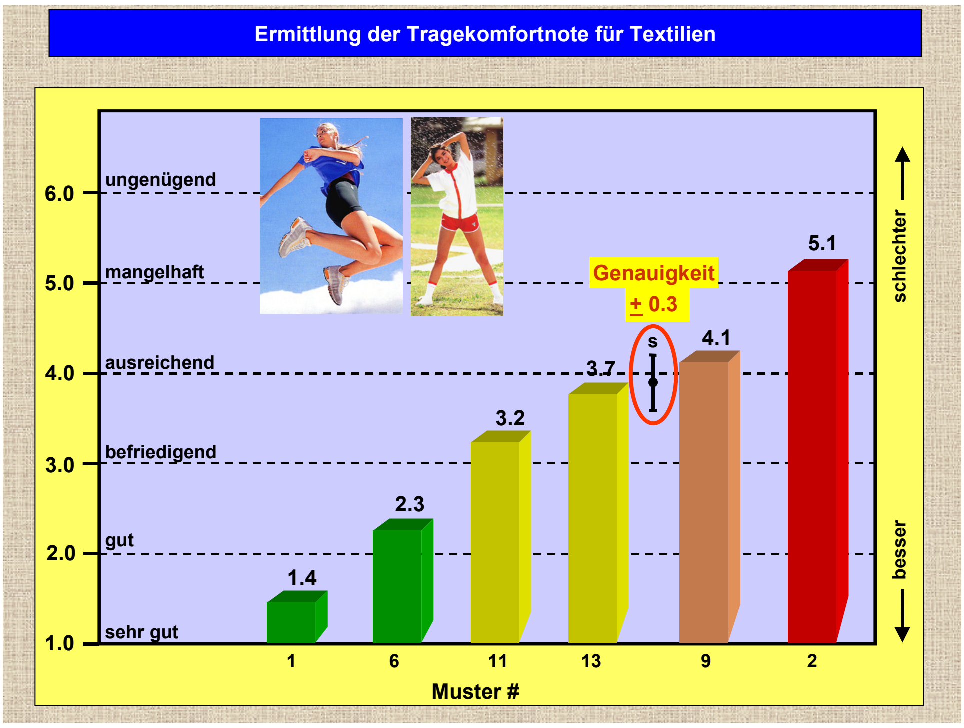
$\alpha_5 = +\ 0.00171$

$\alpha_6 = +\ 0.0386$

Abbildung 4

Heute können mit diesen Vorhersageformeln für den Tragekomfort Web- und Maschenwaren für Alltags-, Freizeit- und Sportbekleidung sowie für Arbeits- und Schutzbekleidung bewertet werden (s. Abbildung 5).

Zahlreiche Trageversuche mit Testpersonen, sowohl in Klimakammern als auch im Alltag oder am Arbeitsplatz, haben gezeigt, daß die mit dem Hautmodell und den sensorischen Apparaturen ermittelte Tragekomfortnote eines Textils mit einer hohen Genauigkeit (Standard-Abweichung s) von ca. ± 0.3 Notenstufen mit dem von Probanden subjektiv ausgedrückten Komfortempfinden übereinstimmt.



Ermittlung der Tragekomfortnote für Textilien

Abbildung 5

Hohensteiner Qualitätslabel

Tragekomfort kann also mit hoher Präzision objektiv gemessen werden. Damit läßt sich die o.g. Frage beantworten, wie man "guten Tragekomfort" von Bekleidung den Kunden am Point of Sale (POS) beweisen kann.

Schon heute existieren für die Bereiche Schutz- und Arbeitsbekleidung zahlreiche nationale und internationale Normen sowie Lieferbedingungen, in denen bekleidungsphysiologische Anforderungen spezifiziert sind, die erfüllt werden müssen, damit die Bekleidung den gesetzlichen Unfallverhütungsvorschriften entspricht. Die Norm DIN 10 524 z.B. fordert für Arbeitsbekleidung, die in Lebensmittelbetrieben aus hygienischen Gründen zu tragen ist, daß sie außer einer akzeptablen "Atmungsaktivität" eine thermophysiologische und hautsensorische Tragekomfortnote von jeweils mindestens 3 ("befriedigend") aufweisen muß.

Offensichtlich ist bezüglich einer ausreichenden physiologischen Funktion von Schutz- oder Arbeitsbekleidung schon viel erreicht worden. Allerdings gibt es für den gesamten Bereich der Alltags-, Sport- und Freizeitbekleidung keine Regelungen, welche die objektive Darstellung der für den Träger spürbaren Funktion "Tragekomfort" verbindlich vorschreiben. Ein hervorstechendes Beispiel dafür ist der Mißbrauch, der vielfach im Handel mit dem Begriff der "Atmungsakti-vität" getrieben wird. Zahlreiche Kleidungsstücke, die als "atmungsaktiv" bezeich-net werden, bestehen einen diesbezüglichen objektiven Test nicht. Die Folge davon ist, daß der Kunde zuneh-mend irritiert und enttäuscht wird, den Marketingaussagen generell nicht mehr glaubt und so möglicherweise mit Kaufenthalt reagiert.

Aus diesem Grund haben die Hohensteiner Institute ein Qualitätslabel kreiert, das in einheitlicher Gestaltung entweder als Hangtag am Produkt, auf Verpackungen oder in Informations- und Werbebroschüren eingesetzt werden kann. Dieses Qualitätslabel ist für die folgenden Produkteigenschaften erhältlich:

- Tragekomfortnote (für Bekleidung) oder physiologische Komfortnote (für Bettwäsche)
- Atmungsaktivität
- Physiologischer Komfort (für Bandagen)
- Antistatik
- Schlafkomfortnote (für Steppbetten)

Qualitätslabel "Tragekomfort"

Das Qualitätslabel "Tragekomfortnote" (s. Abbildung 6) kann für unterschiedliche Bekleidungs-arten wie z.B. Sportkleidung, Alltags- und Freizeitwäsche, Hemden und Blusen, Herrenanzüge, Damenkostüme sowie Arbeits- und Schutzbekleidung eingesetzt werden. Die auf dem Label mit Verweis auf das entsprechende Prüfzeugnis dargestellte Note resultiert aus der Gesamtheit der oben beschriebenen Messungen mit dem Hautmodell und den hautsensorischen Apparaturen, deren Resultate in die für diese unterschiedlichen Kleidungstypen jeweils gültigen Berechnungs-formeln eingesetzt werden. Der Zahlenwert der Tragekomfortnote wird auf dem Label verbal nach der in Abbildung 6 wiedergegebenen Klassifizierung mit "sehr gut", "gut" etc. bewertet.

Abbildung 6

Sinngemäß wird für Bezüge für Steppbetten und Kopfkissen sowie für Bettwäsche das Label "Physiologische Komfortnote" angeboten. Diese wird wie bei Kleidung mit derselben verbalen Bewertung aus den Messungen mit dem Hautmodell und den hautsensorischen Apparaturen ermittelt.

Qualitätslabel "Atmungsaktivität"

Das Hohensteiner Qualitätslabel "Atmungsaktivität" wurde für Wetterschutz-, Outdoor-, Reinraum- und Operationskleidung sowie für Encasings für Matratzen und Bettdecken für Hausstaubmilben-Allergiker geschaffen. Für dieses Label ist der Prüfaufwand wesentlich weniger aufwendig als für das informativere Tragekomfort-Label. Ersteres erfordert lediglich die Messung des Wasserdampfdurchgangswiderstandes R_{et} mit dem Hautmodell nach ISO 11 092 bzw. EN 31 092. Z.B. ist bei Wetterschutz- bzw. Outdoor-Kleidung das Kriterium für das Label erfüllt, wenn der R_{et}-Wert nicht über 13 m²Pa/W liegt und damit eine mindestens "gute" Atmungsaktivität ausweist.

Qualitätslabel "Antistatik"

Das Auftreten elektrostatischer Aufladungen an der Kleidung ist ein sehr störender Qualitätsmangel. Mit dem Label "Antistatik" kann bewiesen werden, daß die Kleidung ein gutes elektrostatisches Verhalten besitzt. Es ist für dieselben Artikelgruppen vorgesehen, bei denen auch das Label "Tragekomfortnote" eingesetzt werden kann. Für Alltags-, Freizeit- und Sportbekleidung wird das "Antistatik"-Label vergeben, wenn deren spezifischer Oberflächen- und Durchgangswiderstand P bzw. R_V unter den in Abbildung 7 angegebenen kritischen Werten liegen, die entsprechend der europäischen Norm EN 1149 Teile 1 und 2 gemessen werden.

Hohensteiner Qualitätslabel "Antistatik"

Vergabekriterien Alltags- / Freizeit- / Sportwäsche

GEPRÜFTE QUALITÄT
HOHENSTEINER INSTITUTE
MUSTER GEPRÜFT AUF:
☑ ANTISTATIK
PRÜF-NR.: FI 03.4.XXXX

Spezifischer Oberflächenwiderstand

Durchgangswiderstand

$P \leq 2 \cdot 10^{12}$ Ohm

$R_V \leq 1 \cdot 10^{11}$ Ohm

Prüfungen : EN 1149 - 1 / 2

Abbildung 7

Qualitätslabel "Schlafkomfort"

Auch bei Bett- bzw. Steppdecken ist der resultierende Schlafkomfort gleichbedeutend mit deren physiologischer Funktion, d.h. deren Fähigkeit, die physiologischen Vorgänge im Körper zu unterstützen. Am wichtigsten dabei ist, wie bei der Bekleidung, die Temperaturregelung des Körpers und das Feuchte- und Wärmemanagement innerhalb der "Schlafhöhle" unter der Decke. Ersteres wird wiederum mit dem Hautmodell geprüft. Für letzteres wird eine in der internationalen Norm ISO 15 831 spezifizierte thermische Gliederpuppe eingesetzt, welche die für den Schläfer effektive Wärmeisolation der Decke mißt und diese in eine von 3 Wärmeisolationsklassen einteilt.

Hohensteiner Qualitätslabel "Schlafkomfortnote"

Vorderseite

GEPRÜFTE QUALITÄT
HOHENSTEINER INSTITUTE
MUSTER GEPRÜFT AUF:
☑ SCHLAFKOMFORTNOTE
Warmes Klima : 1.2 (SEHR GUT)
Kaltes Klima : 1.7 (GUT)
PRÜF-NR.: FI 03.4.48XX

Rückseite

GEPRÜFTE QUALITÄT
HOHENSTEINER INSTITUTE
MUSTER GEPRÜFT AUF:
☑ WÄRMEISOLATION
Klasse 2
**
PRÜF-NR.: FI 03.4.48XX

1.0 - 1.5 : sehr gut
1.6 - 2.5 : gut
2.6 - 3.5 : befriedigend
\> 3.5 : mangelhaft

Prüfungen : ISO 11 092 / BPI 1.2

Prüfung : ISO 15 831

Bettdecken

Abbildung 8

Wie gut das Feuchtemanagement der Bettdecke ist, wird durch die zwei auf dem Qualitätslabel angegebenen Schlafkomfortnoten gezeigt (s. Abbildung 8). Die eine Note gilt bei warmem Umgebungsklima, die andere bei kaltem Klima. Welche dieser beiden Noten für den einzelnen Kunden wichtiger ist und welche Wärmeisolationsklasse er benötigt, kann einem Diagramm entnommen werden, das im Verkaufsraum ausgestellt ist. Dieses Diagramm berücksichtigt zum einen das Körpergewicht des Kunden und zum anderen die Temperatur in seinem Schlafzimmer. Soll eine Bettdecke ganzjährig bei variierenden Umgebungstemperaturen verwendet werden, müssen beide Komfortnoten möglichst gut ausfallen.

Nutzung des Hohensteiner Qualitätslabels

Das Hohensteiner Qualitätslabel wurde für Textil-, Bekleidungs- und Bettdeckenhersteller, für Groß- und Einzelhändler für ihre Produktpräsentationen am POS sowie für die Werbung kreiert. Eine weitere Zielgruppe sind Einkaufsabteilungen z.B. von Krankenhäusern oder Hotels, die das Qualitätslabel zum Bestandteil ihrer Lieferbedingungen machen können.

Um das Label einzusetzen, das in mehreren Sprachen verfügbar ist, muß mit den Hohensteiner Instituten ein im allgemeinen zeitlich unbefristeter Nutzungsvertrag abgeschlossen werden. Mehrere Produkte können in einen Vertrag einbezogen werden, für den eine einmalige Gebühr erhoben wird. Voraussetzung für die Nutzung des Labels ist, daß die darin eingeschlossenen Artikel die für die jeweilige Labelart erforderlichen Vergabekriterien erfüllen, nachgewiesen durch entsprechende Prüfzeugnisse der Hohensteiner Institute. Die dafür notwendigen Prüfungen in den Hohensteiner Labors sind nur einmal und nur an einer Farbe des jeweiligen Artikels erforderlich. Wiederholprüfungen sind nicht vorgesehen, solange das jeweilige Produkt unverändert hergestellt wird. Als Teil des Vertrages wird von dem Hersteller gewährleistet, daß diese Konformität mit dem Prototyp eingehalten wird. Erfolgen jedoch Konstruktionsänderungen, z.B. hinsichtlich Fasermaterial, Bindung, Flächengewicht oder Ausrüstung etc., muß ein neues Prüfzeugnis eingeholt sowie ein neuer Nutzungsvertrag für das Label abgeschlossen werden.

Seit seiner Einführung wird das Hohensteiner Qualitätslabel, das inzwischen als Europäische Bildmarke eingetragen ist, von zahlreichen Firmen bei ihrer Produktpräsentation eingesetzt. Sie haben erkannt, daß dieses Qualitätslabel als Beweis guter physiologischer Funktionen und damit eines Mehrwertes des Produktes am POS für den Hersteller wie auch den Handel die folgenden Vorteile bringt:

- wissenschaftlich belegte und objektive Argumente anstelle von reinen Marketingaussagen,
- einfachere Beratung des Kunden,
- beweisbare Darstellung des Preis-/Leistungsverhältnisses,
- Hilfe für den Verkauf hochwertiger und auch hochpreisiger Produkte.

Dem Kunden gibt das Qualitätslabel die Sicherheit, ein physiologisch funktionierendes Produkt zu kaufen, das auf seine Bedürfnisse abgestimmt ist. Mit zufriedenen Kunden gibt es auch weniger Beschwerden bei Einzelhändlern und Herstellern.

Lenzinger Berichte, 85 (2006), 17-21

CLOTHING EFFECT ON SELECTED PARAMETERS OF OXIDATIVE STRESS

Małgorzata Zimniewska [a], Henryk Witmanowski [b], Ryszard Kozłowski [a]

[a] Institute of Natural Fibres, Poznań, POLAND;
[b] Department of Physiology, University of Medical Sciences, Poznań, POLAND

Abstract

The purpose of this study was evaluating the effect of two types of clothes – linen and polyester on thermo-physiological responses during rest and light exercise. The experiment comprised 8 hours of rest, 20 minutes of exercise on cycloergometer on the level 75 W and rest until full restitution (stabilization of blood pressure and pulse). The basic index of oxidative stress - total antioxidant status, was investigated.

Six healthy, adult males aged 19 – 23 volunteered as subject in this study. Investigation was performed in climatic chamber at air temperature of 20^0 C +/- 2^0 C, relative humidity 50%+/- 2% and air movement less than 0.5 m/s. The fabric structure of both clothes samples was the same.
The results of experiment show that level of total antioxidant status on linen clothes was better than on polyester especially during higher sweating rate conditions.

Introduction

The wear is inseparable requisite in a human's whole life, whether during a day when we are active or at night when we rest. By direct contact with a skin it has a continuous, dynamic and complex effect on our organism. The clothes responsible for a proper microclimate in the area skin-wear should guarantee a perfect comfort and health by ensuring an optimal use comfort.

Today a comfort is a key parameter in wear science. Generally, the comfort is a neutral state, free from pain and discomfort [1]. It is a physiological feeling and a user's opinion in combination of physical activity and atmospheric conditions tightly connected with psychological acceptance of given clothes.

The comfort is very important for the greater part of users. It is visible on the fig. 1, which shows some results from a study on the perceptions of the importance of various attributes of clothing worn at the work place, which covered a number of national groups from Europe, Asia and Australia.

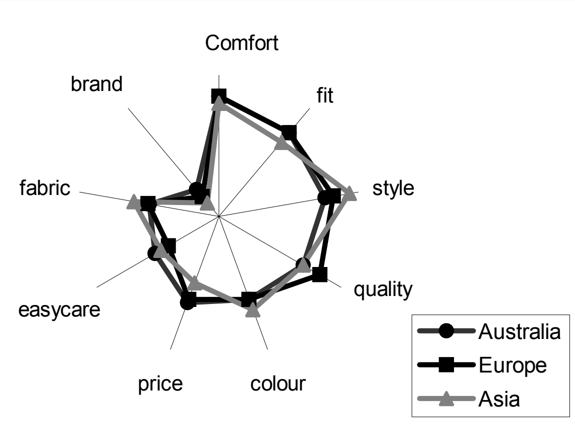


Figure 1. Consumers' requirement of clothing (Y.Li. Wool Sensory Properties and Product Development, Textile Asia, 1998, Vol. XXIX, 5)

The comfort is connected with many complex processes:

1. **Physical processes**
    - visual stimulation – color, light,
    - thermal stimulation – heat and moisture transport,
    - mechanical pressure on the skin,
    - touch stimulation.

2. Physiological processes

- sensory responds of nerve ending to the thermal stimulation, pressure, pain,…
- thermoregulation – sweating, control of blood pressure,…

3. Psychological processes

- sensations of combination of different stimuli – the value and importance of that sensation,

4. General perception – sensation of a state: comfort/discomfort

The effect of wear on human's body is conditioned by a differentiated structure of the skin. The skin has two layers: the outer layer – the epidermis and an inner layer – the dermis, containing among others nerve ends, ducts of sweat gland, hair follicles, muscle filaments, etc

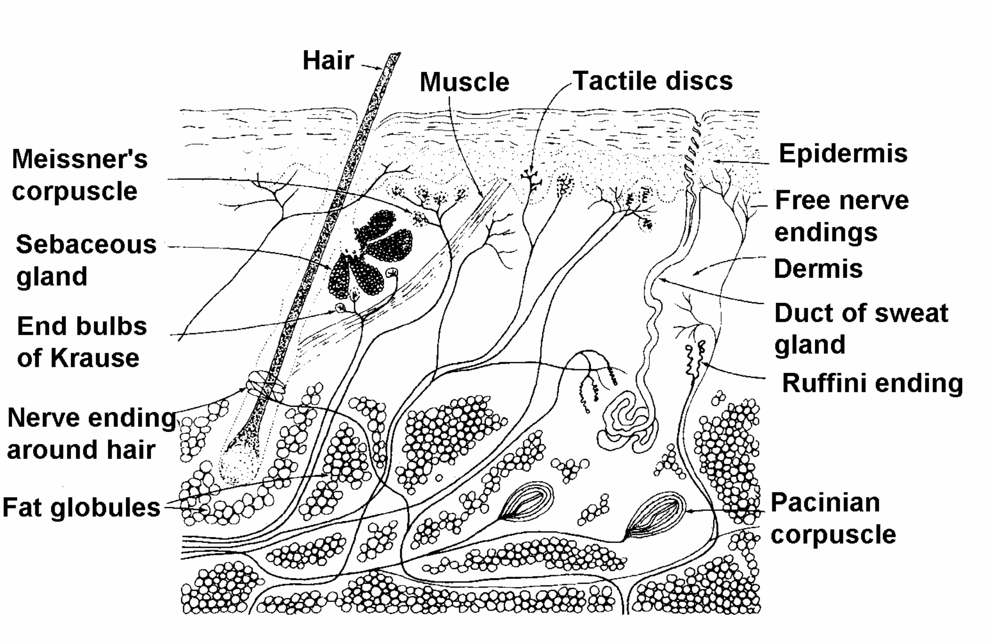


Figure 2. Structure of skin. Source: Y. Li, The Science of Clothing Comfort. [1]

Descriptions to the Fig. 2:

- Meissner's corpuscles or sensory corpuscles (one of the touch receptors) – are the typical touch receptors
- End bulbs of Krause – considered to be the receptors of decreasing temperature of the environment (feeling of cold),
- Pacinian corpuscle – receptors of pressure
- Ruffini endings – there are a lot of disputes on the physiological function of that organ. Traditionally they are considered to be heat receptors. According to some opinions, however, they are a mechanical receptors of touch (feeling of pressure),
- free nerve endings are the simplest and most common form of feeling receptors,
- tactile discs (Merckle tactile discs) – touch receptors

The nerve ends collect the stimuli from skin exposed to clothes and send the information to the brain. This way they stimulate certain processes in human's body.

The sensory comfort is the most intensively perceived element of complex effect of wear on human's body. They are accompanied, however, also by processes that are perceived indirectly and still having an effect on our health.

The paper gives results of studies on the effect of raw material used for production of clothes on the oxidative stress, which is the cause or is found in many diseases. The cause of oxidative stress effect are reactive oxygen species (ROS) [3], especially free radicals, which damage all main components of a cell and show the mutagenic effect. This may be a cause of a cancer. The oxidative stress is observed in situations when cells, tissues or organisms are exposed to additional sources of reactive oxygen species (ROS), ozone, ionizing radiation, cigarette smoke, etc. The cells under stress are not defenseless; the cell is subjected to many adaptation reactions like increase of anti-oxidant concentration and activating enzymes protecting against ROS [2].

Materials and methods

The natural raw materials, including flax, are in all aspects human friendly. They are environmental friendly and guarantee the optimal comfort in use. From the very beginning of human history they serve to man protecting from the unfavorable elements of the environment providing a perfect comfort. The synthetic fibers introduced at the end of 20th century as easier to maintenance had been uncritically accepted, despite they cannot match natural fibers in respect of comfort. However, the question is whether the clothes made of natural fibers provide only a better comfort, or they also have better effect on our health as compared to synthetic clothes. The research has been conducted at the Institute of Natural Fibres in cooperation with the University of Medical Sciences in Poznań, that would attempt to answer that question.

The linen garments represent the natural wear, while synthetics are represented by polyester (PES is the most commonly used synthetic fiber in wear production) garments. The tested materials were men's shirts made of the mentioned above raw materials. They were similar in respect of the model, geometrical form and made in suitable sizes.

The characteristics of chosen metrological parameters of tested fabrics are presented in Table1.

Table 1.

Material	Surface density [g/m^2]	Hygroscopicity		Surface resistance [Ω]	Air Permeability [l/m^2/s]	Thermal conductivity [W/mK]	Heat diffusion [m^2/s]	Heat resistance [Km^2/W]
		at 65% humidity	at 100% humidity					
100% linen	191.6	9.3	17.1	$1.5\text{x}10^{11}$	597	40.3	0.108	14.8
100% PES	90.1	1.0	1.3	$6.5\text{x}10^{9}$	124	38.6	0.050	5.4

The high level of air permeability and heat diffusion of linen fabrics guarantees the right ventilation, removal of excess CO_2 and water vapor from the skin area, which allows for sustaining of the proper temperature of the body. On the other hand, higher level of heat resistance proves that linen better protects against cold as compared to tested polyester fabric. Linen, unlike polyester does not collect the electrostatic charges on the surface. The excellent hygroscopicity of linen fabrics in both 65% and 100% of air humidity means that the sweat will not drain down on the one's back when wearing linen shirt.

The tests were conducted on 6 healthy, untrained, similarly built males of the age 19-23 years of age. The control group was people wearing linen garments, the tested group were the same people wearing polyester clothes. The people stayed in specially adopted climatic chamber (Laboratory of Physiological Testing at the INF) in temperature 20 °C and relative humidity 50 % and air movement smaller than 0.5 m/s.

The tests were conducted in rest – 8 hours, moderate physical exercise – 20 min, and after post-exercise restitution (until blood pressure and pulse was stabilize). The physical activity was on the level of 75 W using the cyclometer (Hellige).

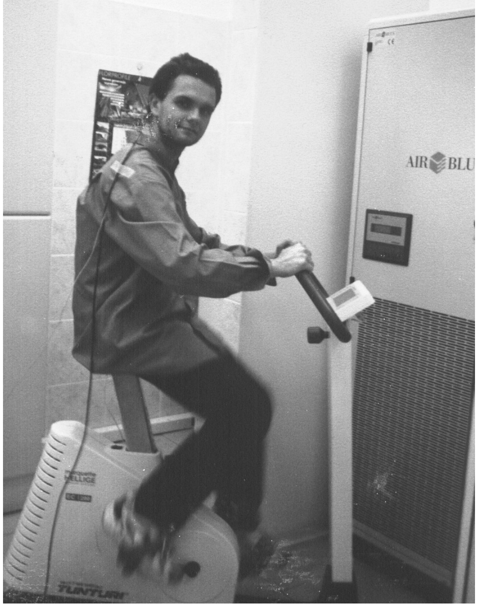


Figure 3. The physical activity with using the cyclometer

In the period before rest, before exercise, after exercise and after restitution, the physiological parameters were tested and blood samples for biochemical assessment ware taken. TAS - total antioxidant status was measured using colorimetric method (Randox Laboratories Ltd. GB). The authors of the study have a permission of the Bioethical Commission at the University of Medical Sciences in Poznan for conducting those tests.

Results and discussion

The aim of the tests was to find the answer to the question, whether staying in different kinds of wear in given conditions, during the rest or exercise may be the cause of the oxidative stress and how the organism defense mechanisms change.

One of the ways to test the ability of the organism to defense itself against the reactive oxygen species is to determine so called total antioxidant status (TAS) [4]. This parameter informs about total ability of tissues to neutralize exactly determined amount of reactive oxygen species.

The results of TAS level testing in people wearing linen and polyester clothes in controlled conditions are shown in figure 4.

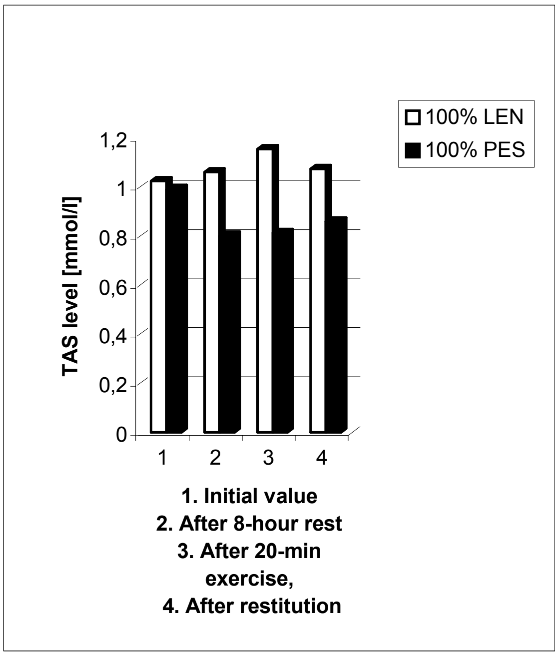


Figure 4. The TAS level in people wearing linen and PES

The results show that the TAS value is lower for individuals wearing PES for 8 hours as compared to linen. The difference is considerable bigger after moderate exercise. Similarly TAS is higher in individuals wearing linen after post-exercise restitution.

Obtained results may show that the antioxidative reserves are over, resulting from increased amounts of ROS in individuals wearing PES. It is supposed that the polyester wear may cause higher production of ROS, which reduces the antioxidative reserves of the organism.

Change of parameters of antioxidative system may reflect the oxidative stress i.e. disorder in physiological defense mechanisms against the reactive oxygen species.

The cause of such test results are most probably the following phenomena accompanying the polyester wear:

- collecting of electrostatic charges on the surface,
- low air permeability,
- low hygroscopicity,
- increased sweating,
- higher body temperature

Conclusions

1. The lower level of total antioxidative status in individuals wearing polyester clothes may show that probably this is an effect of increased production of reactive oxygen species, which are responsible for the oxidative stress.

2. The phenomena observed during conducted tests confirm the stipulations that the wear made of linen – a natural fiber – not only guarantees a comfort, but it also may have a positive effect on users' health. The clothes made from polyester fibers are not without the effect on human organism and it may turn out that this is an unfavorable effect.

3. In the time of environment pollution and threats being a consequence of more and more chemicals in our life, the care for healthy wear (besides healthy food) and proper education will allow users who prefer healthy life style making right choice.

References

[1] Yi Li: The Science of Clothing Comfort, Textile Progress, Vol. 31 nr 1/2

[2] Grzegorz Bartosz: Second face of oxygen, PWN, Warszawa 1995

[3] A. Bast, R.J.A.Goris: Oxidative stress. Biochemistry and human disease. Pharm.Weekbl. Sc. 11, 1989 (6)

[4] H. Witmanowski: The influence of oxidative stress on insulin receptors of perfuse rats liver during experimental diabetes mellitus. Habilitation work. Poznań, 1997

Lenzinger Berichte, 85 (2006), 22-30

THE FUNCTIONAL PROPERTIES OF TENCEL® - A CURRENT UPDATE

Heinrich Firgo[a], K. Christian Schuster[a*], Friedrich Suchomel[a], Johann Männer[a], Tom Burrow[a], Mohammad Abu-Rous[b]

[a] Textile Innovation, Lenzing AG, Austria
[b] Christian Doppler-Laboratory / Chemistry Cellulosic Fibers and Textiles, Institute of Textile Chemistry and Textile Physics of Leopold-Franzens-University Innsbruck, Austria
[*] Corresponding Author: c.schuster@lenzing.com, tel.:+43 -7672 - 701 - 3081

For many years the textile world was very simple when it came to the function of textiles: hydrophilic natural fibers like cotton and wool and the man made cellulosic fibers stood for absorbency and breathability and the synthetic fibers stood for strength and easy care.

With increasing use of the term “functional textile“, the situation has become more complex. The synthetic fiber industry has been developing new products and marketing approaches claiming enhanced “physiological function in textiles” for sportswear and other fields. Consumers have accepted these arguments and there is a general belief that synthetic fibers are the product of choice for active sportswear, even where the hydrophilic fibers may be superior.

In order to redress the situation, Lenzing AG as a leading producer of cellulosic fibers [1][2] decided that a deeper insight into the “inherent physiological properties and functions” of hydrophilic fibers was needed. A research program was started to look at the inherent properties of fibers using new methods and approaches. The objective was to produce the evidence needed to make our customers aware of the excellent “inherent functionality” of Lenzing’s cellulosic fibers and that in many cases there is no need to use highly sophisticated functional synthetic fibers and finishes to achieve a “functional textile”.

There are two ways of developing the physiological functions of a textile product. Properties can be modified or enhanced by work on the fabric development level and/or fibers can be used which offer physiological functions on the fiber level. The best products will result from a combination of the two approaches. However this paper does not consider specific textile product development possibilities; it presents statements of the “inherent physiological fiber properties” of Lenzing’s hydrophilic fibers. For each physiological function that is described, evidence is presented.

To help understand the origins of the “inherent physiological functions” of textile fibers it can be postulated that:

1. When hygroscopic or hydrophilic fibers come into contact with water, they absorb it **into** the fiber structure.
2. Cellulosic fiber type A will not handle/absorb water in the same way as cellulose fiber type B. There are significant differences between different types of cellulosic fibers.
3. Cellulosic fiber plus water gives inherent physiological functions. It is only the combination of cellulose with water that gives interesting physiological properties.
4. TENCEL® plus water gives enhanced physiological properties
5. Hydrophobic synthetic fibers do not absorb water **into** the fiber structure, they can only adsorb water **onto** the fiber surface.
6. Therefore the combination of synthetic fibers with water normally will not result in added physiological properties (or only to a very low extent).

To demonstrate the difference between cellulosic fibers and synthetic fibers, samples of fiber were placed in the specimen chamber of an environmental scanning electron microscope. The atmosphere surrounding the fibers was saturated with water.
Figure 1 shows the result [3]. The fiber on the left is polyester; the fiber on the right is a TENCEL® fiber.

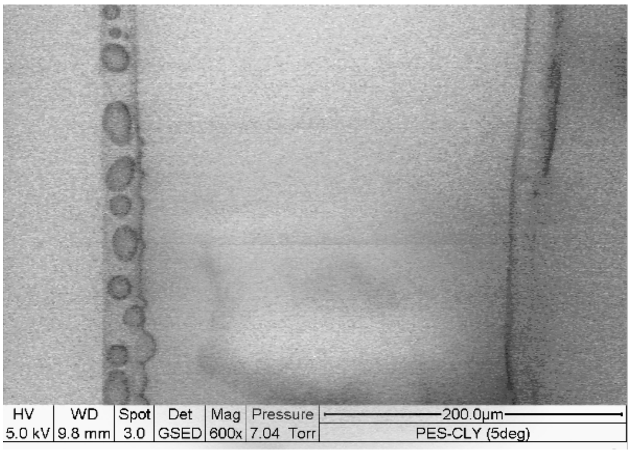


Figure 1: Polyester (left) and TENCEL® fibers (right) in water vapor atmosphere in environmental SEM.

Water droplets have condensed on the surface of the polyester fiber. The TENCEL® fiber does not show any water on the surface. This is the major difference between synthetic fibers and cellulosic fibers. Synthetic fibers such as polyester are non-absorbing, non-hygroscopic and therefore not breathable. They will only adsorb water on the fiber surface. Cellulosic fibers like TENCEL® are hygroscopic, water absorbing and breathable. Water is absorbed into the fiber structure.

The ability to absorb water into the fiber structure is a common feature of all cellulosic fibers and is the basis of some very important physiological properties. All cellulosic fibers show the following eight physiological properties to a certain extent:

- High absorbency
- Warm and dry (as an insulation layer)
- High heat capacity
- Cool and dry to the touch
- Can actively reduce temperature
- Neutral electric properties
- Strongly retards bacterial growth
- Gentle to the skin

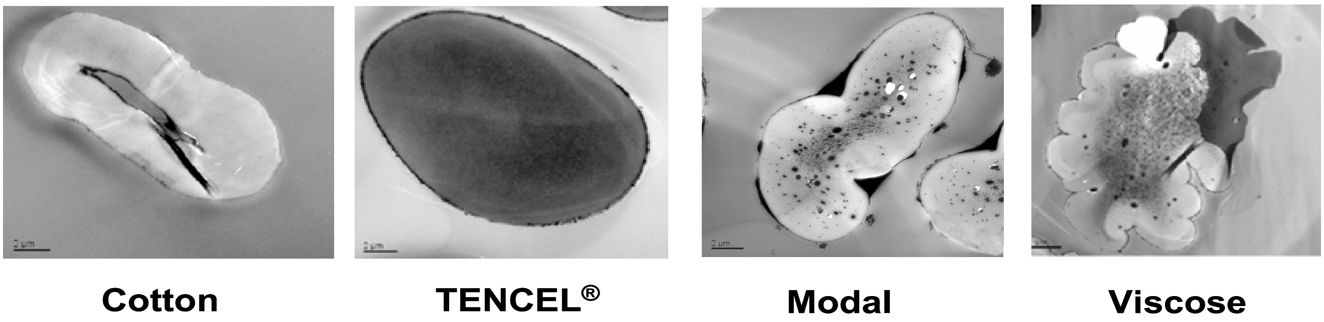
TENCEL® has a very high absorption capability, a unique nano-fibril structure and a very smooth surface. As a result, all these physiological functions are much more pronounced for TENCEL® than for other cellulosic fibers. The inherent physiological properties depend on the amount of water which is absorbed and how it is distributed within the swollen fiber structure.

Absorbency of cellulosic fibers

Transmission electron microscopy can be used to show the location of water in a fiber. For imaging, water-containing pores are filled and stained with a contrasting substance. The water-containing pores show up black, but the cellulose without stain shows up white.
Figure 2 shows the cross-sections of four water swollen cellulosic fibers [4]. Cotton absorbs much less water than TENCEL®, Modal or Viscose. The crystalline skin of Modal contains less water than the core. The water distribution of TENCEL® is very uniform over the whole fiber cross section. Modal and Viscose have a rather coarse pore system with a wide range of pore size distribution from nanometer to micrometer size dimensions The voids in TENCEL® (Lyocell) are very small and quite uniform, in the nanometer range. Latest findings on Lyocell (TENCEL®) fiber structure are reported in [4]-[6].

At a higher magnification using transmission electron microscopy, it can be seen that the pore structure of TENCEL® is a true nano-structure. This is unique amongst the man made cellulosic fibers. TENCEL® consists of countless, very hydrophilic, crystalline nano-fibrils, which are arranged in a very regular manner. The fibrils themselves do not absorb water; water absorption only takes place in the capillaries between the fibrils.

A single TENCEL® fiber, therefore, will behave like an ideally wetting bundle of nano-fibrils with pores in nanometer range in between [4][5][6], something which does not exist in the synthetic fiber world. This is the reason for the excellent water management and the very good comfort in wear of textiles containing TENCEL®.



Cotton **TENCEL®** **Modal** **Viscose**

Figure 2: Position of absorbed water in cellulosic fibers. Transmission electron micrographs. Water appears dark (electron dense), cellulose bright [4]

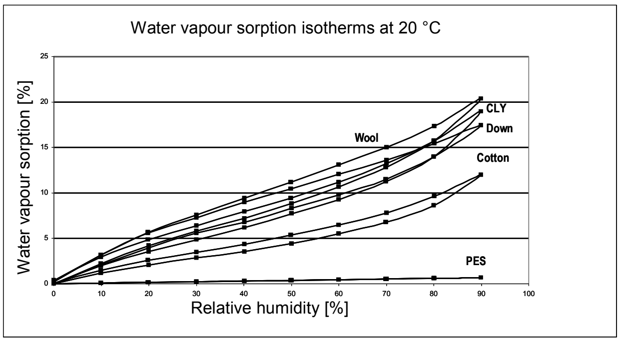


Figure 3. Water vapor absorption isotherms of various textile fibers

Figure 3 is a graph of the “water vapor absorption isotherms” of some fibers [7]. It shows how much water vapor will be absorbed into a fiber from air of a given relative humidity at a given temperature (20°C in this case). Polyester fiber absorbs only negligible amounts of water; cotton absorbs much more. TENCEL® absorbs up to 20% water at 90% relative humidity, which is approximately the same water vapor absorption capacity as wool or down.

The absorption capacity and rate of liquid water absorbency is another important feature of textile fibers. Good water vapor absorbency does not necessarily mean also a high rate of liquid water absorption; the wicking properties of a fabric greatly influence the absorption rate.

One way to measure the absorbency of a fabric for liquid water is the “gravimetric absorbency testing system”, the “GATS” test [12]. In this test the sample is exposed to liquid water from below without any hydrostatic pressure. Therefore the sample will only take up water as it “demands” it. The test allows measurement of the total water absorption and the absorption rate.

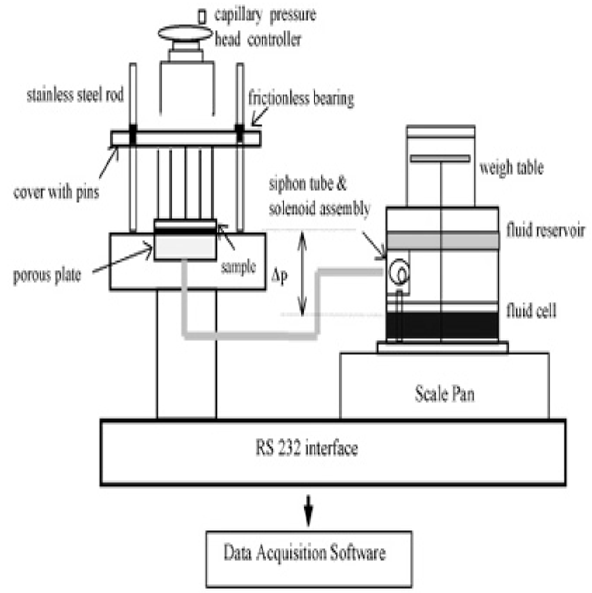


Figure 4. Schematic drawing of the GATS (gravimetric absorbency testing) device [11]

Results with polyester and TENCEL® fabrics of comparable weight which had been washed once before testing have been reported previously. The TENCEL® jersey clearly outperformed the hydrophobic polyester fabric in absorption rate and the amount absorbed [8].

Figure 5 is another example of a GATS test, which was performed on commercial high performance fabrics developed by IBQ in Spain

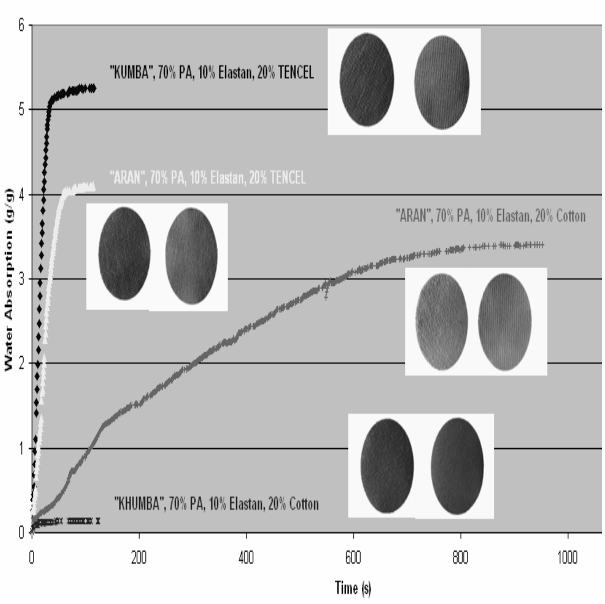


Figure 5. GATS test results on fabrics for sports wear applications

The material is used for mountaineering pants. In two different two-layered constructions (“ARAN” and “KHUMBA”), normally made from 70% Polyamide/ 10% Elastane/ 20% cotton, the cotton was replaced by TENCEL®. Both TENCEL® containing fabrics perform very well in terms of quantity and rate of absorption whereas the cotton variant of “ARAN” absorbs less water more slowly.

The cotton variant of “KHUMBA” did not absorb any water in this test. As the samples were not machine washed before the test, the very bad performance of the cotton - “KHUMBA”- could be due to hydrophobic softeners.

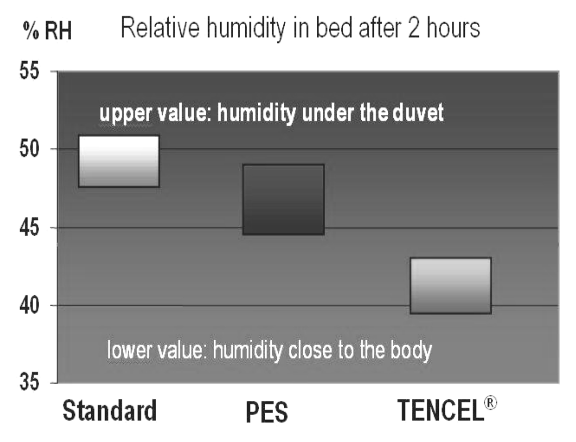
Insulation Properties – Warm and Dry

TENCEL® FILL (a fiber specially designed for use as the filling in duvets) is used to make duvets with very good thermal insulation combined with high water vapor transport, and high absorption of water [7], leading to a high overall comfort compared to polyester fillings [7] and even compared to down fillings [8].

To confirm the laboratory tests for bedding material, a study with test persons was also arranged. Details are reported by Helbig, this volume [13]. Briefly, a group of strongly sweating persons rested in beds with differing bedding materials. Three types of beds were used:

1) a “standard bed” with a mattress having a polyester fleece and a cotton cover. The bed linen was cotton, the duvet and pillow were polyester filled and had a cotton shell.
2) a “polyester bed” with all materials made from polyester and
3) a “TENCEL® bed” with all materials produced from TENCEL®.

The humidity and the temperature were measured in the middle of the duvet filling, under the duvet and close to the body. In Figure 6, the graph shows the humidity under the duvet and close to the body. The TENCEL® bed gave the lowest air humidity both under the duvet (the upper value of the bar) and close to the body (the lower value of the bar).



	Standard	PES	TENCEL®
Mattress			
Fabric	Cotton	PES	CLY blend
Filling	PES	PES	CLY blend
Bed linen	Cotton	PES	µ CLY
Duvet/Pillow	PES	PES	CLY Fill
FillingCover	Cotton	PES	µ CLY

Figure 6. Humidity in bed, and composition of test beds [13]

The insulation properties of TENCEL® fibers in waddings of outdoor jackets were tested under wear conditions. A volunteer cycled on an ergometer in a cooled climate room at -20°C. The jacket she used contained an insulation fleece of TENCEL® / Polyester on the left side and polyester on the right side. The outside surface temperature on the back was measured by an infrared camera. The sides showed a temperature difference of around 1 degree C.

Figure 7 shows the situation after 15 minutes cycling.

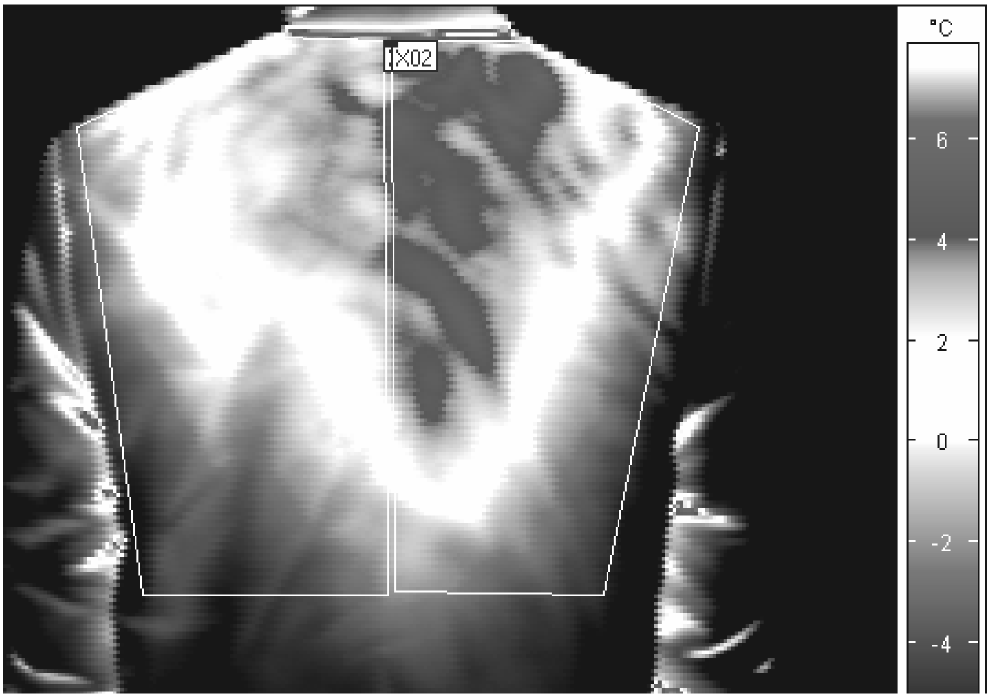


Figure 7. Infrared image of the surface temperature of an outdoor jacket in wear trial at -20°C ambient temperature. Left, TENCEL® /polyester wadding, 0.08 °C average in the marked box, right, polyester wadding, 1.23 °C average in box

Table 1 shows the textile data of the wadding fleeces and the textile physiological measurements taken by the sweating guarded hot plate instrument [10]. It can be seen by the infrared image and by the R_{ct} -value that with basically the same textile properties, the fleece containing TENCEL® fibers shows better insulation. A temperature difference of more than 1 degree on the outside of the jacket will lead to a marked difference in heat loss.

Table 1. Textile physical and physiological data of the waddings used. R_{ct}, , thermal resistance; i_{mt} , water vapor permeability index

Wadding	**Fiber data**		**Area weight [g/m²]**	**Fleece thickness [cm]**	R_{ct}	i_{mt}
	[dtex]	**[mm]**				
100 % PES	3.3	55	120	1.5	0.287	0.73
70% Tencel® 30% PES	1.7 3.3	51 55	120	1.7	0.430	0.68

Heat Capacity and Thermoregulation

Water has a high heat capacity. Therefore, fibers which contain water will also have a high heat capacity. This can be used to help the human body's temperature regulation. On the water vapor absorption isotherm we have seen that TENCEL® FILL always contains water [7].

Figure 8 shows small samples of fiber fill with a defined water content sealed into plastic bags. The samples were placed in an oven at 50°C until they had equilibrated. They were then taken out of the oven at the same time and the cooling rate was monitored with an infrared camera.

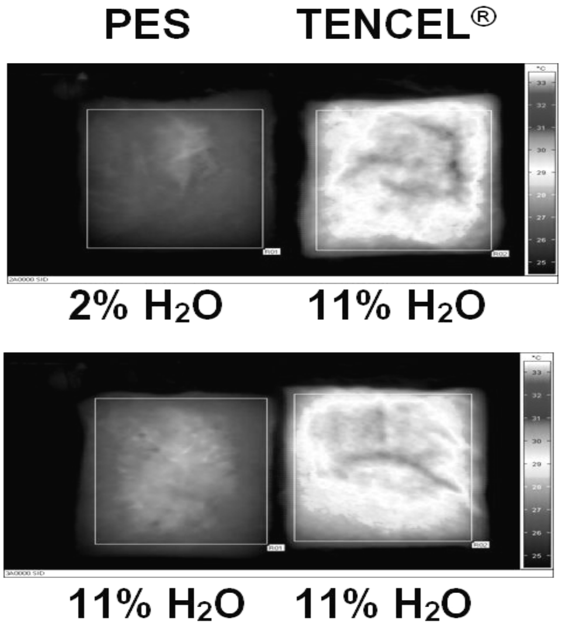


Figure 8: Cooling of duvets. Duvets were heated to 50°C, then left at ambient to cool. The difference is shown by an infrared camera.

The first trial (top) used very realistic conditions with TENCEL® having a moisture content of 11% and polyester 2%. The brighter colors of the TENCEL® sample show that it is retaining heat much more effectively than the polyester sample.

In the second trial both fiber fills had a water content of 11%, but still TENCEL® shows a higher heat capacity and slower cooling rate. The water absorbed within the fiber structure of TENCEL® has a higher heat capacity than the liquid water which is only adsorbed on the surface of the polyester fibers.

TENCEL® FILL in duvets, therefore, acts like a hot water bottle and has a high heat capacity. It can help to smooth out the temperature fluctuations in bed and supports more restful sleep.

Cool and Dry to the Touch

The “Thermal Absorptivity” of a fabric is a measure of the amount of heat conducted away from the surface of the fabric per unit time. A fabric which does not conduct heat away from its surface will feel warm; one that does conduct heat away will feel cold.

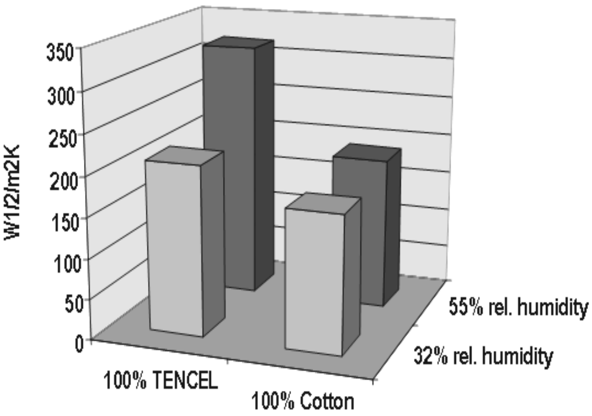


Figure 9: Thermal absorptivity of bed linen

The “Thermal Absorptivity” can be measured using the “Alambeta Test” (Prof. Lubos Hes in Liberec, CZ; [14]).

Figure 9 shows test results on bed linen made from 100% TENCEL® and from 100% cotton. It shows that TENCEL® feels cooler to the touch and that the “cool feeling” increases with increasing air humidity because the moisture content of the fibers increases. With TENCEL® this behavior is much more pronounced than with cotton as the increase in water content with increasing air humidity is much steeper for TENCEL® than for cotton.

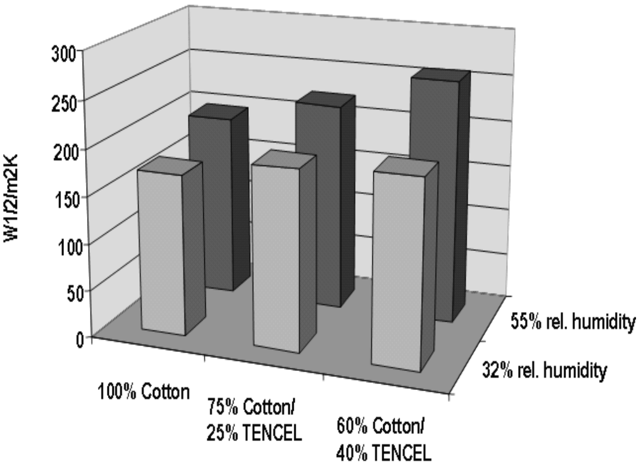


Figure. 10: Thermal absorptivity of shirt fabrics , TENCEL® / cotton blends

Even in minority blends TENCEL® will enhance the “cool feeling” of textiles. Blends of 25% to 40% TENCEL® with cotton in a shirting fabric will give a cooler feeling compared to 100% cotton - especially at higher air humidity (Figure 10). This represents a self-regulating system: In warm and humid ambient conditions, the cool feeling is increased.

Active Cooling

At very high physical activity levels or in very hot and humid climates the temperature control of the human body mainly relies on the production and evaporation of sweat. As the sweat evaporates it carries energy away from the body in the form of the latent heat of vaporization. To do this the sweat must either evaporate from the skin and pass through the covering fabric as vapor or it must be transferred from the skin to the fabric and subsequently evaporate. If the sweat cannot be transported through the fabric, the cooling effect will be too low and the physical performance will drop accordingly.

The ideal "active cooling" textile, therefore, has to have good water transport properties, however it should allow water evaporation next to the skin in order to achieve maximum cooling of the human body. (Many of today's high performance 2 layer sports shirts evaporate the moisture from the surface of the fabric, instead of from next to the skin!)

To investigate the differences of the active cooling properties of TENCEL® and polyester fibers, ergometer tests were performed on subjects wearing T-shirts consisting of 2 halves. The left half was polyester, the right half TENCEL® - both single jersey with the same construction. The test subjects performed a strenuous exercise with the power output increasing in stages to 250 Watts, which guaranteed full sweat production. There were two relaxation stages in between.

The surface temperature of the two halves of the T-shirts was monitored with an infrared camera. In Figure 11, the surface temperature on the right side of the T-shirt – the TENCEL® fabric – is higher.

This demonstrates the better heat dissipation through the TENCEL® fabric during high sweat production. The temperature difference of 0.5 to 1°C seems to be small, however in physiological terms it is significant.

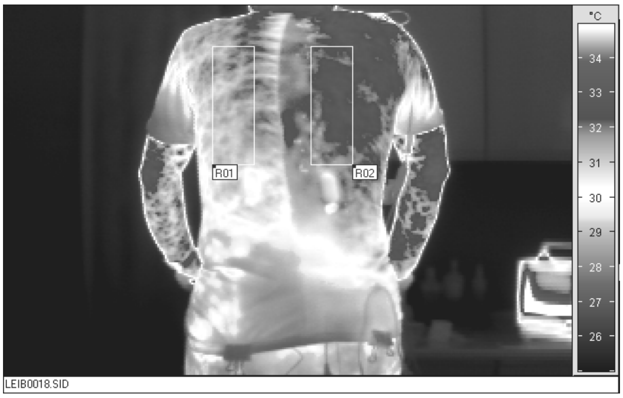


Figure 11: T-shirt in two halves after exercise. Left, polyester. Right, TENCEL® The temperature measured on average over the boxes are 31.5°C (left) and 32.3 °C (right)

Neutral Electrical Properties

Friction induces electrostatic charging of textiles. The extent of electrostatic charging depends on the electrical resistance of the textile surface. A physical measure for the tendency to build up electric charge is the surface resistance of textiles. A surface resistance of higher than 10^{10} Ohm will cause electrostatic charging when friction is applied to a fabric. A high level of electric charge on textiles can cause a very unpleasant experience when the static charge is suddenly discharged and can even cause sparks. Measurements have been made of the electrical surface resistance of TENCEL® and Polyester fabric. Even at a very low air humidity of 25%, the TENCEL® fabric has a surface resistance which is 3 orders of magnitude lower than for the polyester fabric. At higher air humidity (65% RH), the surface resistance of the TENCEL® fibers is 6 orders of magnitude lower [8].

As direct measure for the charge build-up in textiles in contact with the human body, a volunteer stood on an isolated rubber matt and pulled various textiles from his naked shoulders. The electrostatic charging of the body was measured. Polyester and polypropylene cause very high charging in this test (>2500 V); TENCEL® and cotton gave a neutral result; polyamide was much better than the other synthetic fibers but still worse than the cellulosic fibers. An electrostatic charge of more than 1800 Volts can be felt [8].

Not much is known about the impact of this electrostatic charging on the well being of human individuals, but there are hints of negative effects on muscle coordination [15][16].

Strongly Retards Bacterial Growth

If a dry TENCEL® fabric absorbs 60% water, all the water will be absorbed into the fiber, which will cause the fiber to swell. No film of liquid water will cover the surface of the fibers. However if a polyester fabric absorbs 60% water, none of the water will be absorbed by the fibers; all of the water will sit on the surface of the fibers as a water film and/or droplets on and between the fibers of the fabric.

Bacteria and fungi require liquid water for optimum growth. Thus it would be expected that micro-organisms would be more likely to grow rapidly on moist polyester than on moist TENCEL®.

This is the most probable reason for a lower bacterial growth on textiles made from cellulosic fibers as compared to textiles made from synthetic fibers, as was shown by *in vitro* (laboratory) tests [8] under conditions of a challenge test with growth medium (Figure 12).

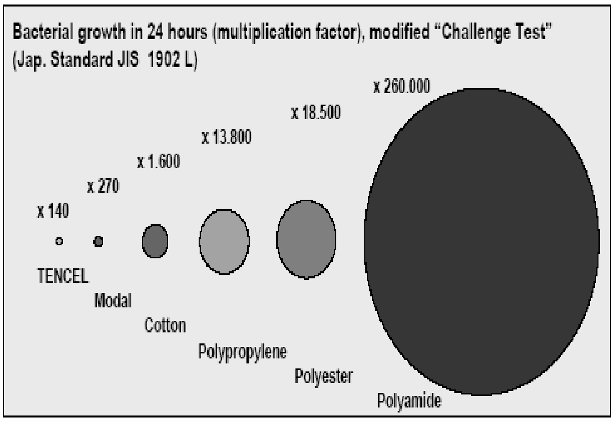


Figure 12: Bacterial growth as multiplication factor in the Challenge Test. Circle areas are proportional to the multiplication factors.

All cellulosic fibers perform well in this test. The bacterial growth on synthetic fibers can be higher by some orders of magnitude. However, within the family of cellulosic fibers TENCEL® shows 10 times lower bacterial growth than cotton. This is probably due to the very good water absorption of TENCEL® in combination with its smooth surface.

In vivo trials (wear trials) with divided T-Shirts confirmed the trend: Under an identical wear situation, on one side of the divided T-Shirt of sports wear fabrics made from synthetic fibers, more bacteria could grow than on the other side made of TENCEL® fabric [6].

For the methods applied to assess interactions of microorganisms and textiles see [17].

Gentle to the Skin

Fibers with poor water absorption capacity result in textiles which cling to the skin when they are wet. Wet skin is much more sensible to irritation than dry skin. The coarseness, the stiffness and the surface character of the fibers will also have an impact on the skin’s sensory perception. Both cotton and wool have rather good water absorbency, however they have a rather rough fiber surface.

TENCEL® combines good water absorbency with a smooth fiber surface which makes it a fiber which is very gentle to the skin.

All these positive inherent properties of TENCEL® - good breathability and moisture absorption, dry and cool micro-climate on the skin, smooth fiber surface, low wet cling effect and no electrostatic charging – mean that textiles made from TENCEL® might offer relief to people who suffer from skin diseases.

A clinical test was organized at the University Hospital in Heidelberg (Germany) which was led by the dermatologist Prof. Diepgen [18]. 60 patients suffering from atopic dermatitis or psoriasis tested commercially available TENCEL® products including bedding, T-shirts, polo-shirts and nightwear. People suffering from these conditions have had to optimize their clothing to identify materials that will cause them the least discomfort.

In summary, approximately 80% of the patients suffering from atopic dermatitis or psoriasis preferred TENCEL® products over their normally used textiles.

A second study was performed by Dr. I. König using a specially designed sleeping overall with scratch protection, tested by children aged 2 to

13. Children and parents were very positive about the properties, reported less itching and scratching, leading to a better night's sleep and a more relaxed overall situation [19].

The outcome of these studies is a very convincing argument for the sensorial properties of TENCEL® textiles [20].The main comfort properties noted by the patients were: thermoregulatory properties, cool, smooth and dry feeling, and the overall excellent skin compatibility.

Conclusion

The combination of absorbent fibers and the water that they absorb is the basis of the positive physiological functions of cellulosic fibers. High absorbency, the unique nano-structure and the smooth surface of TENCEL® result in enhanced physiological functions that make it stand out amongst the family of cellulosic fibers.

Acknowledgement

This work was in part supported by the Christian Doppler Research Society, Vienna, Austria.

References

[1] White P.: Lyocell: the production process and market development. In: Regenerated cellulose fibers, C. Woodings (ed.), 62 – 87, Woodhead Publishing Ltd., ISBN 1 85573 459 1, (2001) Cambridge, England

[2] Schuster K.C., et al.: Environmental Friendly Lyocell and Rayon Fibers, In Natural Fibers, Plastics and Composites, Kluwer Academic Publishers Boston / Dordrecht / New York / London, ISBN 1 4020 7643 6, USA (2003), pp. 123–146

[3] Pölt P., Zankel A., Research Institute for Electron Microscopy and Fine Structure Research (FELMI) of the Graz University of Technology, unpublished

[4] Abu-Rous M., Ingolic E., Schuster K.C., Visualisation of the Fibrillar and Pore Morphology of Cellulosic Fibers Applying Transmission Electron Microscopy, *Cellulose*, (2006) in Print

[5] Abu-Rous M., Ingolic E., K.C. Schuster, Visualisation of the Nano-Structure of Tencel® (Lyocell) and Other Cellulosics as an Approach to Explaining Functional and Wellness Properties in Textiles. Lenzinger Berichte 85 (2006), in press

[6] Schuster, K.C. et al.: Characterization of Fibrillar and Pore Structure in Natural and Man–Made Cellulosic Fibers by Modern Imaging Techniques, Proceeding of Polymer Fibers 2006, Manchester UK, 2006

[7] Schuster K.C., Firgo H., Haussmann F., Männer J., Home Textiles with Feel Good Factor Derived From Wood, Lenzinger Berichte, 83 (2004), pp. 111–116

[8] Männer, J., Schuster, K.C., Suchomel F., Gürtler A., Firgo H., Lenzinger Berichte 83 (2004), 99-110

[9] Umbach K.H., Lenzing AG Customer's meeting, Fuschl, Austria, May, 2003

[10] Mecheels, J., Körper – Klima – Kleidung . Wie funktioniert unsere Kleidung? Schiele & Schön, Berlin, 1998

[11] Website of the North Carolina State University, Textile Protection and Comfort Center, http://www.tx.ncsu.edu/tpacc/comfort/horizontal_wicking_gats.html

[12] Rearick W.A., Martin V.B., Wallace ML, Moisture management: Myths,Magic,and Misconceptions. AATTC Review(3/2004), 43-47

[13] Helbig K., Comparative Research: Microclimate of Bedding Components, Lenzinger Berichte 85 (2006), in press

[14] Hes L., Recent developments in the field of user friendly testing of mechanical and comfort properties of textile fabrics and garments. Proceedings of the World Congress of the Textile Institute, Cairo, 2002

[15] Zimniewska M., Huber J., Krucińska I., Torlińska T., Kozłowski R., The Influence Of Natural And Synthetic Fibers On Activity Of The Motor Units In Chosen Muscles Of Forearm; Fibers and Textiles in Eastern Europe No. 4/ 2002

[16] Zimniewska M., Krucińska I., Kozłowski R., Muscle activity as one of the well-being factors. Lenzinger Berichte 85 (2006), in press

[17] Teufel L., Redl B., Improved methods for the investigation of the interaction between textiles and microorganisms. Lenzinger Berichte 85 (2006), in press

[18] Diepgen T.L., Schuster K.C., Dermatological Examination on the Skin Compatibility of Textiles Made from TENCEL®, Lenzinger Berichte 85 (2006), in press

[19] König I, Project "Polar Bear", a wear study. Available on request from Lenzing AG

[20] Diepgen T.L., Schuster K.C., König I., Emlinger G., Textilien aus TENCEL® und Hautverträglichkeit. Dermatologisches Alpenseminar, Grainau / DE, 25.-27.May 2006

Lenzinger Berichte, 85 (2006), 31-37

VISUALISATION OF THE NANO-STRUCTURE OF TENCEL® (LYOCELL) AND OTHER CELLULOSICS AS AN APPROACH TO EXPLAINING FUNCTIONAL AND WELLNESS PROPERTIES IN TEXTILES

M. Abu-Rous[1], E. Ingolic[2], K. C. Schuster[3*]

[1]Christian Doppler-Laboratory / Chemistry Cellulosic Fibres and Textiles, Institute of Textile Chemistry and Textile Physics of Leopold-Franzens-University Innsbruck - Austria
[2]Research Institute for Electron Microscopy (FELMI); Technical University of Graz, Austria
[3]Lenzing AG, Lenzing, Austria

Based on contributions to the 5th International Textile Conference, Istanbul 2005, and the 3rd International Conference of Textile Research Division, Cairo 2006

The special functional and wellness properties of TENCEL® textiles (generic name: Lyocell) have been demonstrated: the cool and smooth surface (gentle to the skin), the wear comfort properties due to excellent moisture transport and buffering, and the temperature control. The background for this is the nano- structure of Lyocell fibres, which is radically different to the other known cellulosics.
Earlier studies have shown that the pore structure depends on the spinning and treatment parameters. Following a crystallization model of cellulose out of NMMO solution, the fibre cross-section contains a compact core, a porous middle zone and a semi-permeable fibre skin. Classical analysis methods deliver quantitative information about the pore structure and even the pore size distribution, but no information on their spatial distribution.
The major topic of our works is to visualize this pore distribution in relationship with the fibre physical and chemical properties. Applying fluorescence microscopy on fibre cross-sections, different porous zones could be discriminated, partly confirming the model mentioned above. To visualize entirely the fine pore network structure, transmission electron microscopy (TEM) was applied. It was necessary to overcome the problem of the low electron contrast of cellulose material, which does not accept common staining. Here we adapted a contrast-enhancing method to several cellulosics, and to visualize the pore structure of Lyocell and Modal at a high space resolution.

Keywords: *Cellulosic Fibre Structure Properties*

Introduction

For textiles from TENCEL® fibres (generic name: Lyocell), special functional and wellness properties have been demonstrated : they are gentle to the skin by the cool and smooth touch, have excellent wear comfort properties due to outstanding moisture transport and buffering, the temperature control effects, the reduces bacterial growth and odour formation, and the avoided electrostatic charge[1,2]. These special properties have been attributed to the special structure of Lyocell fibres, which is radically different to the other known cellulosics.

TENCEL® (Lyocell) is a round fibre with a smooth surface, which makes the soft touch. The high strength has been explained by the high orientation and crystallinity of the cellulose structure[3]. The nano-fibrillar structure has been studied by scanning electron microscopy after breaking the fibres, leading to a model of a nano-fibrillar structure[1,2,4]. The climate management function seems to be related to the porous water binding internal structure of Lyocell fibres. This internal structure has been a subject of debate. Earlier studies show that the resulting pore structure depends on the spinning and treatment parameters[5,6,7,8]. A recent crystallisation model of cellulose out of NMMO solution proposes a compact fibre core, a porous middle zone and a very thin, semi-permeable fibre skin[9]. Known methods such as water retention measurements give quantitative information about the pore structure. Inverse volume exclusion chromatography gives also the pore size distribution.

Until now, no method was applied to visualise the internal fibril structure of Lyocell in a non-destructive way. The major topic of our works is to visualise this pore distribution in correspondence and with regard to the fibre textile chemical properties applying fluorescence microscopy, and swelling properties by transmission electron microscopy

Experimental

Fluorescence microscopy on fibre cross-sections

A technical 120% oversaturated solution of Uvitex BHT (calcofluor) was resuspended and a 1 g/L aqueous solution was prepared and filtered on a microfilter. 0.2g sample was dyed in 40 ml of this solution 10 min, 4 h and 24 h. The samples were washed twice 10 minutes in water and dried at room temperature.
Fibre cross-sections with an 8 µm thickness were prepared using a Reichert microtome (model: 1140/Autocut) after being embedded in a 2-hydroxyethylmethacrylate resin (Technovit7100™, Kulzer). Fluorescence on fibres and fibre cross-sections was imaged using an Olympus BX microscope equipped with a mercury burner lamp, monochromatic filters and a digital camera system (Analysis). The dye penetration depth was measured.

Transmission electron microscopy (TEM)

The main problem of transmission electron microscopy on cellulosic samples is the absence of contrast in cross-sections. Here, imaging could be performed after contrasting the pores with a substance forming a black stain in the pores[11]. Ultra-thin cross-sections were prepared and TEM was performed at the Research Institute for Electron Microscopy (FELMI) - Graz using a Tecnai 12 (FEI) microscope, equipped with a CCD – Gatan camera system.

Results

Accessibility of pores visualized by a molecular probe and fluorescence microscopy

A comparison of Calcofluor (Uvitex BHT) dye diffusion into Lyocell, Viscose and Modal fibres was done (figure 1). While on Lyocell fibres the diffusion depth increases with the time, the penetration on Viscose and Modal do not exceed an external zone. On Viscose fibres, the dye intensity increases in the shell zone without reaching the core. On Modal the intensity on the surface do not increase after reaching a certain limit.

Having non-accessible core zones, Viscose and Modal have both a relatively narrow dye diffusion zone. The method is more sensitive on Lyocell, where the diffusion can be observed in a larger zone through the cross-section. The further experiments are performed on Lyocell, in order to observe the impact of production and treatment parameters on the pore system.

It was further possible to characterise with a higher resolution the surface and the pore structure of Lyocell (figure 2). The fluorescence microscopy observation gave a

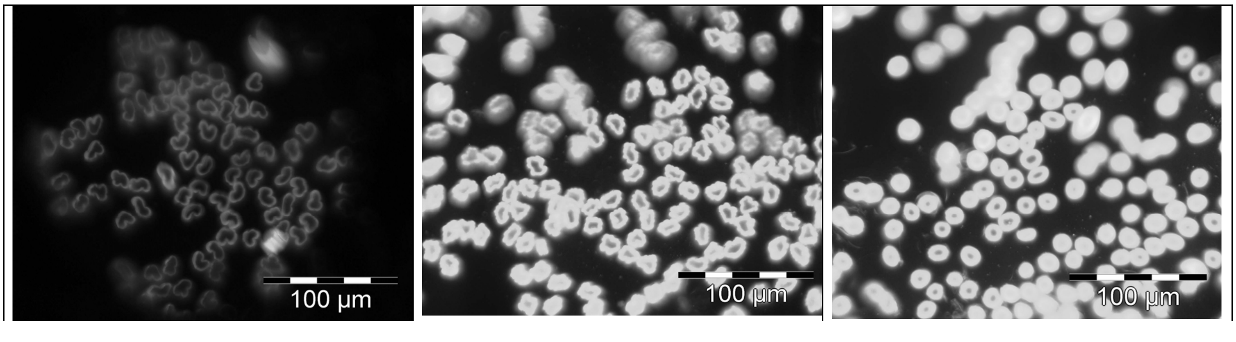


Figure 1: Diffusion of Uvitex BHT into Modal (left), Viscose (middle) and Lyocell (right)

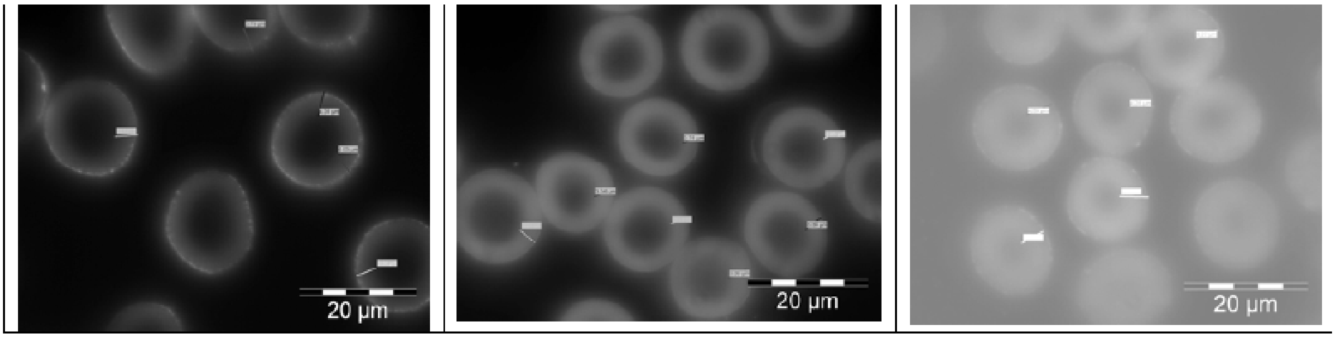


Figure 2: Calcofluor intrusion into a Lyocell cross-section after 10min (left), 4h (middle) and 24 h (right)

dye distribution profile which fits with the model suggested above[9]. The membrane skin on the fibre surface can be illuminated with the fluorescent dye. The dye diffusion through the fibre inside is higher than through the fibre skin, which seems to serve as a semi-permeable membrane. It builds the first obstacle for diffusion into the fibres.

Distribution of pores by TEM imaging

All fibres – except cotton – stained intensively black with the agent applied. Cotton fibres showed only a grey colour, indicating a lower stain inclusion in the less accessible pores (not shown). This corresponds to the lower swelling of cotton compared with the synthetic cellulosic fibres.

TEM images of fibre cross-sections of regenerated cellulosics are shown in figure 3.

The differences in the pore distribution and the internal structure were visualised: A core/shell structure in Viscose fibres, corresponding with the already known structure of fibres produces through the viscose route - a dense shell and a porous, spongy core[10]. Modal fibres show a compact external structure with very small pores (grey shading) and some large pores towards the centre. On Lyocell fibres, a more homogenous distribution of small pores is seen.

Discussion

Pore structure of Lyocell

Earlier models of Lyocell based on x-ray scattering and on SEM of disrupted fibres have mainly focussed on the fibrillar components of the structure[3,8,12]. Following an earlier model[4], the Lyocell fibre is composed of structural sub-units (fibrils) in micro and nanometre range.

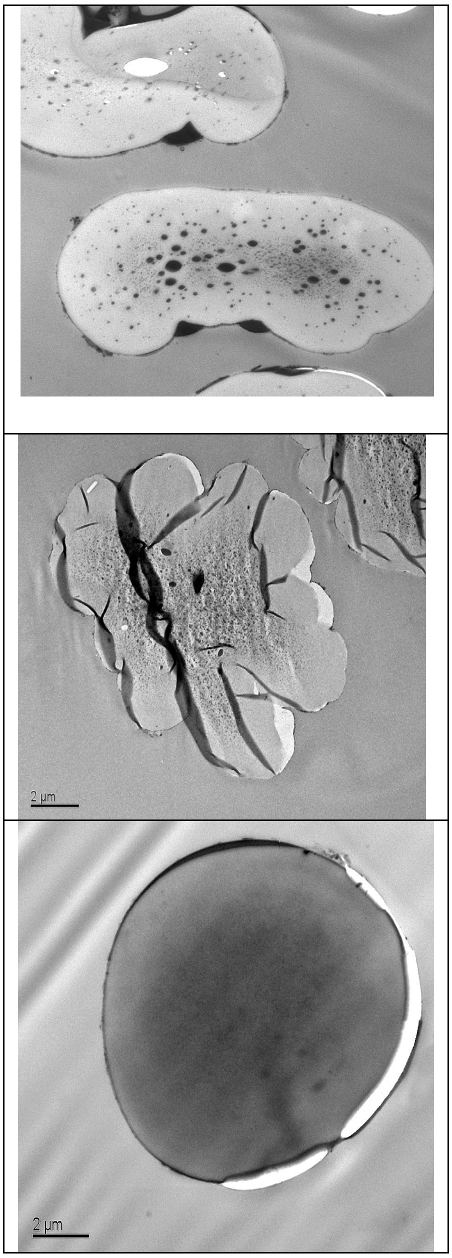


Figure 3: TEM imaging of modal (top), Viscose (middle) and Lyocell (bottom) cross-sections. Pores are stained (black), cellulose structures appear white. The large white areas are parts where the ultra thin sections are ruptured (micrographs from Abu-Rous et al., Cellulose 2006, in Print[11])

Table 1 shows the approximate calculation of the number of fibrils of each dimension within the fibre cross-section.

Table 1: An approximate calculation of the number of Fibrillar sub-units within a Lyocell fibre cross-section

Structure Element	Size	Approximate number of fibrils per fibre cross-section
Nanofibril	10 nm	1,330,000
Microfibril	0.15 µm	5902
Macrofibril	0.75 µm	236
Complete fibre diameter	13 µm	(1)

In this model, swelling was assumed to occur between the crystallites, in the “amorphous zones”. From morphology observed in larger-scale crystallisation of cellulose from NMMO solutions[9], a three- zone model was proposed, a compact skin zone including a semi-permeable membrane, a more porous middle zone, and a compact centre.

Taking up these ideas, and comparing the results from the applied visualisation techniques for the pores, a revised structural model of TENCEL® (Lyocell) fibres is suggested (Figure 5).

Different porous zones could be distinguished, partly confirming the crystallisation model mentioned above[9,13,14]. The profile given by fluorescence microscopy was confirmed by TEM imaging (Figure 3, figure 4). Also in TEM observations, the Lyocell fibre can be divided in three main zones:

A fibre skin or skin zone with a rather compact character:

The very first zones of the skin surface seem to have a high porosity. In high magnification, a highly porous skin layer of about 150 nm thickness becomes visible, giving for the first time an image of the Lyocell skin structure in the wet state. Nevertheless, a compact zone occurs below, which becomes gradually more open towards the next fibre zone. The width of the total “skin zone” is about 1-1.5 µm. Such

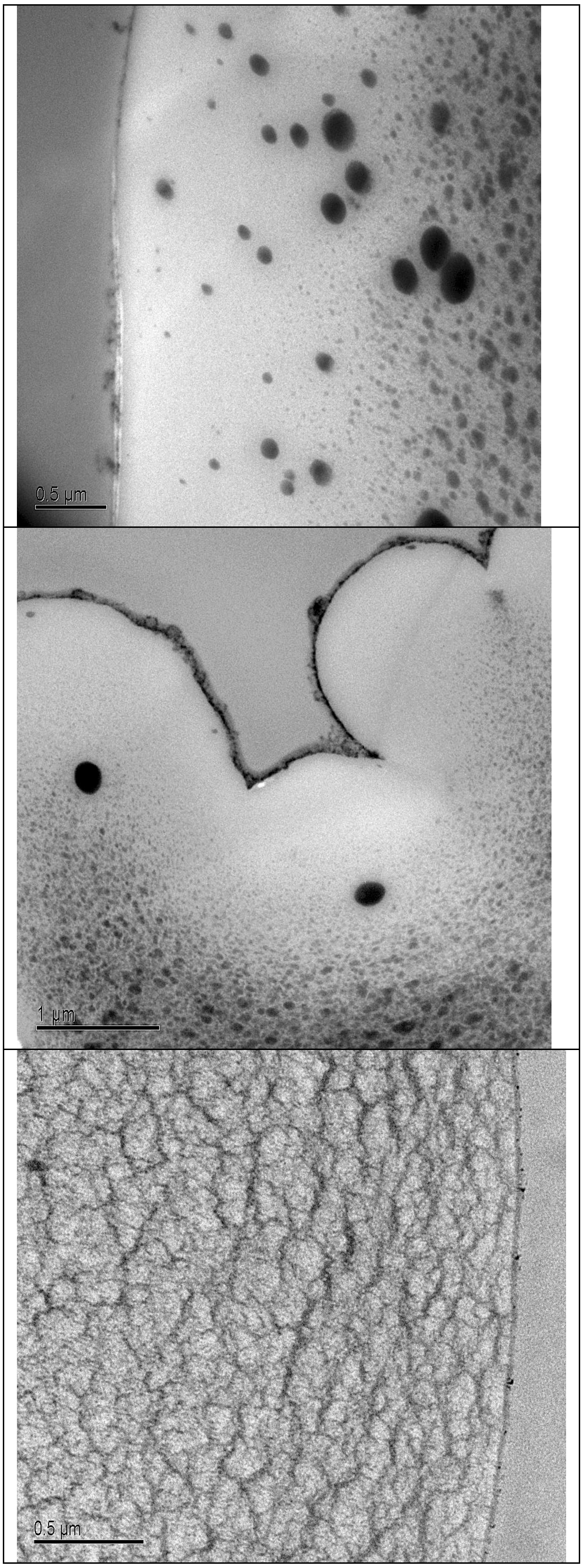


Figure 4: TEM imaging of the internal morphology of modal (top), Viscose (middle) and Lyocell (bottom) cross-sections (micrographs from Abu-Rous et al., Cellulose 2006, in Print[11]).

gradients of porosity have also been observed in TEM images prepared after freeze-etching[15].

Some other sections show radial pores going from the surface into deeper zones inside the fibre. The zone of radial pores showed a depth of ca. 0.2 – 0.5 µm, partly corresponding to the zone where high and very fast calcofluor uptake was observed (Figure 2).

A porous fibre middle zone:

This zone is characterised by a gradual increasing of the porosity. Pores and cellulose domains are observed, in the order of magnitude of 10 to 20 nm. These sizes correspond to the calculations from SAXS data[16,17,18]. Additionally, a network of pore clusters can be observed, presumably surrounding the cellulose bodies which show up as microfibrils when the fibres are exposed to abrasion. Here, the uptake of calcofluor occurs at a fairly high rate (Figure 2). It also ends gradually toward the **compact fibre centre**, where the pores become tighter and the overall structure more compact (Figure 5). Here, the uptake rate of calcofluor decreases sharply (Figure 2).

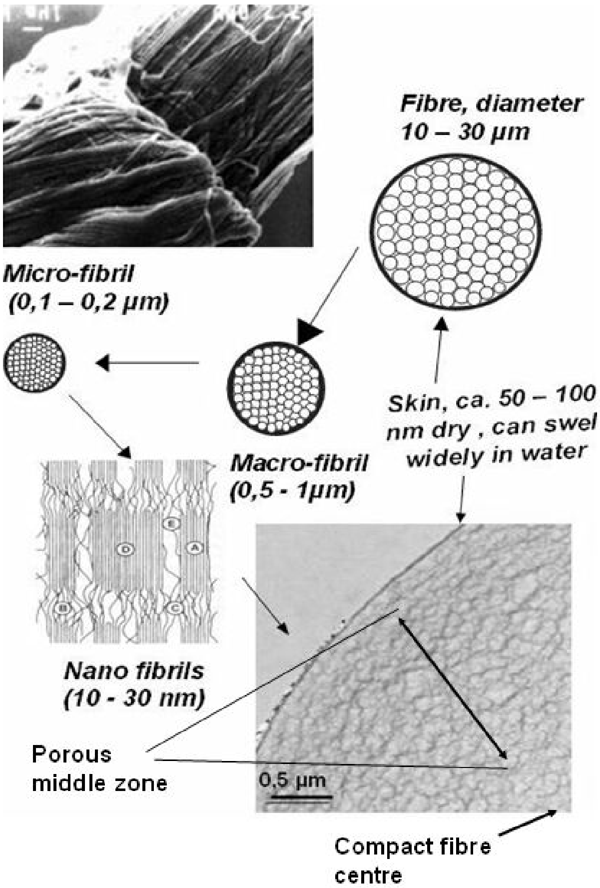


Figure 5: A structural model of TENCEL® fibre

The nanofibrillar-nanoporous structure of Lyocell observed in imaging should also have a strong impact on the kinetics and thermodynamics of water binding into the structure.

Connection to functional and wellness properties

A major difference between synthetic and cellulosic textiles is in the localisation of moisture in the textile (Figure 6). Non-absorptive fibre materials can be wetted overall upon mechanical impact by overcoming the surface tension. In case of polyester, the moisture absorbed by the textile is found between the fibres and/or yarns on the fibre surface. On account of the nano-fibrillary structure of Lyocell fibres, the moisture is transported very swiftly through the micro capillaries and absorbed inside the fibres which swell accordingly. At 60% fibre moisture, a major amount of the moisture is inside the fibre in case of Lyocell without resin finishing.

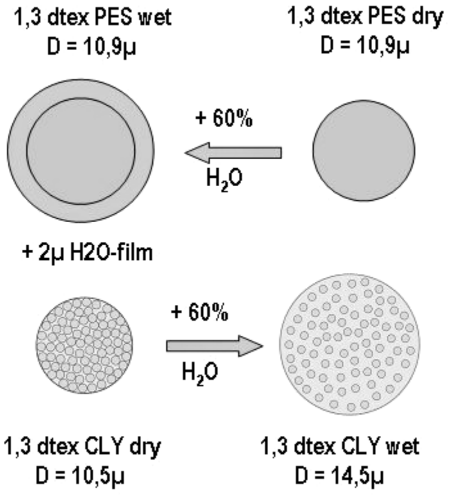


Figure 6: Model of the moisture distribution in polyester and Lyocell fibres

The climate management properties of Lyocell can be related to the porous structure.

High water and moisture (water vapour) uptake: The high porosity and ability to swell is a general feature of cellulosic fibres.

Regenerated cellulosics show higher porosity than natural fibres, leading to outstanding water buffering capacity. In Lyocell, the water-accessible pores are distributed very evenly in the fibre cross-section.

The cool touch of Lyocell can be explained by the quick removal of water vapour from the fibre when the textile is touched and heated up by skin contact. The very accessible interconnected pore network seems to play a role here.

Also for the fast conduction of moisture in the fibre (wicking effect), this pore network seems to be the background.

Additional effects of the high water uptake in Lyocell are less growth of bacteria and thus less odour formation: Experiments for bacterial growth have been done in laboratory tests in vitro[2] (challenge test based on to the Japanese standard JIS1902L) as well as in wear trials in vivo[1]. Both showed on synthetic materials, it is found that bacterial growth is higher by a factor of 100 to 1000 as compared to Lyocell. On cotton, the growth is still higher by a factor of 10, as compared to Lyocell. The considerably higher growth on synthetic fibres may be the cause for the well-known stronger odour formation. The clearly reduced growth on Lyocell can be explained by the behaviour of the fibre towards water (Fig. 5). The water on the surface of synthetic fibres is fully accessible to micro-organisms. In Lyocell materials, the water is absorbed almost entirely into the fibre and therefore offers only little life-sustaining basis for the micro-organisms.

No electrostatic charge[2]: Moisture bound inside the fibre and distributed equally leads to a high electrical conductivity of materials. So, the build-up of electrostatic charge, which may lead to unpleasant electrical shocks from textiles, is avoided in Lyocell textiles.

Conclusion

By the combination of TEM and fluorescence microscopy, the pore structure of Lyocell could be visualised in comparison with the other man-made cellulosic fibres.

The results from fluorescence microscopy show the higher accessibility of Lyocell fibres, which correlates with the water and vapour sorption results. The obtained TEM images visualise for the first time by a non-destructive method the internal pore structure of Lyocell and Modal cellulosic fibres and the fibril and pore structure of Lyocell. The results from fluorescence and electron microscopy correspond and can partly explain the results from water and vapour sorption.

From the results, an understanding for the basis of the functional and comfort-in-wear properties is being developed.

(1) Christian Doppler-Laboratory for Chemistry of Cellulosic Fibres and Textiles, Institute of Tex. Chem. and Tex. Phys. of Leopold-Franzens-University Innsbruck; Hoechsterstrasse 73, A-6850 Dornbirn, Austria; Email: m.aburous.@lenzing.com

(2) Research Institute for Electron Microscopy (FELMI); Technical University of Graz, Austria

(3)* Corresponding author. Lenzing AG, Textile Innovation, 4860 Lenzing, Austria, Email: c.schuster@lenzing.com

References

[1] Schuster K.C., Firgo H., Haussmann F., Männer J., Proc. of the Textile Institute 83rd World conference, Shanghai, May 2004 , 422 – 426 (2004)

[2] Männer, J., Schuster, K.C., Suchomel F., Gürtler A., Firgo, H., Lenzinger Berichte 83 (2004), 99-110

[3] Lenz J., Schurz J., Wrentschur E., Acta Polymer 43, 307-312 (1992)

[4] Schuster, K.C.,Aldred P., Villa M., Baron M., Loidl R., Biganska O., Patlazhan S., Navard P., Rüf H., and Jericha E., Lenzinger Berichte 82, 107-117 (2003)

[5] Zhang Jianchun J., Zhu H., Shi M., Lai K..; Chemical fibres international 49, 494 (1999)

[6] Coulsey H.A., Smith S.B., 35th Int. Chemical Fibres Conference Dornbirn, September 1995

[7] Mortimer S.A., Dissertation, Université Joseph Fourier – Grenoble I, March 1995

[8] Schuster K.C. et al., Environmentally Friendly Lyocell Fibres in *Natural Fibres, Plastics and Composits;* ed.*:* F.T. Wallenberger and N.E. Weston, Kluwer Academic Publishers Boston/Dordrecht/N.Y/Londen;2003; 123 – 146

[9] Biganska O.; Dissertation, L'Ecole Nationale des Mines de Paris; december 2002

[10] See for example Süvern K., Die Künstliche Seide; Springer-Berlin; 4th Edition1921

[11]. Abu-Rous M., Ingolic E., Schuster K.C., Cellulose 2006 (in print)

[12] Ducos F., Biganska O., Schuster K.C., Navard P., *Cellulose Chemistry and Technology*, submitted

[13] Abu Rous M., PhD Thesis, Institute for Textile Chemistry & Textile Physics, Universtiy of Innsbruck, Austria (2006)

[14] Abu Rous M., 6th International ALCERU Symposium,01.-02.09. 2004, Rudolstadt (Germany). Also in Lenzinger Berichte; 83, 92 - 98 (2004)

[15] Purz H.J., Graf H., Fink H.P., *Das Papier*, 12, 714 – 730 (1995)

[16] Schurz J., Lenz J., *Macromol. Symp.*. 83, 273-289 (1994)

[17] Vickers M.E., Briggs N.P., Ibbett R.N., Payne J.J., Smith S.B., Polymer 42, 8241 (2001)

[18] Crawshaw J., Cameron R., Polymer 41, 4691-6 (2000)

Lenzinger Berichte, 85 (2006) 38-43

MUSCLE ACTIVITY AS ONE OF THE WELL – BEING FACTORS

Malgorzata Zimniewska[a], Izabella Krucińska[b], Ryszard Kozłowski[a]

[a]Institute of Natural Fibres, Wojska Polskiego 71b, 60-630 Poznan, Poland
+42-61-84-55-859, 84-55-800, fax: +42-61-841- 830, e-mail: gosiaz@inf.poznan.pl,
sekretar@inf.poznan.pl
[b]Faculty of Textile Engineering and Marketing, Technical University of Łódź, 90 543 Łódź, Żeromskiego 116, Poland, +42-4-631-3317, fax: +42-42-631-3318, e-mail: ikrucins@mail.p.lodz.pl

Abstract

Clothing is an inseparable attribute of whole human life. Human skin is in direct touch with textiles both during the day and during the night. The interaction of skin and apparels depends on many factors. As well raw materials, fabric structure and temperature, humidity, air movement and physical activity and individual characteristic of wearer are responsible for all the features of skin – clothing microclimate. Sensory receptors, the nerve endings in the skin collect signals from the skin surface, regulate the physiological processes in the human body.

This paper will present the analysis of dependence of textile wearer muscle tension on polyester fibers content in blends with flax, which was the basic raw material in clothes, as well as changes of thermal conductivity of the textiles. We have examined the clothes made out of 100% linen, 100% PES and their blends with different percentage of both kinds of raw material. Every sort of raw material has been examined and the parameter of EMG of forearm muscle tension was registered each time with the volunteers wearing the clothes being examined.

The special attention has been put during examination on monitoring of parameters of skin -clothing microclimate, during 5 hours of wearing the clothes by volunteers. The parameters being registered were: temperature of skin of the back and shoulder, and humidity of skin covered by the examined clothes, and also the potential difference of an electrostatic field of electrostatics charges collected on the surface of the clothes. The experiments were performed during the state of rest. The results of tests showed that the increase of the skin temperature covered by clothes is created by other changes of registered EMG than increase of the potential difference of an electrostatic field of charges collected on the clothing surface. We have proved that there are serious changes in the parameters of skin-clothes microclimate which depends on the share of PES fibres in the blends with linen, even if the volunteers taking part in this experiment, has not been doing any physical exercises.

Key words: *clothes, linen, polyester, muscle tension, skin – clothes microclimate*

Introduction

Present studies were undertaken to determine the influence of natural and synthetic fibers and their blends, which were covering transiently the forearm muscles on the activity of motor units of these muscles. The motor units of the tested muscles were studying both in resting conditions and during the voluntary movements.

Among many factors which may influence of the activity of muscle motor units, especially after their covering with the synthetic fibers, there were taken into account the temperature changes as well as the possibility of the electrostatic field emission over the surface of examined muscles. It is supposed, that one of the determinants causing this phenomenon, there are changes in the transmission of motor fibers innervating the investigated muscles. The circadian cycle of the muscles efficiency coming from the fatigue-relaxation rhythm was also considered in these studies [5]. It is commonly known, that typically in the healthy human, the motor units after the relaxation during a sleep (between 1.00 a.m. and 7 a.m.) show a fluctuate activity up to the period of their maximal efficiency in pre- and afternoon hours (more or less between 11.00 a.m. and 1.00 p.m.) as well as later. Furthermore, about 6.0 p.m. - 10.00 p. m., the efficiency of the motor units undergoes exhaustion, because of their natural fatigue, reaching peak in the late evening hours (about 11.00 p.m.) [6]. Therefore, the period of the day when tests were performed (between 2.00 p.m. and 9.00 p.m.), was chosen to adjust changeable activity to the optimal period of the muscle motor units efficiency of the healthy human. The circadian cycle of the temperature rhythm is, in the general, the same as above. The variability in the motor unit efficiency is depends on the sex of the individuals what was especially subjected in these studies, choosing males only from the volunteers.

Aim of the study is also to describe the optimal content of polyester in blends with linen (used for clothes production) for comfort, good feeling and health. The changes of microclimate of skin-clothes sphere according to raw material of garment are also carefully analyzed. The authors try to clear the reason of those phenomena and describe the properties of tested fabrics, which can have influence on muscle tension.

Materials

Clothes made from linen, polyester and blends of these fibres (100% Linen, 75% Linen25% PES, 50%Linen50%PES, 25%Linen75%PES, 100%PES), were used as a tested material. Tests were done on men shirts and trousers made of above mentioned fibres; the same model (long sleeves) and the same construction. Only size has varied due to the differences in volunteers had signed up for the trails. Two kinds of 100% linen with different thickness: thin and two layers linen, were additionally used to the experiment for studying on the effect of heat resistance of fabrics on electromyographic parameters.

Raw material composition is chosen in this way, that analysis of changes of hygienic properties of clothes and microclimate in sphere skin – clothes will be possible according to polyester fibers share in blends with linen. All fabrics (except of “thin linen”) were plain fabrics and they were made from rotor yarn – linear density 100 tex. Table 1 shows the parameters of structure of these fabrics.

Table 1. Parameters of fabrics structure

Raw material	Mass per square meter g/m^2	Density of threads [1 dm]		Thickness [mm]	Clearances [%]
		Warp	Weft		
100% linen	259.1	160	124	0.68	3.49
75% linen 25% PES	286.2	159	128	0.64	2.23
50% linen 50% PES	285.6	158	126	0.68	2.56
25% linen 75% PES	307.7	158	129	0.69	2.53
100% PES	329.8	161	128	0.69	2.69
100% linen thin	127.4	187	179	0.43	7.18

Differences in structure of investigated fabrics are unimportant (except of “thin linen”) and should not have a bearing on their hygienic properties. In the case, recorded differences in fabrics properties and changes of parameters of microclimate in skin – clothes sphere, depend on variety of raw material composition of tested clothing.

Table 2. Properties of tested fabrics.

Raw material	Fabrics Hygroscopicity [%]		Water absorption Speed [s]	Heat Resistance [Km^2/W] x 10^{-3}	Air permeability [$l/m^2/s$]	Electrostatic potential on clothes surface [kV]
	65% relative humidity of air	100% relative humidity of air	JIS 1090: 1990	Alambeta	PN – EN ISO 9237: 1998	HAUG rotation meter
Standard	PN-80/P-04635					
100% Linen	8.05	12.70	0.23	7.68	516	0
75% Linen 25% PES	6.21	8.37	0.31	7,66	352.9	0.03
50% Linen 50% PES	3.90	5.95	0.32	8.5	302.3	0.14
25% Linen 75% PES	2.16	2.78	0.41	9.92	267.6	0.32
100% PES	0.27	0.39	1.00	9.04	266.6	1.26

The fabric properties connected with ability of water sorption worsen considerably with the increase of polyester fibers share in blends with linen. The increase of polyester fibers share of about 25% cause reduction of hygroscopicity level in proportional way. In case of speed of water sorption, big increase of time needed to soak in a water drop is visible for 100% PES fabrics. Reduction of speed of water sorption is not such considerable for blended fabrics. Even 25% share of linen in blends with polyester improves fabrics ability of water sorption.

Considerable decrease of air permeability of fabrics is visible in 25% share of polyester fibers in blend with linen. In spite of the similar structure of the fabrics, polyester fibers clearly reduce level of air permeability.

The man lives in permanent movement, performing every-day works; he moves his hand rubbing tens of times the trunk with the sleeves. In this way, the electrostatic charges are collected on the surface of clothes. During the study, an electrostatic potential was registered on the surface of each kind of clothes direct on the wearers. PES clothes was tested three times: first – after washing, second – after washing with antistatic finish, third – when electrostatic charges was generated by rubbing. The initial measurement of the potential in all tested cases was 0 kV.

The tests on the degree of electrostatic charges collection were conducted by measuring the potential difference of an electrostatic field at the fixed distance from the shirt. The magnitude and mark of the electrostatic field depends on the mark and magnitude of a charge forming this field, i.e. charges collected on the surface of the shirt and a distance from the source of the field.

The measurements were done by a rotation meter of HAUG Company. The detector of this meter has a rotating disk with segment of holes. The charges generate alternated electric signal, which is directed to the electronic unit of the apparatus. The meter gives readings of values of electrostatic field in the position of the detector. The meter can measure the potential difference from 100 V to 100 kV in several measurement ranges [8].

In the case of electrified surface, the value determining the electrostatic field is the surface density of electrostatic charges. To avoid the error connected with the geometry of the tested object and position of a meter in electrostatic field, no density of electrostatic charges was measured. Instead, a size and mark of potential difference of electrostatic field was determined.

In measurements of electrostatic field the distance between detector and the object is very important. The change of a distance causes the change of an electrostatic potential difference value at the same density of the charge. The measurements were done at the 15-mm distance between the detector and shirt surface. To assure the stability of measurement conditions the meter was fixed on a mount.

Regardless to the end-use finish of tested fabric, the man wearing polyester clothes is permanently exposed to an electrostatic field. Household anti-static products only partially improve this situation.

Clothing from the linen fabrics does not collect electrostatic charges on their surface. Even 25 % linen share in blends with polyester in fabrics reduces their ability to collect the charge.

Method

The studies were performed on ten volunteers who worn preliminary linen garments and than by turns blends and polyester garment.

Investigation was performed in Laboratory of Physiological Influence of Textiles on Human Body at stable condition: air temperature of 20^0 C +/- 2^0 C, relative humidity 50%+/- 2% and air movement less than 0,5 m/s. Volunteers were not engaged to the effort movements, they were usually asked for reading, playing with the computer (they chose the computer games), or they were talking. All they were previously informed about the aim of the examination and they gave the signed consent. They could drink the mineral water or eat fruit as necessary. Time of experiment – 5 hours. Humidity and temperature of back skin under the clothes was recorded every half an hour.

The test was repeated three times for each kind of raw material. The electromyographic parameters of muscles were gathered before exposition to the tested garment and after it. The volunteers group consisted of men with similar age, height, weight and constitutional conditions. The exposition duration with each garment was similar as well environmental conditions to avoid any accidental differences in results. Duration of exposition was strictly connected with biological day rhythm [1]. The EMG device recorded the level of muscle tension on surface of forearm during activity and static performance of volunteers, Fig.1.

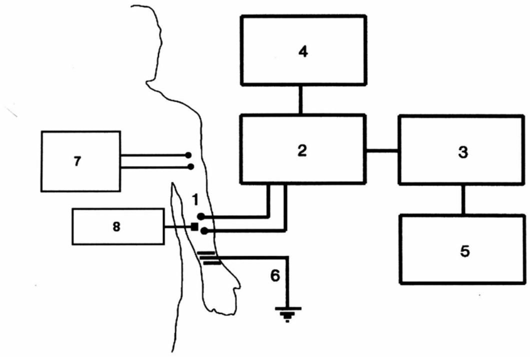


Fig. 1. Experimental arrangement used during tests performed in this study. 1 – surface bipolar recording electrodes, 2 – AC amplifier, 3 – personal computer, 4 – loudspeaker connected to the amplifier, 5 – printer, 6 – reference electrode, 7 – stimulating bipolar electrode, 8 – thermometer measuring temperature over the skin [7].

Results and discussion

Covering most parts of our body for most of the time in our daily life, clothing contacts most parts of the skin dynamically and frequently. This produces various mechanical, thermal, chemical, or electrical stimuli. The result of this effect is the differential microclimate in skin – clothing sphere.

Microclimate In Skin – Clothes Sphere

The microclimate in skin – clothes sphere depends on raw material, from which the clothes were made. Although fabrics structure is similar and tests conditions are constant, skin temperature increases, when the share of polyester grows in the blends with linen. Only in case of two layers of linen clothes (double thickness) skin temperature rises over the skin temperature under synthetic clothes, Fig. 2. In case of skin humidity you observe its significant increase for shirt made from polyester fibers. Even two layers of clothes from linen do not cause increase of skin back humidity, Fig 3. During the experiments, the neckbands were precisely buttoned up. The exchange of heat and air between clothes-skin area and surroundings was made difficult.

Experimental results

The muscles have always some tension even in the rest state (without brain control). The stimuli are sent constantly from the brain to cells of movement and then to muscle with frequency 2–6 Hz.

But temporary covering forearm muscles with different kinds of clothes can change some electromyographic parameters Fig. 4.

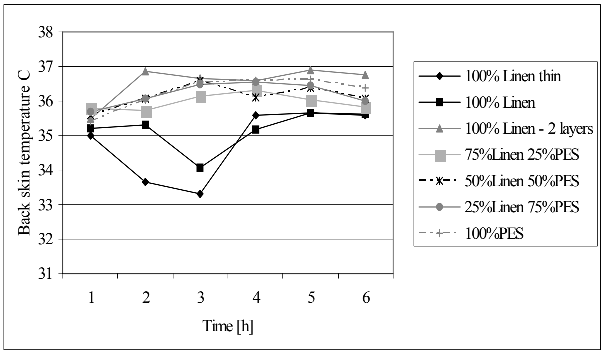


Fig. 2. The temperature of back skin under tested clothes during 5 hours of experiment (Grant 1000 Series Squirrel – Operating Instruction)

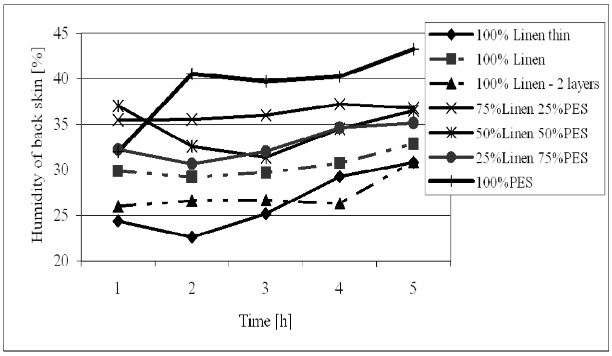


Fig. 3. The humidity of back skin under tested clothes during 5 hours of experiment (Grant 1000 Series Squirrel – Operating Instruction)

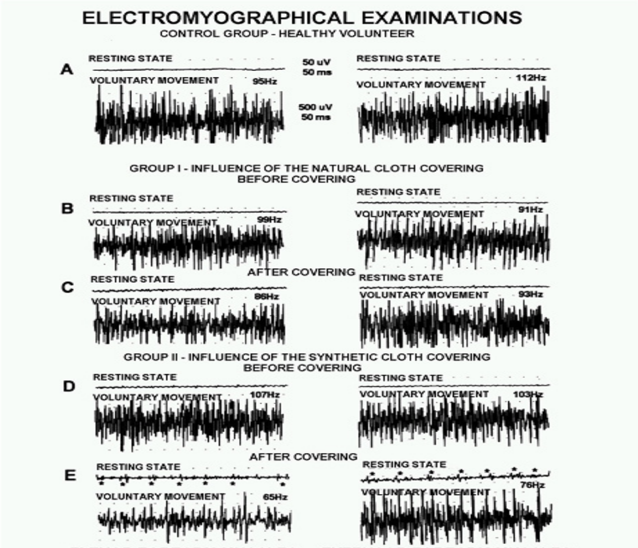


Fig. 4. Examples of EMG recordings obtained in the healthy volunteer (A) and two subjects of group I (B, C) and group II (D, E) before and after covering the forearm with two kinds of clothings. Upper records – recordings at the resting state, lower records – recordings during the voluntary movements. Stars show the presence of the spontaneous discharges. Numbers in the upper right corner show the frequency of the action potentials appearing in each record during the voluntary movements.

The analysis of EMG recording of muscles covered with different kind of clothes give a lot of information.

First of extra spontaneous discharges in resting state become visible in EMG recording under experimental clothes from 25% content of polyester in blends with linen. The bigger content of PE fiber in blends with linen, the bigger number of extra spontaneous discharges in EMG recording of muscles covered with tested clothes, Fig. 5.

It is most probably, that electrostatic field collected on the clothes surface (from 50% PES content in blends with linen) causes some desynchronization in muscle activity

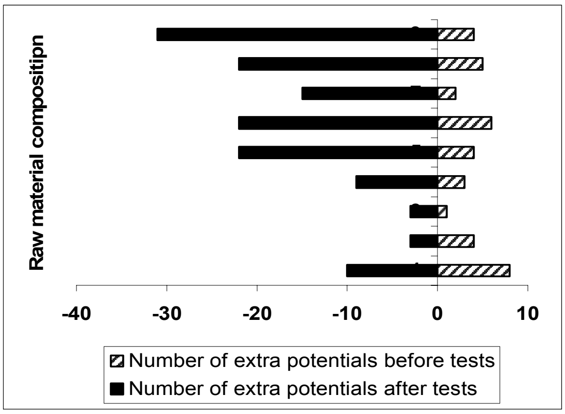


Fig. 5. Number of extra potentials in EMG recording before tests and after 5 hours of covering muscles with different kinds of clothes: 1. 100% Linen – 2 layers; 2. 100% linen; 3. 100% linen thin; 4. 75% linen 25% PES; 5. 50% linen 50% PES; 6. 25% linen 75% PES; 7. 100% PES; 8. 100% PES after antistatic finishing; 9. 100% PES after rubbing

Even if changes in EMG recording (in case of clothes made from polyester and blends polyester with linen) have acceptable range still they confirm existence of some desynchronization in muscle activity. That can lead towards tiredness during longer exposure to synthetics fabrics.

The mentioned occurrence is a result of presence of electrostatic charges on surface of polyester clothes and a higher skin temperature

Conclusion

1. The increase of shares of polyester fibers in blends with linen worsens hygienic properties of clothes and unfavorably influences microclimate in sphere skin – clothes.

2. Electrostatic field from charges collected on the surface of the polyester clothes have a permanent effect on human body and may cause changes in the electromyographic records of muscle tension, which prove desynchronicity of movement units, resulting in higher tendency to getting tired.

3. Higher skin temperature under tested clothes can also influence on EMG recording.

4. During the study on determination maximum of admissible share of synthetic fibers in blends with natural ones in clothes, which ensure positive influence on human body, one should consider 25% share of synthetics as optimum.

5. Everyday clothing can influence human muscle tension, what can be a reason for increase in feeling tiredness. Muscle activity can be consider as one of well – being factors.

References

[1] Holejwijn M., Heus R., Effects of temperature on electromyogram and muscle function, Eur. Appl. Physiol., 65, 541-545, 1992

[2] Huber J., Stryła W., Rogala P., Nowakowski A., Warzecha D., Wilusz A., Electrophysiological picture of different syndromes in the chronic low back pain, Medical News, 70, 3, 187-201, 2001

[3] Li Y., The Science of Clothing Comfort, Textile Progress, Volume 31, Nr 1/2, 2001

[4] “Samson Wright’s Applied Physiology”, Keele C.A., Neil E., (Eds.), London Oxford University Press, New York, 1965

[5] Swansh M., Schwartz M.S., Biopsy Pathology of Muscle, Chapmann i Hall, London, 1984

[6] Winkel J., Jorgensen K, Significance of skin temperature changes in surface electromyography, Eur. Appl. Physiol., 63, 345-348, 1991

[7] Zimniewska M., Huber J., Krucińska I., Torlińska T., Kozłowski R., The Influence Of Natural And Synthetic Fibres On Activity Of The Motor Units In Chosen Muscles Of Foream; *FIBRES & TEXTILES in Eastern Europe* No. 4/ 2002

[8] Zimniewska M., Michalak M., Krucińska I., Więcek B., The Physical Properties of Surface of Apparel Made From Flax and Polyester Fibres. *International Journal of Clothing Science and Technology*, Vol. 15 No. 3 / 4, 2003

Lenzinger Berichte, 85 (2006) 44-50

TENCEL® HIGH PERFORMANCE SPORTSWEAR

Heinrich Firgo, Friedrich Suchomel, Tom Burrow

Textile Innovation, Lenzing AG, Austria

Hydrophilic natural fibers like cotton and wool and the man made cellulosic fibers are recognized as having excellent absorbency and breathability. Most synthetic fibers are hydrophobic and non absorbent but can deliver strength and easy care properties.

Sportswear fabrics need to provide a comfortable environment for the wearer and consequently need to be able to handle moisture vapor and sweat produced by the body, they need to help in controlling temperature and they need to feel good. Modern sportswear is most usually made from synthetic fibers. The objective of this work was to explore whether the natural hydrophilic properties of TENCEL® — a man made, solvent spun cellulosic fiber — could be used to enhance the moisture handling and other properties of sportswear fabrics while at the same time improving the aesthetics.

Moisture Management

“Moisture management” in relation to a fabric refers to its ability to transport, store and dispose of liquid water released from the body. “Breathability” refers to the ease with which gases including water vapor can pass through the fabric.

Liquid water released by the body is known as sensible perspiration. To be removed from the body it must be wicked through the fabric structure and then evaporate from the outside of the fabric. When it evaporates heat is removed which helps to control the temperature of the body.

Water vapor or insensible perspiration can pass through openings between fibers and yarns in a breathable fabric. When water vapor is produced by the body, heat is removed giving a direct cooling effect.

During exercise, both insensible and perspiration and sensible perspiration are produced, but the latter increases in response to rising body temperature producing liquid at the surface of the skin. Fabrics used for active sportswear must have the ability to transport moisture away from the skin to the fabric surface for evaporation. The most effective fabrics will spread moisture over a wide area to maximize the surface area available for evaporation and hence cooling.

Cellulosic fibers in sportswear

100 % cellulose fiber garments are widely used for general sports clothing and street wear, but the only fabrics actively promoted for high performance sportswear are made from synthetic fibers. Consumers and sportswear manufacturers have the view that cellulosic fibers are unsuitable for use in sportswear for high activity where sweat production needs to be dealt with.

The reasons for this view of cellulosic fabrics are real and need to be addressed if the use of cellulosic fabrics in sportswear is to be increased. Cellulosic fabrics absorb water into the fiber structure and become heavy. This leads to stretching of the fabric, sticking to the skin and when activity ceases the fabric may feel cold against the skin. Higher levels of moisture absorbed in the fabric mean longer drying times.

However, cellulosic fabrics are generally perceived to be more comfortable than synthetic fabrics when worn for normal day-to-day activities. They are preferred for a wide range of apparel fabrics where visual aesthetics, handle and comfort are important. In these areas synthetic fibers are only used in blend with cellulosic fibers or where price and/or easy care performance are considered more important.

In order to deliver these positive properties of cellulosic fibers and to eliminate the negative aspects of performance, a new approach is needed. A successful cellulosic containing fabric will need to have a much lower absorbent capacity than a 100 % cellulosic but must also deliver the good visual aesthetics, handle and touch that cellulosic fibers are known for. The fabric would also have excellent moisture handling capability and be easy care. The hypothesis which is tested in this work is based on this thinking.

Basic considerations

The most common strategy used to give high performance in synthetic fiber based active sportswear is to use a two layer fabric with a hydrophobic skin contact layer and a hydrophilic outer layer (Fig. 1). Sweat is pulled through the fabric by the hydrophilic fiber on the outside and then spreads through the fabric outer surface to maximize the area available for evaporation. This leaves the skin contact layer feeling dry because the moisture has been transported to the outside. Because the fabric has a low moisture content — as moisture is not absorbed directly by the fibers — it will dry rapidly.

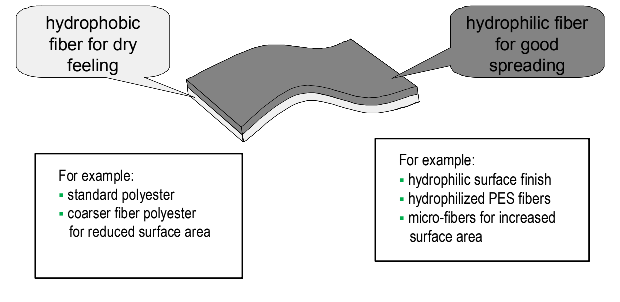


Figure 1. Two-layer fabric strategy

Polyester is the most common fiber for active sportswear although nylon is sometimes used. 100 % polyester two-layer fabrics perform well in general, but do have some disadvantages. The hydrophilic surface finishes used for the fiber on the outside can be removed as the garment is washed and worn. Hydrophilic polyester fibers are specialty products and carry a premium price. For 100 % polyester fabrics the only aesthetic options possible are a synthetic appearance, hand and touch which does not appeal to all users.

Hypothesis

TENCEL® is naturally and permanently hydrophilic. It has a high water absorption capacity which means that if it were used as 100% of the outer layer of a sportswear fabric it would suffer from the disadvantages described above. However, if it were blended with polyester, the absorbent capacity could be controlled to an acceptable level by the blend ratio and the TENCEL® would deliver the hydrophilicity needed for transport of moisture through the fabric and for spreading across the outer surface.

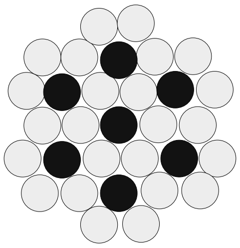


Figure 2. 20 % of the fibres in a yarn

To work effectively, the TENCEL® would need to be present in sufficient quantity to give a continuous network of fibers in the fabric to provide an uninterrupted path for the moisture to follow. To achieve this goal a blended yarn containing at least 20 % TENCEL® should be adequate to give good wicking and liquid spreading.

Basic investigations: test fabrics and test methods

The first trials to test the hypothesis were made with simple single jersey fabrics containing a range of blend ratios of TENCEL® and polyester staple fiber. The fibers were intimately blended during yarn production.

- 100% PES
- 10% TENCEL®/ 90% PES
- 20% TENCEL®/ 80% PES
- 30% TENCEL®/ 70% PES
- 40% TENCEL®/ 60% PES
- 50% TENCEL®/ 50% PES
- 100 % TENCEL®

The following tests relevant for physiology were done on the fabrics

- Water absorbency/wetting (GATS test)
- Spreading of water
- Drying velocity
- Water vapor permeability resistance, Ret value (guarded sweating hot plate)
- Thermal resistance, Rct value (guarded sweating hot plate)
- Water vapor permeability index, imt value
- Wet cling index

Basic investigations: water absorbency and wetting – Fig. 3

The GATS test measures the amount of water absorbed by a sample when water is delivered at zero pressure to a point at the centre of a disc of fabric. For the fabric to absorb, it must positively pull the water into its structure.

The 50 % TENCEL® / 50 % PES fabric has the highest water absorption capacity and absorbs at a similar rate to the 100 % TENCEL® fabric. The 30 % TENCEL® / 70 % PES absorbs at a lower rate but matches the total absorbency of the 100 % TENCEL®. Normal hydrophobic polyester (100PES) does not wet at all.

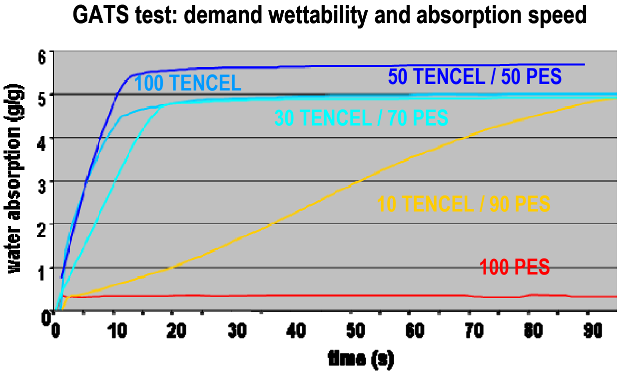


Figure 3. Basic Investigations – GATS

Basic investigations: spreading of moisture – Fig 4

500 mg of water containing a dye is applied with a syringe to the center of a 15 cm disc of fabric. The area over which the water spreads is measured.

Spreading of moisture is best for 30 % TENCEL® / 70 % PES fabric. On the 100 % PES fabric moisture does not spread at all.

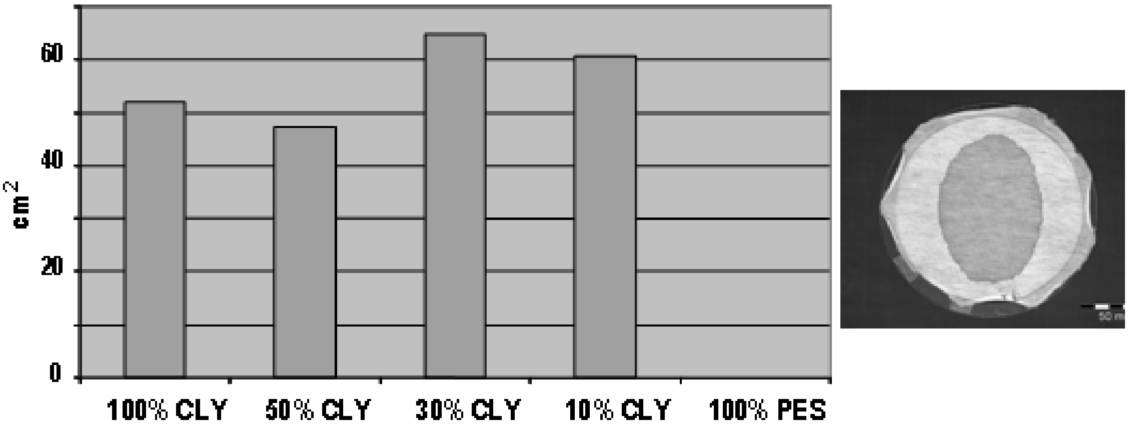


Figure 4. Basic investigation – moisture spreading

Basic investigations: Drying velocity – Fig 5

The sample from the moisture spreading test above is placed on a balance in a conditioned atmosphere and continuously weighed as it dries.

The 30 % TENCEL® / 70 % PES fabric dries about 25 % faster than the other blends. The 100 % PES dries very slowly because the applied water did not spread. The surface available for evaporation is small.

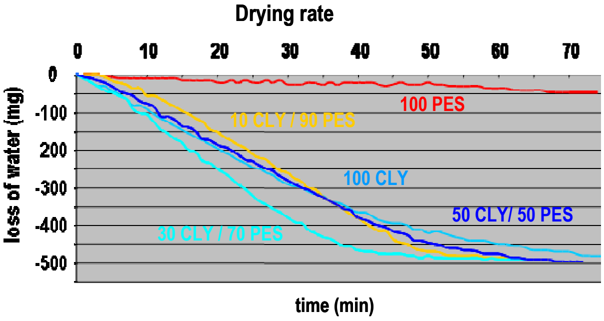


Figure 5. Basic investigations – drying rate

Basic investigations: breathability and thermal behavior – Fig 6

The sweating guarded hotplate method is used to measure the evaporative resistance (Ret) and thermal resistance (Rct) of a fabric by careful ly monitoring heat and vapor transmission in a closely controlled environmental chamber. From these measurements, the water vapor permeability index can be calculated as in eq. 1.

$$imt = 0.6 \times \frac{Rct}{Ret} \quad (1)$$

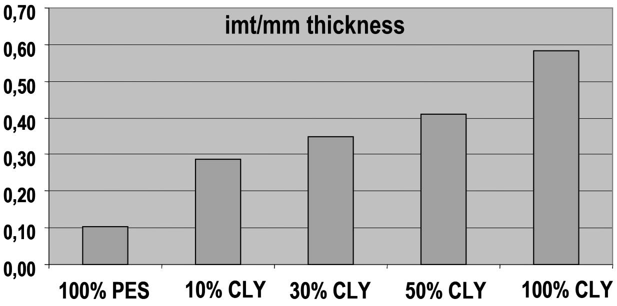


Figure 6. Basic investigation – SGHP

The imt – value is a measure of the balance between water vapor permeability and thermal conduction of a fabric and should normally be as high as possible.
The 30 % TENCEL® / 70 % PES blend still gives an intermediate imt – value.

Basic investigations: Wet cling behavior – Figure 7

The wet cling index is a measure for the tendency of a fabric to cling to the wet skin. It is determined by measuring the force required to pull a wet fabric over a standard wet surface. According to the Hohenstein Institue, Germany, an acceptable performance is generally lower than ik = 15.

With increasing TENCEL® content of the fabric, the wet cling index becomes smaller TENCEL® therefore improves the wet cling performance of PES fabrics

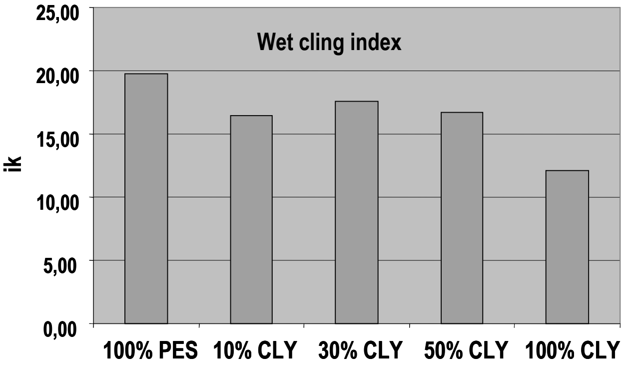


Figure 7. Basic investigation – Wet cling

Overall results of basic investigation

The PES rich single jersey made from 70% PES/ 30% TENCEL® yarn showed the best overall performance giving:

- good absorbency
- best moisture spreading
- fastest drying rate
- intermediate water vapor permeability index
- good wet cling behavior

These are the properties that are needed for the outer layer of a two-layer active sportswear fabric.

Two-layer fabric trials

Based on the results of the basic investigation, a range of fabrics was produced which included fabrics using a 30 % TENCEL® / 70 % PES intimate blended yarn on the outside face and a 100 % PES filament yarn on the inside as the skin contact layer. The physiological properties have been compared to single jersey constructions. As a benchmark polyester running shirts with "Nike DriFit" and "Reebok PlayDry" technologies have been used.

Examples

- Double layer 1 ("DL SJ")
  - Outside Single Jersey 70 % PES / 30 % TENCEL®
  - Inside Single Jersey 100 PES filament

- Double layer 2 ("DL PIQ")
  - Outside Pique 70 % PES / 30% TENCEL®
  - Inside Single Jersey 100 % PES filament

- Single Jersey 1 ("SJ 80/20")
  - 80 % PES / 20 % TENCEL®, 5 % Dorlastan plated

- Single Jersey 2 ("SJ 70/30")
  - 70% PES/ 20% TENCEL, 9% Dorlastan plated

- Single Jersey 3 ("SJ 30/70")
  - 100% TENCEL® yarn alternating with 100% PES filament yarn, 5% Dorlastan

- Nike DriFit ("Nike")

- Reebok PlayDry (Reebok")

Two-layer fabric trials – moisture absorbency (GATS) – Figure 8

The two layer fabrics have best water absorption properties of those tested. The fabrics that contained Elastane gave lower Gats - test absorbency due to tighter fabric construction.

Two-layer fabric trials – moisture spreading – Figure 9

Moisture spreading performance of the TENCEL® two-layer fabrics is between the Nike and Reebok fabrics. The 70 % PES / 30 % TENCEL® intimate blend single jersey shows better spreading than the TENCEL® rich 30PES/70TENCEL® system blend single jersey because the TENCEL® fibers absorb the moisture as well as spreading it.

Two-layer fabric trials – Drying rate – Fig 10

The drying rate of the TENCEL® two-layer fabrics is comparable to the Nike and Reebok benchmark shirts. The Elastane containing single jersey fabrics dry slower than the two-layer fabrics. The TENCEL® rich single jersey dries the slowest.

Two-layer fabric trials – "Water vapour permeability index – Fig 11

The water vapor permeability index for all of the TENCEL® containing fabrics is much better than for the Nike and Reebok benchmark fabrics. The double layer piquet construction shows extremely good breathability.

Two-layer fabric trials – Wet cling – Fig 12

The wet cling properties are OK for all of the fabrics (ik < 15). The TENCEL® containing two-layer fabrics show excellent wet cling behavior.

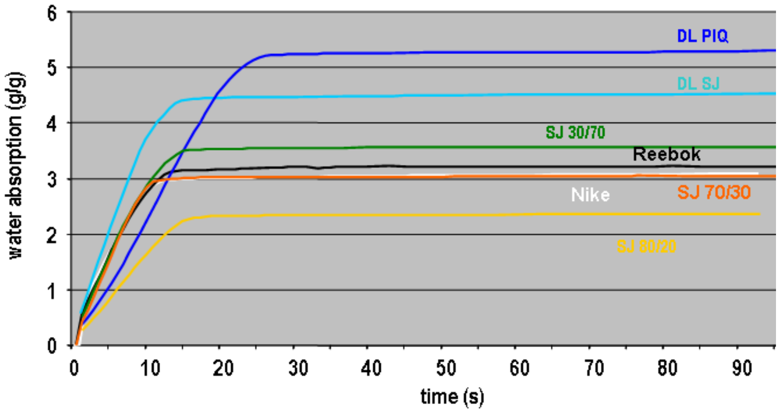


Figure 8. Two-layer fabric trials – GATS

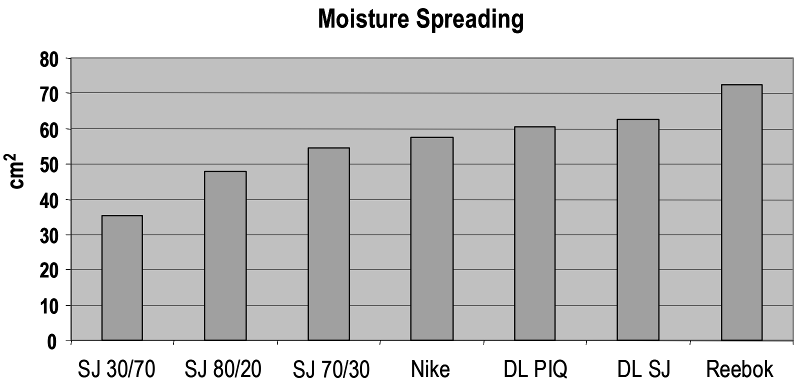


Figure 9. Two-layer fabric trials – Moisture spreading

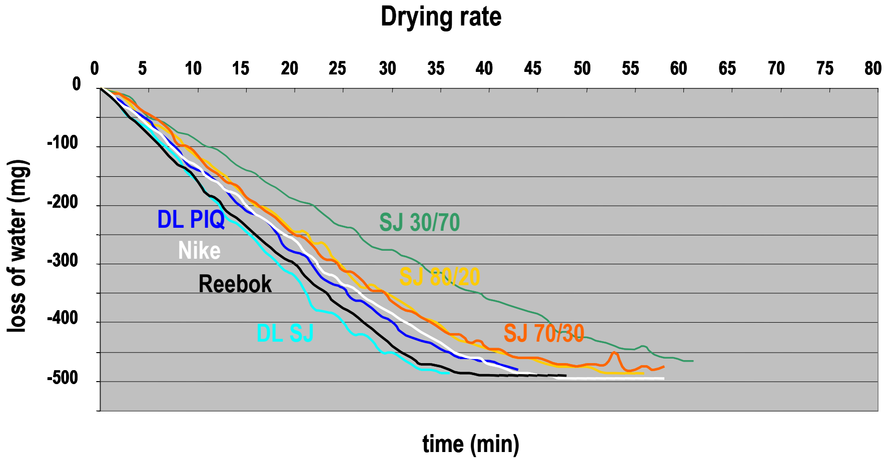


Figure 10. Two-layer fabric trials – Drying rate

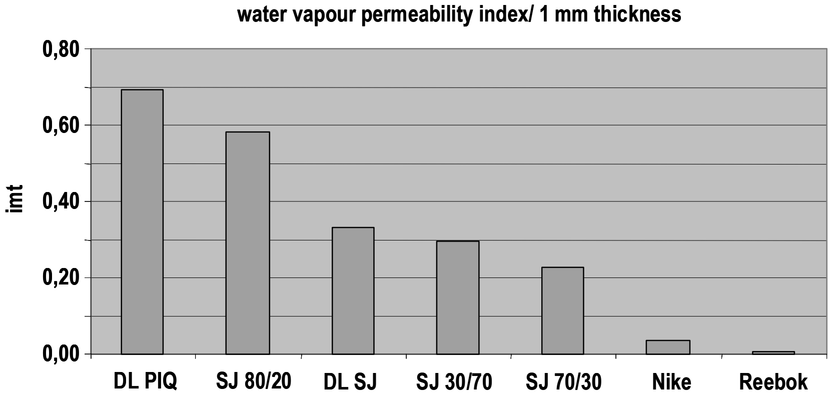


Figure 11. Two-layer fabric trials – Water vapour permeability

Conclusions

TENCEL® can be used effectively for the development of high performance sportswear provided that the fabric is carefully designed to maximize the contribution the TENCEL® makes to the performance of the fabric.

TENCEL® can serve as a permanent hydrophilic component as an alternative to hydrophilic topical treatments of polyester or expensive hydrophilic PES fibers.

Compared to high quality 100% polyester sportswear, two-layer fabrics made using TENCEL® in the outer layer give:

- better moisture absorption and buffering
- equal moisture spreading
- same drying rate
- equal wet cling behavior
- a much better balance of water vapor permeability and thermal comfort
- a less synthetic look and touch

TENCEL® can be used in minority blends with polyester as the outer layer of a two-layer construction to give high performance sportswear for athletic activities where sweat production is high. The fabrics produced have a non-synthetic look and touch.

Lenzinger Berichte, (85 (2006) 51-53

COMPARATIVE RESEARCH: MICROCLIMATE OF BEDDING COMPONENTS

Dr. Konrad Helbig

Research Group Physiological Anthropology, University of Kiel, Legienstraße 35, D-24103 Kiel

Abstract

Technical examination of textile materials focuses on a comparison of their characteristics, e.g. in checking their thermal insulation and humidity transport, while microclimactic testing of products with test subjects attempts to assess the significance of these characteristics for the climate close to the body of the users.

In this paper, test methods are described (measurement of temperature and humidity close to the body, in the cavity between sleeper and bed components, inside blanket and pillow) which serve to describe the influence of the material of the used bed components on the general climactic situation. This situation is evaluated under the aspects of comfort and suitability. In this respect, product evaluation by physiological anthropologists is always founded upon the knowledge on the variability of subjective preferences, of physiological factors and of the respective environmental conditions.

The test methods are exemplified with a recent test of bedding components made of different fiber materials.

1. Preliminaries

A physiological assessment of products is conducted in the dynamics between standardized technical testing and research with test subjects. The results of technical testing describe material properties while the assessment with test subjects (according to German Standard DIN 33419) show the effects of these characteristics on humans.

The interrelationships of the complex of human characteristics and the resulting technical requirements can be very simple (body length – bed length), but also quite complex in the realm of physiological features (thermoregulation on the bed – bedding components).

2. Methods

Technical testing of textile materials in human contact usually results in a good comparability in properties such as insulation-weight index or water vapor permeability. Thus, utilization of materials can be allocated and particular material suitability can be assessed.

In testing microclimate with test subjects, there are two major differences compared to technical testing:

- The direct effects of the material on human beings is assessed, e.g. through measurements of temperature and relative humidity in the sleeping cavity.
- The variability of physiological features – as for instance sweating – can be taken into account in working with test subjects.

Thus, while technical testing is the means of comparison for material properties, usually not allowing for a categorization of the effects of these properties on different human beings, testing with test subjects is used to assess the effects of these characteristics on humans directly and to describe them in their variation.

This type of research is conducted with a quoted collective of test subjects (e.g. who represent the upper 25% of the total population in their transpiration capacity) in various standardized environmental climates. Test subjects are acclimatized and measurements are usually performed over a span of 120 minutes. Previously, bedding components are climatized over a time span of over 12 hours in the respective environmental conditions. Between testing, the climactic chambers are ventilated, so that every test can be performed in initially similar climactic conditions.

Measured values are continually registered in intervals of 60 seconds and represented as sequences (here every 10th value, see fig. 1).

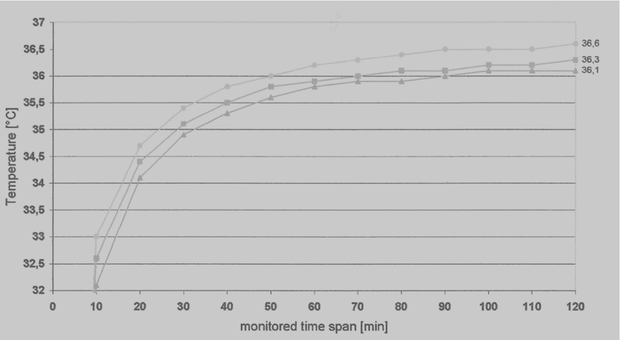


Figure 1. Exemplary temperature sequences

The following table (Table I) compiles the locations for measuring temperature and relative humidity. Measurements are performed using combination sensors and data loggers of the type testo 454.

Table I. Measurement locations

Location	Sensor-Application	Parameters	
		Temperature [°C]	Humidity [%rH]
Skin	abdominal area above the pelvic bone	x	
Sleeping cavity	lateral of the waist without direct body contact	x	x
Body-sphere	contact area in the lumbar region	x	x
In the blanket	abdominal area, center of the filling	x	x
On the pillow	contact area in the upper spinal lordosis	x	x

3. Results

In product testing, the usual procedure is to test a new or modified product in a standardized environment, keeping as many factors as possible constant to be able to make a statement about the new product.

In drawing comparisons between complete bed equipments, as presented exemplarily in this paper, an inverse method was chosen. A standard bed with complete current equipment was compared to a bed with polyester components and one with Lyocell components, respectively. The objective was to illustrate possible differences between the three equipments more clearly. The measurements were performed in an environmental climate of 18°C and 50%rH.

3.1. Temperature

The most telling differences resulted in the comparison of the sleeping cavity, the contact area (body-sphere temperature) and the blankets. It was ascertained that polyester has the lowest insulation properties, while Lyocell has a clearly higher value lying marginally above the one of the standard bed, i.e. Lyocell has better insulation effect in the sleeping cavity and in the contact area as well as a lower value inside the blanket (less loss of warmth). Figures 2 and 3 illustrate the final values after 120 minutes of monitoring.

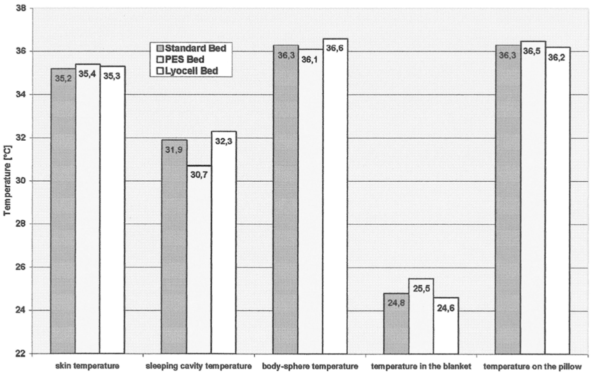


Figure 2. Average temperature values

3.2. Relative Humidity

In the relative humidity of the sleeping cavity, the best result was reached by the Lyocell bed (43.5%rH). The relative humidity in the contact area between the prostrate test subject and the support system shows similarly clear differentiation between standard bed, PES-bed and Lyocell-bed, the latter reaching values under 40%rH (the resulting climate is adverse to house dust mites).

When taking into account that relatively similar temperatures were measured in all three equipment variants, yet clearly lower values of relative humidity occurred in the Lyocell equipment, it can be ascertained that there is a better humidity transport or absorption in this variant. This assessment is supported by the finding that a practically identical relative humidity to the other variants was measured **in** the blanket (despite low relative humidity in the sleeping cavity and the contact area, see fig. 3).

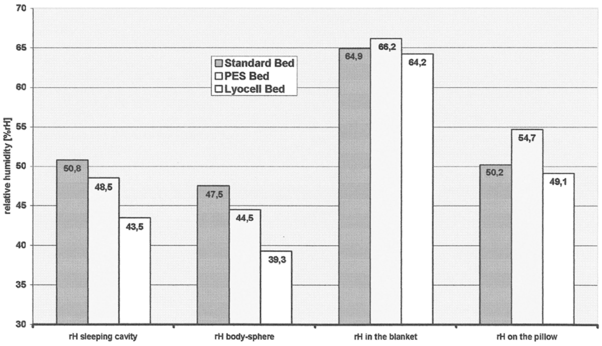


Figure 3. Average humidity values

Since the monitoring was not performed at the regular environmental conditions of 23°C and 50%rH, in which the major factor for a comfortable sleeping climate is humidity transport, but at a relatively cool temperature of only 18°C (and 50%rH), the favorable combination of insulation and humidity transport of the Lyocell materials could be clearly differentiated.

4. Summary

Comparative microclimatic research of bedding components was performed, in which the effects of different materials on the microclimatic conditions were assessed. This research differs from mere technical testing, as test subjects chosen according to German standard DIN 33419 were employed.

In summary, it could be shown that the employed conditions allow for a clear differentiation of textile materials concerning their suitability for bedding. The results illustrated that the specific properties of lyocell used in bedding components can influence positively the temperature as well as the relative humidity.

Lenzinger Berichte, 85 (2006), 54-60

IMPROVED METHODS FOR THE INVESTIGATION OF THE INTERACTION BETWEEN TEXTILES AND MICROORGANISMS

Linda Teufel[1,2] and Bernhard Redl[2]

[1]Christian Doppler Laboratory for Textile and Fibre Chemistry in Cellulosics, Institute of Textile Chemistry and Textile Physics, Leopold- Franzens University Innsbruck, Hoechsterstr. 73, A-6850 Dornbirn, Austria
[2]Division of Molecular Biology, Biocenter-Innsbruck Medical University, Fritz Pregl Strasse 3
A-6020 Innsbruck, Austria

ABSTRACT

Clothing textiles are in permanent contact with microorganisms, which can cause serious problems, including fabric rotting, staining, unpleasant odours and health concerns ranging from simple discomfort to physical irritation, allergic sensitization, toxic responses, infection and disease. Therefore, the control of undesirable effects of microbes on textiles is becoming an important issue in textile industry. One possible approach to limit growth of microorganisms is the use of biocides in textile finishing. However, this may lead to health and environmental concerns in everyday use of textiles. Another approach might be the use of materials with inherent activity to reduce microbial growth. In this context the evaluation of biofilm development on the various materials and the interaction between microorganisms and textiles will be an essential part in textile research. In moderate climate most problems arise from bacteria transferred from human skin. The bacterial skin flora is highly complex with a large number of microorganisms, some of which can hardly be cultivated. Therefore, similar to other complex microbial communities there are serious difficulties to analyze these systems. This article summarizes the current microbiological methods used in textile research and gives some outlook for future developments in this field of research.

Keywords: *microbial growth, textiles, DNA quantification, testing*

Introduction

Textiles and clothing are in permanent contact with microorganisms from the environment and the human skin. Whereas in hot and wet climate major problems arise with microorganisms from environment, which produce enzymes to degrade organic materials, in moderate climate major problems arise with bacteria transferred from human skin. Generally, textiles might be an excellent substrate for microbial growth, because they are made of organic materials providing a good base for biofilm attachment and the human sweat, which is retained by the textiles, provides nutrients necessary for bacterial growth. The human skin contains a complex mixture of microorganisms, even with "clean" skin having a typical population of between 100-1000 microbes/cm^2 (1, 2, 3). At these levels microbes pose neither a health or odour problem. To the contrary, their presence and balanced population is essential for human health (3). But when ideal growth conditions are provided, microbes rapidly multiply and can then cause problems preferentially with smell generation, loss of performance, discolouration of textiles and possibly infection (4). Most ideal growth conditions occur at high moisture, which is normally found under increased production of sweat. In extreme cases, microorganisms can cause serious problems, include fabric rotting, staining, unpleasant odours and health concerns ranging from simple discomfort to physical irritation, allergic sensitization, toxic responses, infection and disease (4). Many of the characteristic malodours associated with the human body are due to the presence of large populations of microorganisms (5, 6). Whereby the associated malodours are the result of these microorganisms digesting nutrients in the perspiration and releasing volatile pungent waste products (7, 8, 9). Therefore the control of undesirable effects of microbes on textiles is becoming an important issue in textile industry. Currently, there is much interest in hygienic fabrics that offer an advantage in respect of cleanliness and odour prevention as a result of their antimicrobial properties or inherent reduced bacterial growth. Such fabrics include clothing, especially that worn next to the skin (lingerie, T-shirts, socks etc.), but also other domestic textiles, such as wipes and cloths.

This article provides an overview of the current methods for investigating the interaction of microorganisms and textiles and describes some novel applications. In addition, aspects for a critical evaluation of some methods, which are related on bacterial „model organisms“ and do not consider the complexity of the human skin flora, are discussed.

Methods based on „classical“ microbiological procedures

Originally, most of these methods have been developed for testing of antibacterial finishes on textile materials (Table 1). However, under certain conditions they can be adapted to be used as a general procedure for determination of growth of microorganisms on different textiles.

Tab.1 Conventional culture-based antimicrobial activity tests

Agar plate tests, semi quantitative	Textile fabrics: Determination of the antibacterial activity	SN 195920- 1992
	Textile fabrics: Determination of the antimycotic activity	SN 195921- 1992
	Antifungal activity, assessment of textile materials: Mildew and rot resistance of textile materials	AATCC 30- 1993
	Antibacterial assessment of textile materials: Parallel streak methods	AATCC 147- 1993
	Antibacterial activity of fabrics, detection of	AATCC 90- 1982
	Antimicrobial activity assessment of carpets	AATCC 174- 1993
Challenge test, quantitative	Antibacterial finishes on textile fabrics, assessment of	AATCC 100- 1993
	Testing method for antibacterial textiles	JIS L 1902- 1998 and - 2002
	Textile fabrics: Determination of the antibacterial activity: Germ count method	SN 195924- 1983
	Properties of textiles- Textiles and polymeric surfaces having antibacterial properties. Characterisation and measurement of antibacterial activity	XP G39- 010- 2000
Dynamic shake flask test, quantitative	Testing methods for organic man-made fibres with antibacterial activity	BISFA booklet, 2002, chapter 4.4
Fouling tests, soil burial tests	Methods of test for fungus resistance	JIS Z 2911- 1992
	Textiles- Determination of resistance of cellulose containing	ISO 11721- 1- 2001

For testing of the antimicrobial activity a first overall classification of the method to be used is carried out on the basis of the kind of the evaluation of the micro-organism population into intimate contact with an agar culture medium inoculated with the test bacteria (DIN EN ISO 20645 - 2001, AATCC 147). If a diffusable antibacterial activity is present, it will be possible to observe a clear zone around the treated sample comparing to the zone of bacterial growth around and the untreated control sample after the same contact time. However this method cannot be applied for non diffusable antimicrobial substances.

The Parallel Streak Method (AATCC 147-2004) has filled a need for a relative quickly and easily executed qualitative method to determine antibacterial activity of diffusable and non-diffusable antimicrobial agents on treated textile materials. In the „classical“ Parallel Streak Method (for diffusable agents), the agar surface is inoculated making it easier to distinguish between the test organism and contaminant organisms which may be present on the unsterile specimen. The Parallel Streak Method has been proven effective over a number of years of use in providing evidence of antibacterial activity against both Gram positive and Gram negative bacteria. A modified Parallel Streak Method can be used to evaluate the antimicrobial activity of non-diffusable agents. Thereby, a piece of textile is pressed onto an agar plate and the test bacteria are inoculated over the specimen by three or four parallel streaks.

DIN EN 1650, AATCC 30, is a further semi-quantitative test for anti-mycotic properties, which shows the effectiveness of anti-microbial finishes on fungi and moulds. Samples are treated with a specific spore suspension of a germ and incubated on agar plates. After evaluation, it is possible to establish the effectiveness of the anti-mycotic treatment. When testing resistance to moulds, it has to be considered that the incubation time must be at least twenty-one days.

Quantitative methods are based on the determination of the number of bacteria, still living after an opportune contact time. The quantitative evaluation can be differentiated reduction: qualitative or quantitative.

In the qualitative methods the test specimen and an untreated control are pressed further in other two classes according to the main test conditions. In the „Challenge Test“, a small amount of liquid culture medium is used to cover a specimen, while the fibre specimen is immersed in a larger amount of liquid culture when the dynamic „Shake Flask Test Method“ is carried out. Most quantitative methods are adequately sensitive but cumbersome and time consuming for routine quality control and screening tests.

In Challenge-Tests JIS L 1902, DIN EN 1276, AATCC 100, ASTM E 2149-01, ASTME 2180-01 samples with and without anti-microbial substances are treated with a specific test germ suspension. The fluid is immediately washed off of one portion of the test bed, whilst incubation is allowed to take place on the remaining samples, before they are also washed off. The number of germs on each can then be counted and compared to quantify the effectiveness of the anti-microbial finishing. Test variants under growth conditions (nutrients supplied) and non-growth conditions (no or very little nutrients supplied) are in use.

The dynamic Shake Flask Test Method (BISFA) (10) is designed to evaluate the resistance of non-leaching antimicrobial treated specimens to the growth of microbes under dynamic contact conditions. This dynamic shake flask test was developed for routine quality control and screening tests in order to overcome difficulties in using classical static antimicrobial test methods to evaluate substrate-bound antimicrobials. These difficulties include ensuring contact of inoculum to treated surface (as in AATCC 100), flexibility of retrieval at different contact times, use of inappropriately applied static conditions (as in AATCC 147), sensitivity, and reproducibility.

Although the methods described above have been originally developed to test the antimicrobial activity of modified fibres and textiles, they can be adapted for the assessment of bacterial colonization on various materials which have not been treated with antimicrobial agents.

The results of such an experiment are depicted in Fig. 1. In this experiment we have used the Challenge test (JIS L 1902) under growth conditions to compare different materials in their susceptibility for bacterial colonization under conditions of different humidity. For this purpose fibres made of the hydrophilic material cellulose, TENCEL® fibres, (from Lenzing AG, Lenzing, Austria; a fibre of the generic name Lyocell) (CLY), and fibres made of hydrophobic materials, polyester (PES) an polypropylene (PP), were incubated with different amounts of medium to ensure either 50% humidity or 100 % or 200% humidity. *Staphylococcus* sp. was used as a test organism.

From this experiment (Figure 1) it can be concluded that in a certain range of humidity, the hydrophilic materials reduce microbial growth, probably by limiting the amount of free medium and / or available water on the fibre surface.

The effect is especially pronounced with the hydrophilic fibre below the fibre saturation point (which is at 60 % absolute humidity for TENCEL®).

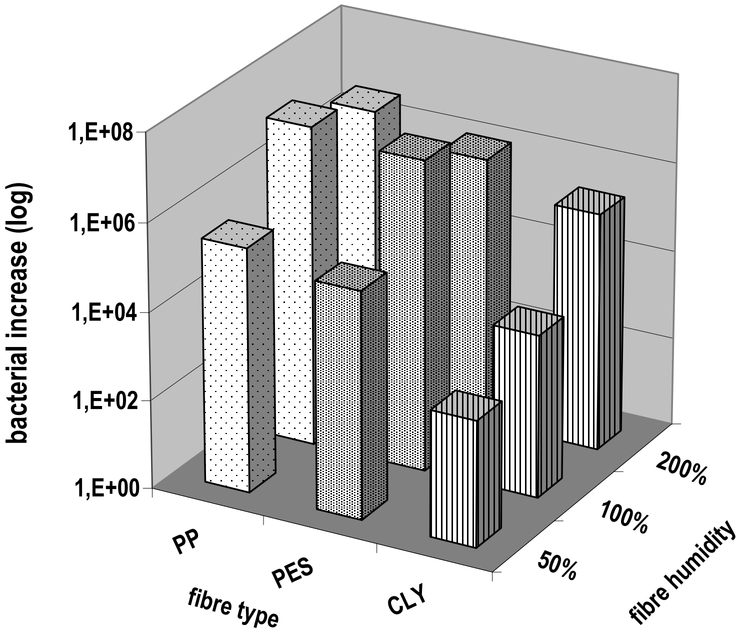


Figure 1. Challenge tests according to JIS L 1902 were used to investigate the growth of *Staphylococcus* sp. on hydrophilic TENCEL® (CLY) and hydrophobic (PES/PP) fibres. Humidity is given as % water added to 100 % dry fibre material

Novel culture-independent methods

The bacterial skin flora is highly complex with a large number of microorganisms, some of which can hardly be cultivated (2, 3). Therefore, similar to other complex microbial communities there are serious difficulties to analyze these systems. As described above most of the present methods used to assess textile susceptibility and biocide efficacy are culture-based procedures, and are thus inadequate to reflect the *in vivo* situation. In addition, many methods are done using specific bacterial test strains, some of which do not have relevance in the normal skin flora. Therefore, methods for the *in situ* determination of microbial communities present on standard textiles as well as on biocide-treated textiles are of crucial importance (11).

A first attempt to overcome the limitation of culture-based methods in textile research was done by McCarthy (12). In this work measurement of adenosine 5`-triphosphate (TP) by the luciferin-luciferase reaction was used for estimation of microbial growth on textiles. The presence of ATP is a useful marker of „life“ and chemoluminescent detection of ATP using luciferase is a highly sensitive assay. However, this method needs a quantitative extraction of ATP, which is not easy to perform. And the amount of ATP is not strictly related to the number of microorganisms, but is dependent of the physiological status of microorganisms.

Recently, we have established a method for **assessment of microbial colonization and growth on textile by DNA quantification**, based on a suitable DNA extraction protocol and quantification of the extracted DNA with the highly sensitive fluorescent dye PicoGreen (13). This method provides a fast and sensitive procedure to compare the amount of microrganisms present on different material after *in vivo* trials.

This method was used to compare the bio film development on sportswear made of hydrophobic or hydrophilic materials. Therefore, T-shirts made of polyester (PA), polypropylene (PP) and cellulosics fibres, TENCEL® (CLY) and cotton (CO), were cut into halves and sawn together to obtain different combination of materials. These T-shirts were used for an *in vivo* trial of 44 test persons during soccer training for 2h at a moderate temperature (15 – 18 °C). Samples were then cut out at defined positions (2 pieces from each, back, front and axilla) from each half of the shirt and analyzed by the DNA-quantification procedure. Tab. 2 shows the summary of the results obtained by this test. Significant amounts of DNA could be extracted from all materials tested. However, under the conditions used the biofilm development on CLY was significant lower than on other materials. From 11 halves made of CLY, 9 (81.8 %) showed a significant reduced bacterial growth compared to their counterparts.

Tab. 2. Quantification of bacterial growth on T-shirts made from different materials after an *in vivo* test trial

Sample Nr.	**Material**	**ng DNA / cm^{2**}**
61A	CLY	11,70*
61B	PA	15,15*
64A	CLY	5,21
64B	PP	6,00
66A	CLY	6,56
66B	PA	8,03
67A	CLY	20,92*
67B	PES	50,36*
77A	CLY	8,70
77B	PA	13,35
80A	CLY	12,11*
80B	PES	11,06*
89A	CLY	13,65*
89B	CO	10,69*
90A	CLY	6,52
90B	CO	12,60
91A	CLY	8,10*
91B	WO	18,19*
92A	CLY	4,13
92B	WO	7,54
98A	CLY	14,78*
98B	CO	32,29*

* T-shirt was incubated at 37°C for 24h
** mean amount of 6 samples per T- shirt

Fluorescent microscopy might also be used for investigations of the interaction between textiles and microorganisms. The development of yeast and bacteria specific fluorescent dyes and dyes which allow discrimination between live and dead cells have highly improved this research. Fig. 2 shows a comparison of biofilm development on textile fibres by a pure culture of *Staphylococcus sp.* and a mixed culture of sweat bacteria. The results indicate that with Staphylococcus, which is also used in „in vitro“ Challenge tests, there is only very limited biofilm development, whereas a massive biofilm can be seen with sweat bacteria. Therefore, this experiment demonstrates the disadvantage of experiments using selected bacteria as test organisms.

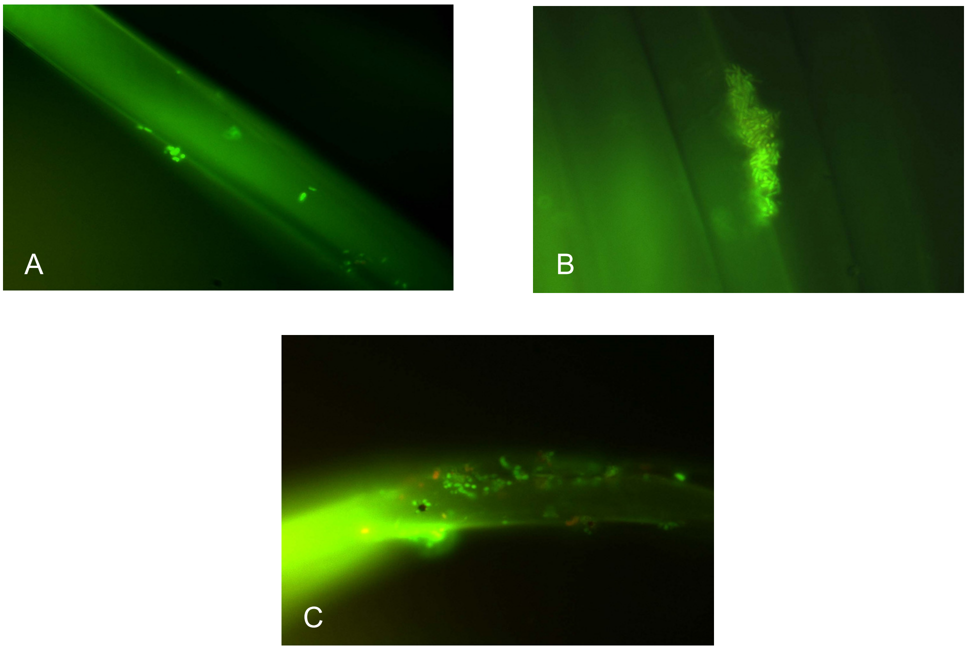


Figure 2. Biofilm development on textile fibres by different bacterial populations. (A) *Staphylococcus* sp., and (B, C) a mixture of sweat bacteria. (C) green staining represents living bacteria whereas read staining are dead cells

Conclusions

Since microorganisms have a number of deleterious effects on textiles there is some need to reduce microbial growth on the material. The current strategy is mainly based on the use of antimicrobial additives. Therefore, as outlined in this article, most methods used for investigations of the interaction between microorganisms and textiles have been developed for this specific purpose so far. However, the use of antimicrobial additives may have harmful effects, e.g. they might disturb the normal skin flora or might cause allergic reactions. Thus, there is some need for materials impeding microbial growth *per se*. However, to test and investigate such materials, methods have to be developed, which allow investigations on the overall growth of microorganisms *in vivo*. Here, we have presented some methods which are based on modification of classical tests and described some new developments to overcome the limits of culture based assays and use of specific test organisms. Especially, the use of DNA quantification might be a highly suitable method for investigations under *in vivo* conditions.

Acknowledgements

The authors acknowledge the Christian Doppler Research Society, Vienna, Austria, for financial support of this work.

References

[1] Jackman, R., and W. Noble. 1983. Normal axillary skin microflora in various populations. Clin. Exp. Dermatol. 8: 259-268.

[2] Leyden, J. J., K. J. McGinley., K. M. Nordstrom, and G. F. Webster. 1987. Skin microflora. J. Invest. Dermatol. 86: 65-72.

[3] Roth, R. R., and W. D. James. 1988. Microbial ecology of the skin. Ann. Rev. Microbiol. 42: 444-464.

[4] Szostak-Kotowa, J. 2004. Biodeterioration of textiles. Int. Biodeter. Biodegr. 53:165-170.

5] Leyden, J. J., K. J. McGinley, E. Hölzle, J. Labows, and A. M.Kligman. 1981. The microbiology of the human axilla and its relationship to axillary odour. J. Invest. Dermatol. 77: 413-416.

[6] Rennie, P. J., D. B. Gower, and K. T. Holland. 1991. In vitro and in vivo studies of human axillary odour and the cutaneous microflora. Br. J. Dermatol. 124: 596-602.

[7] Austin, C., and J. Ellis. 2003. Microbial pathways leading to steroidal malodour in the axilla. J. Steroid. Biochem. Molec. Biol. 87: 105-110.

[8] James, A. G., D. Hylianders, and H., Johnston. 2004. Generation of volatile fatty acids by axillary bacteria. Int. J. Cosmet. Sci. 26: 149-156.

[9] Rennie, P. J., D. B. Gower, K. T. Holland, A. I. Mallet, and W. Watkins. 1990. The skin microflora and the formation of human axillar odour. Int. J. Cosmet. Sci 12: 197-207.

[10] BISFA (The international bureau for standardisation of man-made fibres), 2002. Testing methods for organic man-made fibres with antibacterial activity . BISFA, 1160 Brussels, Belgium.

[11] Hamlyn, P. F. 1995. The impact of biotechnology on the textile industry. Textiles Mag. 3: 6-10.

[12] McCarthy, B. J. (2001) Bioluminescent assay of microbial contamination on textile materials. Int. Biodeter. Biodegrad. 48, 79-83.

[13] Teufel L., Schuster K.C. , Merschak, P., Bechtold T. and Redl B. (2006) Development of a fast and reliable method for the assessment of microbial colonization and growth on textiles by DNA quantification. J. Appl. Microbiol. *Submitted*

Lenzinger Berichte, 85 (2006) 61-67

DERMATOLOGICAL EXAMINATIONS ON THE SKIN COMPATIBILITY OF TEXTILES MADE FROM TENCEL® FIBRES

Thomas L. Diepgen [a] **, K.Christian Schuster** [b]

[a] University Hospital Heidelberg , 69115 Heidelberg, Germany
[b] Lenzing AG, Textile Innovation, 4860 Lenzing, Austria

Based on a Lecture at the 43rd International Man-Made Fibres Congress, Dornbirn, Austria 15-17 September, 2004

Summary

Background*:* Textiles play an important role in well-being, as the human body is in close contact with textiles most of the time. Especially, subjects with diseased or sensitive skin are able to feel small differences in well-being by using different textiles. It is well known that their skin is easily aggravated by contact with clothes of synthetic or woollen fibres.
Objectives*:* To evaluate the skin compatibility of commercially available TENCEL® (generic fibre name: Lyocell) textiles in patients suffering from atopic dermatitis or psoriasis in an everyday situation.
Methods*:* 30 patients with atopic dermatitis and 30 patients with psoriasis should wear and use TENCEL® textiles over the testing period of one week, during day and night. All textiles were commercially available products made from TENCEL®, produced through standard textile process routes, with no special additional treatment or finishing: 100% TENCEL® bedding (duvets, covers, bed linen, sheets), clothing from 70% TENCEL® / 30% Cotton (t-shirts, polo-shirts, pyjamas). As a control, patients used their own clothing and their own bedding textiles. All patients were evaluated by a dermatologist at baseline and 7 days after the initial examination. The overall severity of atopic eczema was evaluated using the SCORAD index, and the severity of psoriasis the PASI score, respectively.
Results*:* During the test period the severity of atopic dermatitis and psoriasis improved significantly ($p<0.01$). Over 90% of the patients reported that TENCEL® textiles are superior in comparison to their own clothing and their own bed textiles regarding the skin compatibility. The patients gave excellent scores for TENCEL® textiles regarding improvement of itching, skin sensitivity, thermoregulatory properties, for its properties of cool, smooth and dry feeling, and for its compatibility with the local topical treatment.
Conclusions*:* TENCEL® textiles significantly contribute to well-being also under dermatological conditions. From a dermatological point of view these textiles can be recommended not only for healthy subjects but also for people with sensitive skin or even patients with skin disease, especially atopic dermatitis or psoriasis.

DERMATOLOGISCHE UNTERSUCHUNGEN ZUR TEXTILVERTRÄGLICHKEIT VON TENCEL ®

Univ.-Prof. Dr. T.L. Diepgen [a] **, Univ.-Doz. Dr. K.Ch. Schuster** [b]

[a] University Hospital Heidelberg , 69115 Heidelberg, Germany
[b] Lenzing AG, Textile Innovation, 4860 Lenzing, Austria

Zusammenfassung

Hintergrund: Die menschliche Haut kann sehr differenziert das subjektive Wohl- bzw. Missempfinden unterschiedlicher Bekleidungsstoffe unterscheiden. So ist es ein bekanntes Phänomen, dass vor allem Textilien aus Kunstfaser auf der Haut als unangenehm empfunden werden und Kratzen und Juckreiz auslösen können. Diese Missempfindungen werden häufig bei körperlicher Anstrengung oder

Sport verstärkt. Personen mit atopischer Diathese (genetische Disposition zur Entwicklung von Allergien, wie z.B. Neurodermitis, Heuschnupfen, Asthma, die bei etwa 20% - 30% der Bevölkerung vorkommt) haben häufig eine sehr empfindliche Haut und vertragen bestimmte Bekleidungsstoffe nicht bzw. bevorzugen Textilien aus Baumwolle. Eine sogenannte „Textilunverträglichkeit“ wird von Dermatologen auch als Minorkriterium des atopischen Ekzems bezeichnet. Neben irritativen Eigenschaften von Textilien ist auch die mögliche Auslösung von Typ-IV Allergien und Kontaktekzemen zu bedenken. Auch der Einsatz antibakteriell ausgerüsteter Fasern ist aus dermatologischer Sicht kritisch zu hinterfragen.

Material und Methode: In einer dermatologisch kontrollierten, offenen Trage- bzw. Anwendungsstudie wurde die Hautverträglichkeit von verschiedenen Alltagstextilien aus TENCEL® auf der Haut von 30 Patienten mit atopischem Ekzem (= Neurodermitis) und 30 Patienten mit Psoriasis vulgaris untersucht. Dabei kamen folgende Gebrauchstextilien aus TENCEL® zur Anwendung: Langarm T-Shirt sowie Kurzarm Polohemd für den Tag, Pyjama sowie Bettbezug incl. Leintuch und Zudecke für die Nacht. Wichtige Zielgrößen waren die subjektiv empfundene Verträglichkeit der Textilien, deren Einfluss auf das atopische Ekzem bzw. die Psoriasis und die Kompatibilät mit der jeweiligen Lokaltherapie. Der Untersuchungszeitraum betrug jeweils eine Woche. Zu Beginn und am Ende des Trageversuches wurde der Schweregrad des atopischen Ekzems mittels SCORAD bzw. für Psoriasis mittels PASI durch den untersuchenden Dermatologen erhoben. Zusätzlich wurde von den Versicherten ein eigens hierfür konzipiertes Tagebuch geführt, in dem täglich Parameter zur Hautverkrankung und Textilverträglichkeit eingetragen wurden. Als Vergleich dienten die bisher getragenen Textilien, die subjektiv von den Patienten bezüglich Hautverträglichkeit über viele Jahre optimiert worden waren.

Ergebnisse: Innerhalb der 1-wöchigen Beobachtungszeit verbesserte sich der Schweregrad des atopischen Ekzems und der Psoriasis signifikant. Insgesamt wurden die Textilien in allen Anwendungen sehr gut vertragen, zeigten eine deutliche Verbesserung hinsichtlich des Juckreizes, sehr gute hautsensorische und thermoregulatorische Eigenschaften, auch bei körperlicher Anstrengung, sowie einen sehr hohen subjektiven Tragekomfort, insbesondere auch gegenüber der bisher getragenen Kleidung / Bettwäsche. Im Vergleich zu den bisher getragenen Textilien, die in über 90% aus Baumwolle bestanden, wurden die Alltagstextilien aus TENCEL® auf der Haut von Patienten mit atopischem Ekzem und Psoriasis fast immer als „deutlich besser“ oder „besser“ im Vergleich zu den sonst getragenen Textilien beurteilt

Schlussfolgerungen: Sowohl auf gesunder als auch kranker Haut können daher Textilien aus TENCEL® dermatologisch bestens empfohlen werden.

Introduction

Atopic Dermatitis (AD) is a common, chronically relapsing, inflammatory skin disease, clinically characterized by typically distributed eczematous lesions, dry skin, intense pruritus, and a wide variety of pathophysiologic aspects. Recent European studies indicate a lifetime prevalence of atopic dermatitis in 15-20% of subjects, with a 4-12% point prevalence (Diepgen 2003). There is a strong evidence that the prevalence of the disease has increased substantially over the past decades (Diepgen 2000), which seems to be associated with a change of environmental and lifestyle factors, especially in Western countries (Diepgen 2001). There are many factors known to worsen the disease, including allergens, climatic factors and chemical or physical irritants. Triggering factors include skin exposure to allergens and/or irritants such as harsh textiles and clothing, particularly wool and synthetic fabrics. The itching produced by direct contact with wool in patients with AD is characteristic and the irritation is likely to be caused by the “spiky” nature of the fibres. Dry and rough skin in combination with a defect of the epidermal skin barrier, causing the development of eczematous lesions after exposure to repeated irritants, seems to play an important role in the pathogenesis of AD. Because of the frequently observed worsening of the disease due to harsh fabrics, patients with AD have often been advised to wear cotton clothes. However, studies have suggested that cotton may also present a roughness that irritates the skin of individuals affected by AD or with sensitive skin (Diepgen et al. 1990, 1995, Salzer et al. 1994, Bendsoe et al. 1987)

Psoriasis is a chronic skin disorder characterized by erythematous scaly patches which typically affect the extensor surfaces of the body and the scalp. The lifetime prevalence of psoriasis is estimated to be between 2 % and 3 % within Europe.

The aim of our study was to evaluate the skin compatibility of commercially available TENCEL® textiles in patients suffering from atopic dermatitis or psoriasis in an everyday situation.

Methods

Patients

We studies 30 patients with atopic dermatitis (11 males, 19 females, mean age 37.6 years, range 18 to 73 years) and 30 patients with psoriasis (21 males, 9 females, mean age 45 years, range 19 to 73 years). Atopic dermatitis and psoriasis were diagnosed by trained dermatologists.

Patients were assessed by a dermatologist on inclusion and after 1 week of having used the textiles. All adverse events during the study were recorded. All participants gave consent for study enrolment.

Severity of atopic dermatitis and psoriasis

The severity of atopic dermatitis and psoriasis was assessed before (T_1) and at the end (T_2) of the testing period. The extent and severity of atopic dermatitis was assessed using the SCORAD scale (European Task Force on Atopic Dermatitis 1993). The SCORAD was used as well-known international accepted severity score to determine the disease severity. The SCORAD scale is based on the extent of eczema, the morphology of the lesions, and the two subjective characteristics sleep disturbance during the night and itching. The SCORAD scale can vary from 0 to 103, with higher scores representing a greater degree of atopic dermatitis severity. The extent and severity of psoriasis was evaluated using the Psoriasis Area and Severity Index (PASI) (Fredriksson et al. 1978). The Psoriasis Area and Severity Index (PASI) scoring system assesses four body regions: the head (h), the upper extremities (u), the trunk (t) and the lower extremities (l), corresponding to 10%, 20%, 30% and 40% of the total Body Surface Area (BSA), respectively. The area of psoriatic involvement for each of the four regions is assigned a numerical value (A) of 0-6 corresponding to 0-100% involvement: 0, no involvement; 1, < 10%; 2, 10 < 30%; 3, 30 < 50%; 4, 50 < 70%; 5, 70 < 90%; 6, 90-100%. For each region, erythema (E), induration (I) and desquamation (D) are rated according to a five-point scale: 0, no involvement; 1, slight; 2, moderate; 3, marked; 4, very marked. The PASI score can vary from 0.0 to 72.0, with higher scores representing a greater degree of psoriatic severity.

Textiles

The study was designed to assess the skin compatibility of textiles based on TENCEL® fibres (generic name: Lyocell) in sensitive patients in an everyday situation. Therefore, the textiles used here were not medical products made specifically for the study, but selected to represent a range of everyday products based on TENCEL® fibres. The patients should wear and use TENCEL textiles over the testing period of one week as continuously as possible, during day and night. All textiles were commercially available products made from TENCEL®, produced through standard textile process routes, with no special additional treatment or finishing.

Clothing textiles were produced by Odem, Fürstenfeld, Austria. The ring yarns were made of 67 % TENCEL in a blend with 33 % cotton, yarn metric count Nm 50. The fabrics were knitwear, single jersey of 180 g/m^2 mass per unit area, enzyme finished and resin finished for protection against fibrillation. T-shirts, long arm polo shirts, and pyjamas in various colours (white, black, red, navy, platinum grey, beige) were included in the study.

The following bedding textiles were used: Duvets from Hefel, Schwarzenberg, Austria, made of 100 % TENCEL® FILL (6.7 dtex, siliconised) in the filling, and a ticking of 100 % TENCEL® woven fabric. Bed sheets were also from Hefel, 100 % TENCEL® Micro, full plated with Lycra, single jersey knitwear, resin finished. Duvet and pillow covers were from Dierig, Leonding, Austria, 100% TENCEL® Micro, satin weave, resin finished, calandered, with printed dessins in various colours. As a control, patients used their own clothing and their own bed textiles. Adult patients have individually optimised their textile use for decades, providing the toughest possible control.

Statistical methods

All statistical analyses were performed by using the SAS statistical package. For statistical tests nonparametric methods were used. The distributions of the severity of the skin diseases before and after the testing period were presented as box and whisker plots. A box and whisker plot displays the mean, quartiles, and minimum and maximum observations for a sample.The box has lines at the lower quartile, median, and upper quartile values. The whiskers are lines extending from each end of the box to the minimum and maximum to show the extent of the rest of the data. A dot represents the mean.

Results

At the beginning of the study 26 out of 30 patients with AD and 29 out of 30 patients with psoriasis reported that they are normally using textiles made from cotton during the night. During the day, 29 out of 30 AD patients and 28 out of 30 patients with psoriasis reported using clothes made from cotton. At the end of the study most patients reported that the skin compatibility of TENCEL® textiles was superior in comparison to their own clothing and their own bed textiles in an everyday situation (Table 1).

Table 1: Overall skin compatibility of TENCEL® textiles in comparison to their own clothing and their own bed textiles in an everyday situation in 30 patients with AD and 30 patients with psoriasis.

	Atopic Dermatitis	Psoriasis
	TENCEL® textiles superior	TENCEL® textiles superior
Bedding textiles	86 %	84 %
Pyjama	82 %	84 %
T-Shirt	79 %	83 %
Long arm Polo-shirt	76 %	73 %

During the test period the severity of atopic dermatitis and psoriasis improved significantly ($p<0.01$) (Fig. 1). The average SCORAD decreased within one week from 37,9 points to 29,9 points ($p<0,01$), the average PASI scale from 7.7 points to 3.7 points ($p<0,01$).

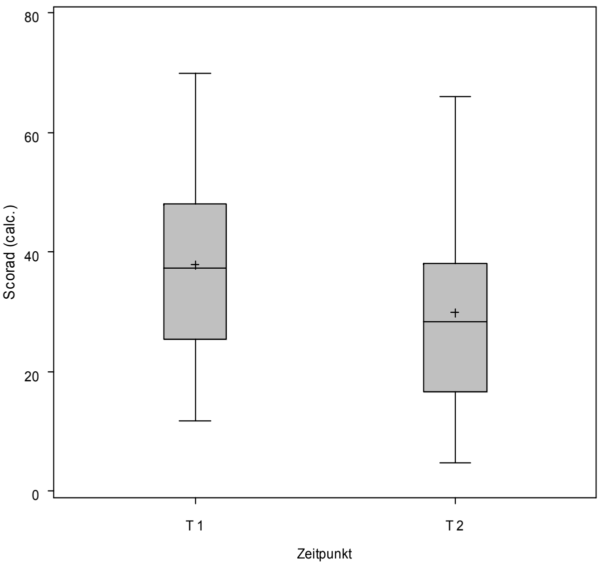


Figure 1 Severity of atopic dermatitis according to the SCORAD scale before (T1) and at the end of the study (T2). ($p<0.01$)

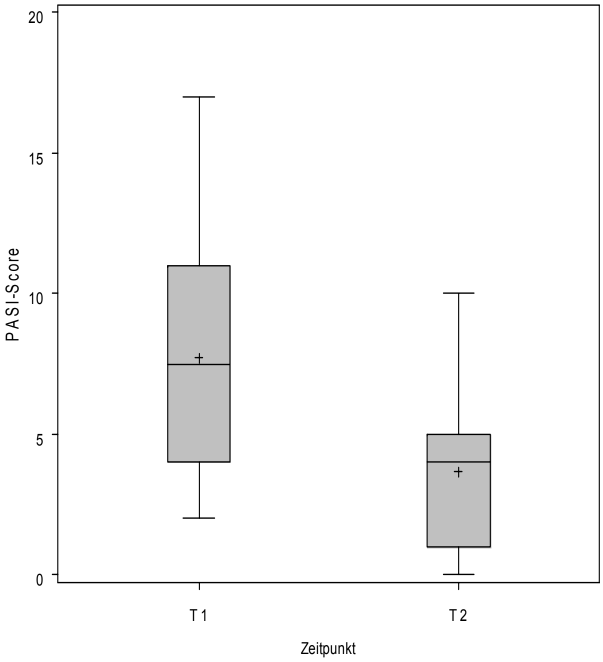


Figure 2 Severity of psoriasis according to the PASI score before (T1) and at the end of the study (T2). ($p<0.01$).

Nobody of the 60 patients reported worsening of itch. Surprisingly, even 30% of the AD patients and 10% of the psoriasis patients reported improvement of itch after wearing the TENCEL® textiles. The patients gave excellent scores for TENCEL® textiles regarding skin sensitivity, thermoregulatory properties, and for its properties of cool, smooth and dry –feeling (table 2). Nobody reported uncomfortable properties for the TENCEL® textiles.

Table 2. Subjective scores for skin compatibility, thermoregulatory properties even after exercise, and for its properties of cool, smooth and dry–feeling for TENCEL® textiles in an everyday situation in 30 patients with AD and 30 patients with psoriasis during the one week use-test.

	Atopic Dermatitis (n=30)			Psoriasis (n=30)		
	Excellent Skin compatibility	Excellent thermoregulatory properties	Smooth, soft	Excellent Skin compatibility	Excellent thermoregulatory properties	Smooth, soft
Bedding textiles	90 %	87 %	93 %	93 %	97 %	100 %
Pyjama	90 %	87 %	90 %	93 %	97 %	100 %
T-Shirt	93 %	87 %	93 %	90 %	97 %	100 %
Long arm Polo-shirt	83 %	80 %	83 %	80 %	97 %	87 %

The patients were asked to rank their subjective skin compatibility and skin comfort for the TENCEL® textiles on a visual analogous scale between 0 (most uncomfortable skin compatibility) and 10 (better skin compatibility not possible). The results are presented in table 3. Over 90% of the patients with AD and psoriasis reported a good or excellent compatibility of the different TENCEL® textiles with the local topical treatment.

Table 3. Subjective skin compatibility and skin comfort for the TENCEL® textiles on a visual analogous scale between 0 (most uncomfortable skin compatibility) and 10 (better skin compatibility not possible). The results are presented as means and standard deviation according to the scores given by 30 patients with AD and 30 patients with psoriasis.

	Atopic Dermatitis (n=30)	Psoriasis (n=30)
	Mean scores for skin compatibility	Mean scores for skin compatibility
Bedding textiles	8.6 ± 1.3	8.8 ± 0.7
Pyjama	8.6 ± 1.0	8.7 ± 1.0
T-Shirt	8.7 ± 1.0	8.7 ± 1.2
Long arm Polo-shirt	8.6 ± 1.1	8.7 ± 1.1

Discussion : Background in Textile Properties

When the patients taking part in the study were asked for the reasons for the good skin compatibility of the TENCEL® textiles, the outstanding properties mentioned were coolness, good skin sensory perception, and thermoregulatory properties.

The thermal contact feeling of textiles is an important component of the sensation of textiles on the skin. Textiles are available in a wide range from cool to warm sensation, depending mainly on the smoothness and heat conductivity of the textile construction, and on the basic fibre material. An objective measure for this sensorial property is the thermal absorbtivity (Hes, 2002). A high thermal absorbtivity is connected to a cool feeling. Textiles from TENCEL® are characterised by a very high thermal absorbtivity , compared to textiles of similar constructions made from other fibres , e.g. cotton. The reason is the combination of the smooth fibre surface with high water vapour absorption at ambient conditions (Firgo et al., 2006). With increasing ambient humidity , as in hot and humid summer weather, the cool feeling increases, leading to a pleasant sensation on the skin and reduced itching for individuals with skin problems.

The skin sensory perception depends on the smoothness of the textile and the friction between textile and the skin. Fibres with a rough surface (like wool, and to a certain extent also cotton) and stiff fibres, like wool (Bendsoe et al. 1987), and some types of synthetic fibres (Diepgen et al. 1990.1995) can lead to skin irritation. TENCEL® fibres have a very smooth surface and a circular cross-section, similar to many synthetic fibres. The fibres bend easily. The smoothness and easy bending is a basis to avoid mechanical irritation. Additionally, the high water uptake of TENCEL® has the effect that humid textiles shown less friction to the skin compared to other textiles, as measured objectively by the wet cling index (Männer et al., 2004). The combination of the smooth fibre surface, the low fibre stiffness, and the low wet cling helps to avoid skin irritation by textiles in moist or wet conditions.

The thermoregulatory properties of textiles are a combination of several physical effects, which in combination assist the human body's natural temperature regulation mechanisms (Mecheels, 1998).

Generally, a good moisture transport from the skin through the textile to the environment is advantageous; the water vapour resistance is the objective measure. Fast and high absorption of sweat, as characterised by the short term water vapour absorption capacity is another important factor. A high heat capacity of textiles adds to thermoregulation. In all of these features, TENCEL® textiles show advantages (Schuster et al, 2004; Männer et al 2004). In warm environments and at high activity, the human body cools by sweat evaporation. Active cooling is improved in TENCEL® clothing by spreading of moisture and a high heat conductivity of the wet fabric (Firgo et al. 2006).

In bedding textiles, a high water vapour transport together with good insulation is desired, as well as a heat capacity of materials . Advantages of in TENCEL® products over synthetic materials and even natural fibres (wool, down) could be shown (Schuster et al., 2004), These factors together lead to a pleasant climate in bed, as shown in a field trial (Helbig , 2006).

Conclusions

TENCEL® textiles significantly contribute to well-being also under dermatological conditions. From a dermatological point of view these textiles can be recommended not only for healthy subjects but also for people with sensitive skin or even patients with skin disease, especially atopic dermatitis or psoriasis. The subjective skin compatibility and skin comfort for the TENCEL® textiles and its thermoregulatory properties even after exercise, and its properties of cool, smooth and dry feeling are superior to cotton textiles even in patients with sensitive skin or inflammatory skin diseases.

References

[1] Bendsoe N, Bjornberg A, Asnes H (1987) Itching from wool fibres in atopic dermatitis. Contact Dermatitis 17: 21-2

[2] Diepgen TL, Stäbler A, Hornstein OP (1990) Textilunverträglichkeit beim atopischen

[3] Ekzem – eine kontrollierte klinische Studie. Zeitschrift für Hautkrankheiten 65: 907-910

[4] Diepgen TL (1991) Die atopische Hautdiathese. Gentner Verlag Stuttgart

[5] Diepgen TL, Salzer B, Tepe A, Hornstein OP, Albrecht W (1995) Hautreizung durch Textilien unter standardisierten Schwitzbedingungen bei Patienten mit atopischem Ekzem. Melliand Textilberichte 12: 1116-1121

[6] Diepgen TL (2000) Is the prevalence of atopic dermatitis increasing? In: HC Williams (Ed.) Epidemiology of Atopic Eczema. Cambridge University Press, Cambridge 96-109

[7] Diepgen TL (2001) Atopic Dermatitis – The role of social factors. J Am Acad Dermatol 45: S44-48

[8] Diepgen, TL (2003) Epidemiology of Atopic Dermatitis. In: T. Ruzicka, S. Reitamo (eds.) Tacrolimus Ointment. Springer-Verlag Berlin, Heidelberg, New York, 3-21

[9] European Task Force on Atopic Dermatitis. Severity scoring of atopic dermatitis. The SCORAD-Index. Dermatology 1993; 186:23-31.

[10] Firgo, H., Schuster KC, Suchomel F., Männer J, Burrow T, Abu Rous M., The functional properties of TENCEL® - A current update, Lenzinger Berichte 2006, in press

[11] Fredriksson T, Pettersson U (1978) Severe psoriasis—oral therapy with a new retinoid. Dermatologica 157: 238 44.

[12] Hes, L., Proceedings of the World Congress of the Textile Institute, Cairo, 2002

[13] Helbig K., Lenzinger Berichte 2006, in press

[14] Männer J, .Schuster KC, Suchomel F, Gürtler A, Firgo H, (2004). Higher performance with natural intelligence. Lenzinger Berichte 83, 99-110

[15] Mecheels, J., Körper – Klima – Kleidung . Wie funktioniert unsere Kleidung ? Schiele & Schön, Berlin, 1998

[16] Salzer B, Tepe A, Diepgen T:L:, Hornstein OP (1994) Textilunverträglichkeit unter standardisierten Schwitzbedingungen bei Patienten mit atopischem Ekzem. Dermatosen in Beruf und Umwelt 42: 226-230

[17] Schuster KC, Firgo H, Haussmann F, Männer J , (2004) Higher performance with natural intelligence., Lenzinger Berichte 83, 111-115

Correspondence address:

Univ.- Prof. Dr. med. Thomas L. Diepgen, University Hospital Heidelberg, Dept. of Clinical Social Medicine, Occupational & Environmental Dermatology, Thibautstr. 3, D-69115 Heidelberg, Germany.
E-mail: thomas.diepgen@med.uni-heidelberg.de

Lenzinger Berichte, 85 (2006) 68-76

CHARACTERIZATION OF COTTON FIBRES MODIFIED BY CARBOXYMETHYL CELLULOSE

L. Fras Zemljič [a]*, P. Stenius[b], J. Laine[b], K. Stana-Kleinschek[a], V. Ribitsch[c]

a. Laboratory for Characterization and Processing of Polymers, Faculty of Mechanical Engineering, University of Maribor, Smetanova 17, SI-2000 Maribor, Slovenia
b. Laboratory of Forest Products Chemistry, Helsinki University of Technology, P.O. Box 6300, FI-02015 HUT, Finland
c. Institute of Chemistry, Rheology & Colloid Science, Karl Franzens University, Heinrichstraße 28, AT-8010 Graz, Austria

Abstract

In order to introduce charged groups onto cotton fibres the adsorption of carboxymethyl cellulose (CMC) onto fibre surface was investigated. The increase of charge was determined indirectly by phenol-sulphuric acid method and directly by conductometric titration. It was found that the total charge of cotton was increased by more than 50 % in the case of all used CMC products. Modification of cotton by adsorption of CMC introduces new carboxyl groups on the fibre surfaces, which increases the adsorption capacity of the fibres for cationic surfactant (cetylpyridinium chloride). The modified fibres appeared to have better mechanical properties. It is expected that this modification procedure can be used for practical applications.

Keywords: *cotton fibres, modification; carboxymethyl cellulose; acid groups, in fibres; conductometric titration, phenol-sulphuric acid test; adsorption capacity*

Introduction

The importance of the acidic groups in fibres lies in their capability of ionisation without going to extreme values of pH [1]. These dissociable groups can have a large impact on final fibres properties, such as strength, wetting, adsorption and absorption capacity etc. Their effects on fibre swelling are well known [2]. It is also known that an increase in the acid group content of cellulose fibres can result in increased strength properties of the paper sheets made from the fibres [2]. The adsorption of different compounds onto cellulose fibres may increase with increased content of acidic groups, but this effect has not yet been investigated systematically in the field of textile chemistry. Therefore, the purpose of this study was to evaluate to what extent there is correlation between an increased amount of –COOH groups and adsorption of cationic substrate onto cotton fibre surfaces, by systematically changing the amount of carboxylic acid groups in the fibres.

Numerous methods exist to introduce acidic groups (i.e., to increase the total charge) in cellulose fibres. One way is to use different oxidation procedures. Thus, in many cases the cellulose has been oxidized with nitrogen dioxide, ozone, hydrogen peroxide or oxygen [2]. In the case of wood cellulose other pathways include addition of sulfonic acid groups to lignin, grafting of carboxylic acids to cellulose and the formation of free radicals using devices such as electron beams [2]. Carboxymethylation and use of substantive dyes have also been employed to introduce carboxyl groups [3]

In our work the methodology for attaching more carboxyls to cotton fibres was based upon application of a previously published method used for wood fibres. Laine et al. have developed a method based on topochemical modification of wood cellulose fibres with carboxymethyl cellulose (CMC) [3,4]. It was shown that by appropriate choice of conditions, CMC can be attached quantitatively. The CMC has two functionalities: it modifies the surface by strong adsorption, and it increases the charge density of fibres [3,4]. The irreversible attachment of CMC onto cellulose surfaces is thought to be due to cooperative hydrogen bonding between the free cellulose segments on the CMC-backbone and the cellulose fibre surfaces on the fibre. It may be viewed as a co-crystallisation process, but this remains conjectural [5].

This paper describes the modification of cotton fibre surfaces by irreversible adsorption of carboxymethyl cellulose (CMC) in order to achieve higher surface charge, using the same chemical conditions as in the method developed by Laine et al. [3,4] for wood fibres. The adsorption of CMC onto cotton fibres was determined using phenol-sulphuric acid method [6] and conductometric titration. The phenol-sulphuric acid method was used for indirect determination of the adsorbed amount of CMC, while the total charge of non-modified and modified fibres was obtained by conductometric titration.

The functionality of CMC has been quite well described for cellulosic fibres used for papermaking. In spite of all that, there are no data describing the effect of CMC attachment on the adsorption capacity of fibres. In this paper we therefore also summarize an evaluation of the correlation between increased amount of charge, which is a consequence of CMC adsorption onto cotton fibres, and the adsorption capacity of the fibres for cationic surfactant. As a model system, the interactions between a cationic surfactant, cetylpyridinium chloride CPC, and CMC-modified fibres were studied. This system was chosen because, apart from well - known practical applications, such systems are important in the modelling of complex fluid and fluid/solid mixtures, including biological systems [7]. A full account of these results is given in [8].

To our knowledge, there are no reports on the use of CMC for modification of textile fibres in order to get higher total charge and consequently better adsorption capacity of cationic compounds. CMC-modified cotton fibers could find application in one of the most prospective textile fields - production of biodegradable, sustainable and highly absorptive materials [9,10,11]. Carbon-14-labeled sodium CMC has been employed to measure its adsorption on textile fibres, and in the case of cotton, to investigate the relationship between adsorption and detergency action. It was found that CMC adsorbed onto cotton has a significant function in preventing redeposition of particulate soil materials [12].

It has also become clear that cotton fibres treated according to the present method provide better mechanical properties.

Experimental

Materials

***Cotton fibres*:** The fibres were natural cellulose cotton fibres (originating from Russia, type Ronda), with mean fibre length 29 mm, micronaire value 4.4 and regain 7.7 %. In order to obtain a well-defined reference substance the following cleaning treatments of these fibres were applied:

- Alkaline boiling: removal of non-cellulose compounds (hemicellulose, waxes, pectin, proteins) by treatment for 90 min in 0.5 M NaOH at 95 oC.
- Oxidative bleaching: degradation of natural dyes and pigments by treatment for 30 min with 0.1 M H2O2 at pH = 11.2 and 95 oC.

After each treatment the fibres were washed with distilled water until the conductivity of the water was less than 5 μS/cm. The processed material was air-dried.

***Carboxymethylcellulose*:** Four commercial CMC samples with different average molecular weights $\overline{M}_w$ were used for modification of the cotton fibres (Table 1). CMC:s I-III were manufactured by Mare from Austria and CMC IV by Noviant Oy, Äänekoski, Finland. Their properties are summarised in Table 1.

The concentration of simple electrolyte in the CMC solutions that were used for cotton modification was measured in order to check if the ionic strength was constant for all samples.

This was done conductometrically as described by Ander and Sonesa [13]. The ionic strength was about 0.001 M in all solutions. The percentages of salt in each CMC product are given in Table 1.

The average molecular weights of the CMC products were calculated from viscosity measurements.

Table 1. Amount of salt and average molecular weight ($\overline{M}_w$) of CMC products

CMC		Amount of salt wt%	$\overline{M}_w$
Product	Notation		
Niklacell T30	I	14	167 000
Niklacell T50	II	10	281 000
Niklacell T100	III	15	452 000
Nymcel ZSB-16	IV	9	591 000

Other chemicals. Cetylpyridinium chloride monohydrate (CPC, C21H38NCl·H2O) (Mw = 358.0 g/mol) of analytical grade was manufactured by Aldrich and used without further purification.

In all analyses ion exchanged, distilled and degassed water and analytical grade chemicals were used.

Methods

***Adsorption of CMC on the cotton fibres*:**

Prior to the adsorption experiments with CMC, cotton fibres were washed with an excess of 0.1 M HCl for 30 min in order to remove metal ions and to convert ionizable groups on the fibres into their acid form. After this treatment the fibres were washed with distilled water until a conductivity of the water less than 5 µS/cm was reached. The ionizable groups were changed into their Na-form by washing in 0.001 M NaHCO3 at pH 9 (adjusted with 0.1 M NaOH) followed by washing with distilled water until a conductivity less than 5 µS was obtained.

The notation of fibre samples modified with CMC is given in Table 2. CMC was adsorbed on the fibres using the following procedure in all cases:

The fibres (consistency 25 g/L) were soaked in a solution of 20 mg CMC/g fibre in 0.05 M CaCl2 at pH 7-8 and 80 oC for 2 h. After this treatment the fibres (which were now in Ca-form) were washed with deionised water and ion-exchanged to their H-form or Na-form as described by Fras et al. [14]. The fibres were stored wet in a refrigerator at 4 - 6 °C and were not dried before analysis. The reference sample (A) was treated in the same way but without CMC addition.

Table 2. Topochemical modification of cotton fibres. CMC attachment conditions: fibre consistency = 25 g/l, CMC addition level = 20 mg/g fibre, 0.05 M CaCl2, t = 2 h, pH =7 -8, T =80 °C.

Sample	Treatment of fibres
A	Pre-treated (alkaline boiling and oxidative bleaching) fibres
AI	Sample A modified with CMC I
AII	Sample A modified with CMC II
AIII	Sample A modified with CMC III
AIV	Sample A modified with CMC IV

The adsorption of CMC onto the cotton fibres was analysed:
i)indirectly by spectrophotometric determination of the decrease in CMC concentration of the solution equilibrated with fibres (phenol-sulphuric acid method)
ii) directly by measurement of the content of acidic groups in the fibres (conductometric titration).

Phenol-sulphuric acid method
After equilibration in CMC solution, fibre suspensions were filtered through weighted filter paper using a Büchner funnel. 200 µL of the filtrate and a blank (control) solution were first mixed with 400 µL of water and shortly afterwards with 200 µL of a 5 % solution of phenol in water. 1 mL of concentrated sulphuric acid was added. The solution was shaken and heated at 90 °C for 15 minutes. The samples were cooled down and after a further 30 min the absorbance of samples was determined at 490 nm. The method based on the fact that polysaccharides give an orange yellow colour when treated with phenol and concentrated sulphuric acid [6], and thus implies that the sample and blank solution were analysed for dissolved carbohydrates. A standard curve was obtained by treating solutions of glucose in the same way.
The amount of CMC adsorbed onto the fibres is assumed to be equal to the difference in concentration of dissolved carbohydrates between an initial CMC solution and the same CMC solution after equilibration with fibres. The amount was corrected for the concentration of carbohydrates dissolved from fibres equilibrated with the same amount of electrolyte solution without dissolved CMC. The details about method are described in Ref. [6].
All solutions were prepared and analysed in triplicate.

Conductometric titration
The amount of charge introduced into the modified fibres was determined using conductometric titration, using a Metrohm 712 conductometer. For a detailed description of this titration technique see Fras et al. [15]. An amount of wet fibres corresponding to 1 g oven-dry fibres were suspended in 500 cm^3 1 mM NaCl, acidified with 0.5 cm3 0.1 M HCl and titrated at (25 ± 0.5) °C under argon atmosphere with 0.1 M NaOH added from a precision burette in steps of 0.04 cm3 with one-minute intervals.Typically, titrations were finished at pH ≈ 10.5, which made reliable extrapolation of linear parts of the titration curves possible [16,17]. A blank titration without fibres was performed in order to calibrate the system and to eliminate impurity effects. All reported amounts of acid are the mean values of three separate titrations.
The CMC modified cotton fibres were characterised by determination of: adsorption properties for cationic surfactant using UV spectroscopy and of mechanical properties using standard procedures

UV spectroscopy. Adsorption of CPC onto CMC-modified cotton at (25 ± 0.5) oC was evaluated by determination of the surfactant concentration in solutions (pH 8.5 ± 0.5) in contact with the fibres by on-line using a Cary 50 UV spectrometer at wavelength 260 nm during 3 h of adsorption. During the first hour absorbance was measured every 30 s and afterwards every 30 min. In the adsorption kinetics experiment, 1.5 g of cotton fibre was stirred in a solution prepared by mixing of 200 mL of 0.001 N KCl with 50 mL of 0.002 N CPC. For details, see [8].

The equilibrium surfactant uptake cF (g surfactant/kg fibre) and the degree of exhaustion de (usually quoted as a percentage) were calculated using the following equations [15]:

$$c_F = \frac{m_{\mathrm{sur}}}{m_{\mathrm{fibre}}} = \frac{\left(A_0 - A_{\mathrm{eq}}\right) \times V}{k \times l \times m_{\mathrm{fibre}}} \qquad (1)$$

$$d_e = \frac{A_0 - A_{eq}}{A_0} \times 100 \qquad (2)$$

where A_0 = absorbance at the start of the experiment; A_{eq} = absorbance at equilibrium time; V = solution volume; k = absorbance coefficient; l = thickness of sample; m_{sur} = surfactant mass; m_{fibre} = fibre mass.
If cF is divided by the surfactant molar mass M, the surfactant equilibrium uptake is expressed in mol of surfactant per kg of fibres.

Table 3. Standard procedures for mechanical properties determination

Properties	Measuring units	Standard
Titer	dtex	SIST EN ISO 1973:1999
Tenacity	cN/tex	SIST EN ISO 5079:1999
Elongation	%	SIST EN ISO 5079:1999
Force	cN	SIST EN ISO 5079:1999
Young module	cN/tex	SIST EN ISO 5079:1999

The surfactant concentration in all experiments was well below the critical micelle concentration (c.m.c.). Thus, the surfactant bath could be treated as a monomer solution [18].

Standard procedures for determination of fibre mechanical properties.
Mechanical properties of CMC-modified fibres were measured using standard procedures shown in the table 3.

Results and discussion

Adsorption of CMC by phenol/sulphuric acid method
The amount of CMC adsorbed (attached from solution) onto fibres is presented in Table 4.

The amount of CMC attached onto to the fibres from treating solutions is in all cases between 50 % and 85 %. On the average, 65 % of the CMC initially present in solution was adsorbed onto the fibres, which gives the average content about 13 mg of attached CMC charge onto g of cotton fibres.

Table 4. The attached amount of CMC

Sample	Amount of CMC adsorbed	
	% of CMC initially in solution	mg/g fibres
AI	70	14
AII	83	16.6
AIII	51	11.8
AIV	59	10.2

Determination of charged groups by conductometric titration
The amount of acidic groups (total charge) on CMC-modified fibres obtained by conductometic titration is presented in Table 5. The amount of groups in acidified (H-form) of fibres was about 100 % higher in sample AIV than in fibres without CMC (sample A) and more than 100 % higher for samples AI, AII and AIII.

Table 5. Anionic groups (total charge) of fibres in acid and neutral forms determined by conductometric titration. The uncertainty (coefficient of variation) of the charge determination was less than 2 % for all samples

Sample	Total charge (carboxyls) mmol/kg		Desorption	Charge increase
	H-form fibres	Na-form fibres	%	%
A	11.3	-	-	-
AI	22.8	18.2	20	61
AII	25.5	21.3	17	88
AIII	23.1	17.9	23	58
AIV	20.4	16.1	21	43

In an earlier study of wood fibres it was shown that if the fibres are converted to their Na-form and stored in deionized water this leads to desorption of CMC from the fibre material [3,4]. Therefore, in order to evaluate the degree of desorption of CMC from cotton fibres during storage, they were transformed into their Na–form as described by Laine et al. [3]. Then the residual charge density was determined by conductometric titration. Clearly, a small amount of CMC was desorbed by weakening the interactions of CMC with the fibres. Table 5 shows that around 17 % to 23 % of the CMC were desorbed from the fibre material i.e., the total charge of the fibres in Na-form increased from 43 % - 88 % (Table 5) due to CMC adsorption

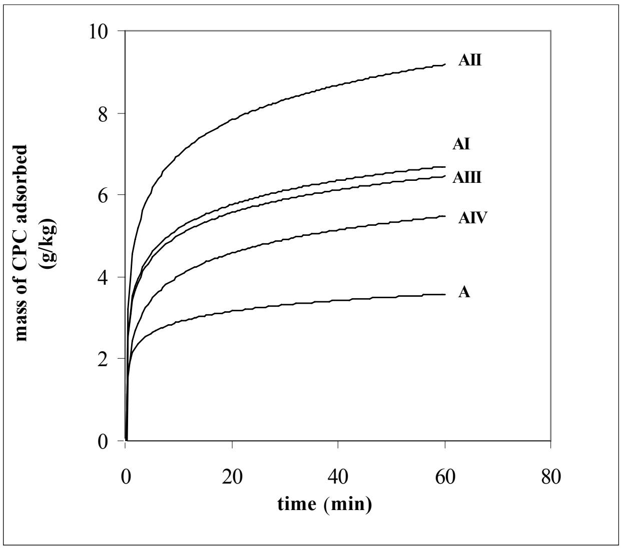


Figure 1. Kinetics of adsorption of CPC on cotton samples [8]

Cationic surfactant adsorption on CMC-modified fibres

The adsorption of CPC as a function of time from a $4\cdot10^{-4}$ M solution on cotton samples at pH 8.5 is shown in Figure 1 [8].

Equilibrium concentrations of CPC (cF) and the fraction of the total surfactant in the system that was adsorbed at equilibrium (expressed as the degree of exhaustion of the solution, de) for cotton modified with different CMCs are summarised in Table 6.

A significant amount of CPC is adsorbed almost instantaneously and a plateau value is reached in 10-30 min for all cotton samples. Adsorption curves of this type, in which initially rapid reactions tend asymptotically towards an equilibrium position, occur commonly and may be described in terms of two parameters, namely the equilibrium value and the rate at which the equilibrium is approached [19]. As shown in the following, the equilibrium values correspond to a stoichiometric formation of ionic bonds between the CPC and the carboxylic groups in the fibres.

The opposite charge of the fibre and the surfactant suggests that the primary driving force for the uptake of CPC by cotton fibres is electrostatic attraction between the anionic carboxylic groups of cotton, ionised at pH 8.5, and the cationic pyridinium groups in the CPC [8]. The shapes of the curves in figure 1 suggest adsorption in a monolayer i.e., sites of the fibres are occupied by CPC; when these are filled, the adsorption ceases.

It can be seen from Table 6 that the adsorbed amount of CPC (and, concomitantly, dE) increases due to fibre modification with CMCs. The equilibrium CPC concentration is almost the same for samples AI and AIII (18.4 mmol/kg and 17.9 mmol/kg, respectively) and an average increase of more than 80 % of adsorbed CPC is reached in both cases. Sample AIV adsorbs up to 15.9 mmol/kg of CPC (+ 62 %) during the first 30 min.

The highest adsorption is that of sample AII, giving equilibrium CPC concentration of 24.3 mmol/kg (+148 %).

Table 6. The equilibrium CPC concentration cF and the exhaustion degree of surfactant at equilibrium, de. The uncertainty (coefficient of variation) of equilibrium CPC concentration cF was less than 5 % for all samples [8].

Samples	cF mmol/kg	Increase of adsorbed CPC mmol/kg	Increase of adsorbed CPC %	de %
A	9.8	-	-	20
AI	18.4	8.6	89	36
AII	24.3	14.5	148	45
AIII	17.9	8.1	83	32
AIV	15.9	6.1	62	29

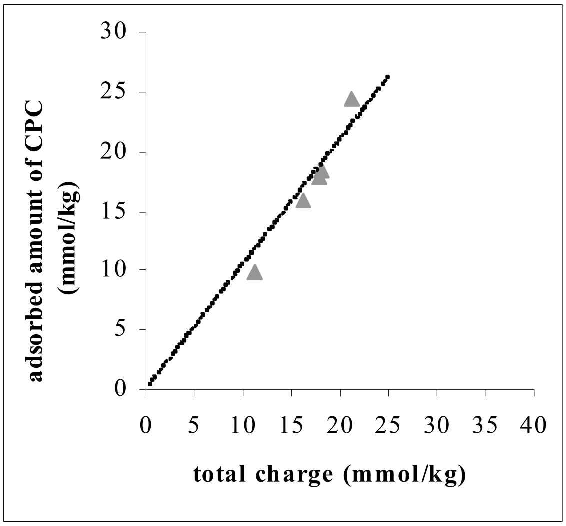


Figure 2. The adsorbed amount of CPC at the plateau level as a function of the total charge of the fibres as determined by conductometric titration [8]. The uncertainty (coefficients of variation) of the charge determination using conductometric titration was less than 2 % for all samples and less than 5 % in the case of adsorbed amount of CPC determination.

Figure 2 [8] shows the relationship between the fibre charge as determined by conductometric titration and the maximum amount of adsorbed CPC on the five fibre samples. The relationship is linear with a correlation coefficient of 0.99 and closely follows the line defining 1:1 stoichiometry. Obviously all dissociating carboxyl groups in the fibres are easily accessible to CPC molecules. Thus, the primary driving force of adsorption is ion exchange, resulting in the formation of a 1:1 ionic complex between the anionic carboxyl groups in the fibres and the CMC and the cationic pyridinium groups of CPC. There are no indications of multilayer formation. Neither does the adsorption kinetics give any indication of cooperative interactions between adsorbed CPC leading to formation of admicelles on the fibre surfaces. This is somewhat unexpected, as this type of interaction is often observed in the adsorption of cationic surfactants on anionic surfaces [20]. The reason may be that the surface charge density of the fibres is rather low. On the other hand, adsorption driven predominantly by electrostatic forces as observed for these fibres has been reported for the adsorption of other surfactants on various substrates [18,22,23]. Maximum adsorption of CPC depends largely on the cationic ion exchange properties of the fibres which follows the alkali number (acidic group amount-anionic charge) [12]. The fact that there is a 100 % stoichiometric reaction between CPC and the carboxyls on CMC-modified fibres implies that no steric hindrances prevent the formation of ionic bonds.

Table 7. Mechanical properties for AIV.

Sample	Titer dtex	Tenacity cN/tex	Elongation %	Force cN	Young modulus cN/tex
A	1.84	31.94	11.61	5.66	105
AIV	1.94	33.24	13.57	6.39	82

Figure 2 implies that there is a linear relationship between the mass of any of the CMC:s adsorbed and the amount of CPC adsorbed, showing that the initial CPC concentration ($4 \cdot 10^{-4}$ M) was sufficient to saturate the fibres in all cases [8].

Mechanical properties of CMC modified fibres

Table 7 presents the mechanical properties for sample AIV. Sample A is a reference.

The topochemical modification of cotton with CMC results in better mechanical properties of cotton fibers. Titer and tenacity of CMC-modified fibers (AIV) can be increased by about 5 %, while with respect to elongation and force about 15 % increase is obtained in comparison with non-modified fibers (reference sample A). Obviously, the mechanical fibre properties of fibres modified by CMC are improved.

Conclusion

Topochemical modification with CMC can be used to increase the charge density of cotton fibres, resulting in an increase of the total fibre charge by ≥ 50 % for all used CMC products.
This increased charge results in a higher capacity of the fibres to adsorb cationic surfactant as well as better mechanical properties.
Presently there is growing interest in different areas (textile, pharmaceutical industries, and reinforcement-materials industry) to find applicable and useful modification of cellulose with the aim to improve the interactions between cellulose and specific (first of all cationic) component with unchanged or improved mechanical fibre properties at the same time. Thus, it is believed that this modification procedure can be used for practical applications

Acknowledgments

We thank the Finnish Centre for International Mobility (CIMO), which provided financial support for this work. We also thank Katja Routanen, Timo Pääkkonen_and Ritva Kivelä, Laboratory of Forest Products Chemistry, as well as Tanja Kos and Vida Žižek, Laboratory for Characterization and Processing of Polymers, for their skilful technical assistance. We wish to thank Mr. Dieter Lehner, the general manager of Mare Austria GmbH, who generously offered CMC samples for our research

References

[1] Scallan, A.M.1983. J.Tappi, 66:73

[2] Barzyk, D., Page, D.H., Ragauskas, A. 2000. J. Pul Paper Sci., 23(2): 520

[3] Laine, J., Lindström, T.2001. Das Papier, 40.

[4] Laine, J., Lindström, T. 2000. Nordic Pulp and Paper Res. J., 15(5): 520

[5] Fors, C. 2000. The effect of fibre charge on web consolidation in papermaking. Licentiate thesis, Royal Institute of Technology, Stockholm, Sweden.

[6] Chaplin, M.F., Monosaccharides. In: Chaplin M.F. and Kennedy J.F., *Carbohydrae analysis:*A practical approach, IRL Press, Oxford, 1986, 1-36.

[7] La Mesa, C. 1999. Colloids Surfaces A., 160: 37.

[8] Fras-Zemljič, L., Stenius, P., Laine, J. and Stana-Kleinschek, K. 2005. The effect of adsorbed carboxymethyl cellulose on the cotton fibre adsorption capacity for surfactant",. *Cellulose*, accepted for publication.

[9] Edwards, J. V. and Vigo, T.L. 2001. Bioactive Fibers and Polymers. American Chemical Society, Washington, DC.

[10] Speakman, J.B. 1941 J. Textile Inst., T83-T108.

[11] Wollina, U., Heide, M., Müller-Litz, W., Obenauf, D. and Ash, J. 2003. Curr Probl Dermatol. Basel, Karger, 31: 82.

[12] Evans, P.G. and Evans,W.P. 1967. J. Appl. Chem., 17: 267.

[13] Ander, P. and Sonessa, A.P. 1965. Principles of Chemistry, Macmillan Co., New York, USA.

[14] Fras, L., Johansson, L. S., Stenius, P., Laine, J., Stana-Kleinschek, K. and Ribitsch, V. 2005. Colloids Surfaces A, Phys. Chem. Asp. 260: 101.

[15] Fras, L., Laine, J., Stenius, P., Stana-Kleinschek, K., Ribitsch,V. and Dolecek,V. 2004. J. Appl. Polym. Sci., 92: 3186.

[16] Katz, S., Beatson, R.P. and Scallan, A.M. 1984. Svensk. Papperst., 87: 48.

[17] Sjöström, E. and Enström, B. 1966. Svensk. Papperst., 69: 55.

[18] Fras, L. 2004. Določitev disociacijskih constant funkcionalnih skupin kemijsko modificiranih celuloznih vlaken ter opredelitev površinskega naboja, dissertation; Faculty of Chemistry and Chemical Engineering, University of Maribor, Maribor, Slovenia.

[19] Jungerman, E. 1970. Cationic Surfactants, Marcel Dekker, Inc. New York.

[20] Mahanta, D., Chaliha B.P. and Baruah, J.N. 1987, Colloids & Surfaces, 25: 101.

[21] Atkin, R., Craig, V.S.J., Wanless, E.J. and Biggs, S. 2003. Adv Coll. Interface Sci.,103: 219

[22] Kabanov,V.A. and Zezin,A.B. 1984. Pure Appl. Chem., 56: 343.

[23] Espinoza-Jimenez, M., Gimenez-Martin, E. and Ontiveros-Ortega, A. 1997. Textile Res. J., 67: 677.

Lenzinger Berichte, 85 (2006) 77-86

CHARACTERISATION OF THE POROSITY OF REGENERATED CELLULOSIC FIBRES USING CLASSICAL DYE ADSORPTION TECHNIQUES

R. N Ibbett*, S Kaenthong, D.A.S Phillips, M A Wilding

Christian Doppler Laboratory for Textile and Cellulose Chemistry, School of Materials,
University of Manchester, Manchester, M601QD UK;
*Author for Correspondence (e-mail: roger.ibbett@manchester.ac.uk)

Abstract

The use of classical dye adsorption techniques can provide information which relates quantitatively to fibre porosity. The modeling approach applied in this study allows the determination of a value for internal accessible volume, which can be used to interpret difference between fibres and the effects of fibre modification. In some cases the accessible volume correlates with the value for total pore volume determined by centrifugation. However, in this study it has been found that lyocell has a greater than predicted accessibility, consistent with its high dye uptake. This can be rationalized in terms of the known fibrillar structure of this fibre compared to other regenerated fibres manufactured using the alternative viscose process. The measurement of accessible volume will be of value in predicting the uptake behaviour of other textile process chemicals.

Keywords: *Lyocell, Viscose, Modal, isotherms, dyeing, porosity, accessibility, fibre, structure, cellulose*

Introduction

Cellulosic fibres have strongly hydrophilic character due to the presence of hydroxyl groups on each polymer repeat unit. This explains their ability to absorb moisture from the atmosphere and also their swelling properties in liquid water. Both natural and regenerated cellulosic fibres take up significant quantities water by the expansion of void spaces within the semi-crystalline morphology, forming a water-cellulose two-phase structure [1]. The expansion of the internal structure leads to a very high internal wetted surface area, meaning that a high proportion of the polymer hydroxyl groups become accessible to the swelling medium. Dissolved reagents are therefore transported through the void structure and can interact either physically or chemically with the available surface functional groups. Wet state treatments are often preferred for cellulosic fibres, in order to maximize the amount of available substrate to achieve highest uptake efficiency. A uniform distribution of chemical throughout the material may be achieved rather than the buildup of a limited layer of chemical at the fibre surface.

The ability of dissolved chemicals to interact within the cellulosic structure will depend on the nature of the two-phase water-cellulose texture developed during fibre swelling. The responses of different fibres are often rationalized according to some measurement of wet-state porosity, which may differ widely between regenerated or natural cellulosic types [2]. However, the measurement of fibre pore character is highly technique dependent and may be influenced by preparation conditions. Methods are required which can be operated without risk of altering the fibre structure and which provide information under realistic processing conditions [3]. Such techniques would ideally be sensitive to the sizes and interconnectivity of the pores within the fibre as well as the amounts and chemical nature of the internal cellulose-water interfaces.

Dyestuffs for cellulosic fibres are highly water-soluble, with molecular structures designed to interact at the cellulose-water internal interface.

The uptake of dyes is often used to monitor changes in fibre properties, brought about by variations in manufacturing conditions or fibre post treatment. Often the small variations in fibre colour are the first indication of some alteration to process variables. Dyes can therefore be considered as coloured probe molecules, which will report on the details of the internal pore texture [4,5]. They are usually quite bulky molecules and therefore will be sensitive to pore sizes and interconnectivity. The effectiveness of their interaction will also be influenced by the chemical and physical nature of the internal cellulose surfaces. Theories that relate dye uptake to fibre pore character will be valuable in understanding factors affecting product consistency during manufacture or during subsequent fibre or textile processing. The control of the response of fibre products under dyeing conditions is also of commercial importance.

Theory

Theories have been developed in an attempt to explain the response of natural and regenerated fibres towards solutions of direct dyes, which interact with cellulose by purely physical means. [6-9]. However, the same models will also be of value in understanding the behaviour of reactive dyes, which are covalently bonded to the internal cellulose surface during an alkali catalysed fixation reaction. Such dyes are often applied initially under non-fixing neutral conditions where uptake is governed by the same physical interactions affecting direct dyes [10]. Both direct and neutrally applied reactive dyes are therefore capable of reporting on the internal pore structure of cellulose. The anionic nature of reactive and direct dyes means that their uptake is enhanced by the addition of electrolyte to the dyebath. The successful theories account for such electrolyte effects and also the influence of charged functional groups on the fibre.

The most widely applied model, developed by Peters and Vickerstaff, was originally proposed to explain the response of direct dyes [11]. This model assumes that the chemical potential (μ) for a direct dye (D) can be expressed in terms of its activity (A) according to equation (1), where μ^o is the chemical potential of the reference state, R is the gas constant and T the absolute temperature. The approximation is also made using electrolyte-solution theory that the activity of the dye corresponds to the product of the concentrations of its constituent ions, as in equation 2, where (z) is the ionic charge of the dye. The dye anion and its counter-ions (usually Na^+) are assumed to move together in close association, in order to preserve electrical neutrality, so the concentration gradient of both species will influence the final equilibrium across the fibre-dyebath boundary.

$$\mu = \mu^\circ + RT\,ln(A) \tag{1}$$

$$A = \left(\left[D^-\right] \times \left[Na^+\right]^z \right) \tag{2}$$

$$-\Delta\mu^\circ = -\Delta G^\circ = RT\,ln\left(\frac{A_f}{A_s}\right) \tag{3}$$

The anion of the direct dye is substantive towards cellulose and will tend to move from the external dye solution into the fibre. An equilibrium is reached when the chemical potential (μ) of the dye is the same on each side of the fibre boundary, which leads to an expression for the standard change in chemical potential ($-\Delta\mu^o$). This is alternatively described as the standard affinity of the dye, or the standard free energy of dyeing ($-\Delta G^o$), according to equation (3), where (A_s) and (A_f) represent the dye activity in the dye-bath solution and fibre respectively. The important feature of the activity terms is that they involve the freely moving cations as well as the substantive anions and therefore the position of the dye equilibrium depends on the concentration of additional cations from added salt.

The amount of dye on fibre [D_f] at equilibrium can be determined from either the depletion of the dyebath or by extraction from the fibre, however, the units will be expressed in mols per kilogram of cellulose and not the mols per litre required in the ionic product terms. A factor (V) is introduced which describes the specific internal volume of the fibre, which modifies the activity term for the fibre phase to give equation (4), (where the charge signs have been dropped for clarity). The concentrations of both adsorbed and internal free dye are included within this volume and they are considered to exert an identical influence on the chemical potential. The factor (V) has units of litres/kilogram and represents the internal pore or void space of fibre that is accessible to the dye. Peters and Vickerstaff and others appreciated that this parameter could be used to contrast different fibre structures, with the dye considered as the molecular probe.

$$A_f = \frac{[D_f][Na_f]^z}{V^{z+1}} \quad (mols/l) \qquad (4)$$

The concentration of sodium ions within the fibre [Na$_f$] will be different from that in the external bath [Na$_s$] and must be deduced using the Donnan electropotential equilibrium theory [12]. Peters and Marshall derived equation (5), for calculation of the internal sodium ion concentration, expressed in terms of measurable or deducible quantities except for the accessible volume (V).

$$[Na_f]_{Cor} = 0.5\left\{z[D_f] + \left(z^2[D_f]^2 + 4V^2[Na_s][Cl_s]\right)^{0.5}\right\} \qquad (5)$$
$$+[C] \quad (mols/kg)$$

Cellulosic fibres usually carry a slight negative charge due to carboxylate functional groups at aldehydic endgroups or oxidized hydroxyl groups. Peters and Vickerstaff suggested that the carboxyl anions in the fibre would carry a stoichiometric quantity of sodium counter ions, which would add to the internal fibre sodium ion concentration [Na$_f$] predicted from the Donnan equilibrium [13]. Equation (5) therefore carries a correction for the carboxyl content of the fibre [C], which may be determined from the model or by a direct chemical or spectroscopic method.

An assumption is made that the large excess of the bath volume over the internal fibre volume would ensure that the equilibrium chloride concentration in the bath [Cl$_s$] would not deviate significantly from the made-up concentration at the start of dyeing. It is also assumed that the concentration sodium ions in the solution phase [Na$_s$] would be equivalent to the sum of all counter anions, according equation (6), which includes chloride and also the external dye as measured by visible spectroscopy.

$$[Na_s] = [Cl_s] + z[D_s] \quad (mols/l) \qquad (6)$$

The dye activity in the solution phase (A$_s$) required for equation (3) is then established according to equation (7).

$$A_s = [D_s][Na_s]^z \quad (mols/l) \qquad (7)$$

To establish a value for the accessible volume (V) Peters and Vickerstaff were obliged to carry out a fitting exercise, based on the assumption of a linear unitary relationship between the logarithms of dye activity in the solution and the fibre, according the reworking equation of (3) giving equation (8). The model parameter (V) is adjusted to achieve a least-squares fit, which should be independent of both dye and salt concentration.

$$log(A_f) = log(A_s) + \frac{\Delta G°}{2.303RT} \qquad (8)$$

Experimental

Stocks of factory produced 1.3dtex lyocell, 1.4dtex viscose and 1.3dtex modal were made available in loose fibre form, courtesy of Lenzing AG. Lyocell is manufactured by a direct dissolution dry-jet method and viscose is manufactured by a chemical derivatisation wet-jet method. These fibres were available in factory-dried state or in the never-dried washed state. The never-dried state refers to the condition after coagulation and removal of process chemicals, where the fibre has highest porosity, preceding the structural collapse on initial drying. A further batch of factory-dried lyocell fibre was immersed for 10 minutes in a 10% weight/volume solution of sodium hydroxide. This was then rinsed in repeated quantities of demineralised water until at neutral pH, then squeezed and allowed to dry under ambient laboratory conditions.

Two sets of dyeings were carried out on each of the as-received lyocell, viscose fibre and causticised lyocell samples, using a commercially available Direct Blue 71 dye (Mwt = 1299, z = 4). Solutions of the dye were made up at six concentrations, to give from 0.33 up to 2.0wt% on fibre, at a 20:1 fibre:liquor ratio, using either 2 or 4 g/l stock solutions of sodium chloride. [14] Dyeings were carried out at 80°C for 2 hours using a laboratory dyeing machine, after which samples of the final solutions were taken for spectroscopic analysis, according to Beer's law (λmax = 589nm).

Five commercial monochloro-triazinyl type reactive dyes were also selected. These were CI Reactive Red 120, CI Reactive Red 141, CI Reactive Yellow 84, CI Reactive Orange 84, and CI Reactive Navy 171. Single dyeings were carried out on both factory-dried and never-dried fibres, under neutral exhaustion conditions, with a liquor-to-fibre ratio of 20:1, at 80°C [15]. The restriction of the investigation to the neutral phase of dyeing ensured that uptake would be due only to physical adsorption, without chemical fixation. Dyebaths were made up to a concentration equivalent to 2% by weight of dye on fibre, together with 4gl/l of sodium chloride. Initial and final dyebath concentrations were determined by visible spectroscopy.

Dye concentrations were used to calculate the final equilibrium amount of dye on fibre [D_f] and remaining dye in the bath [D_S]. The purity of the direct dye was provided by the manufacturer, and was determined for the reactive dyes by titremetric reduction of the dye azo group using titanous chloride solution [16]. The inorganic buffer in the Direct Blue 71 dye formulations was estimated to be 5% of total weight and 30% by weight in the reactive dyes. It was assumed that under neutral conditions this electrolyte contribution to the thermodynamic model could be expressed on the basis of an equivalent weight of sodium chloride.

The total pore capacity of the fibre samples was determined separately by the centrifugation method [17]. Approximately 1 gram duplicate portions of fibre were immersed in distilled water for 10 minutes. Centrifugation was carried out using capped tubes at 1300G. Centrifuged samples were accurately weighed and then dried for 18hours at 60°C before reweighing. The internal water content or Water Retention of the fibres (WR) was calculated according to equation (10).

$$WR(\%) = 100 \times \frac{(Centrifuged\ weight - Dried\ weight)}{Dried\ Weight} \qquad (11)$$

The carboxyl contents of the dry and neverdried fibres determined by adding samples to a solution of 600mg/l of Methylene Blue (CI Basic Blue 9, MWt 374), buffered to pH8.5, at a liquor to goods ratio 100:1, according to the method of Davidson [18]. Dye-fibre liquors were continuously rotated for 20 hours using a laboratory dyeing machine, at 25°C. The visible absorbances of the dye liquors for each sample were measured initially and at equilibrium (λmax=666nm). The molar quantity of dye taken up was assumed to correspond to the fibre carboxyl content, expressed in milliequivalants per gram.

Results

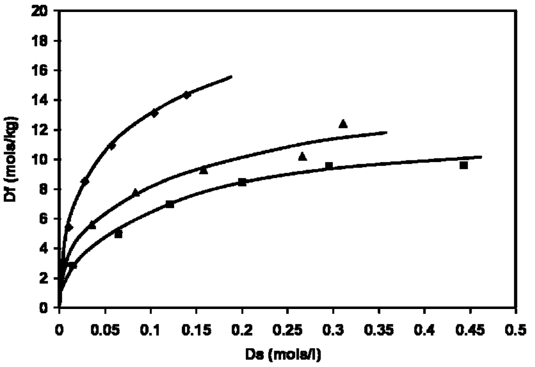


Figure 1 Direct Blue 71 adsorption isotherm at 2 g/l NaCl at 80°C. Causticised lyocell (◆), factory-dried lyocell (▲), factory-dried viscose (■).

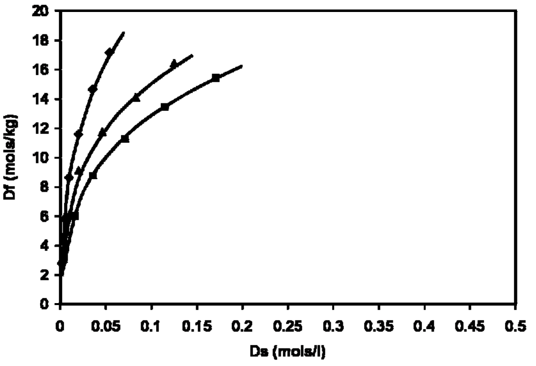


Figure 2: Direct Blue 71 adsorption isotherm at 4g/l NaCl at 80°C. Causticised lyocell (◆), Factory-dried lyocell (▲), factory-dried viscose (■).

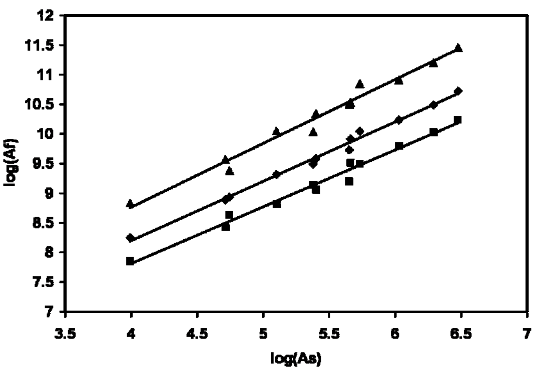


Figure 3 Linear fit of Peters and Vickerstaff model with varying accessible volume (V). 0.3mls/g (▲), 0.45mls/g (◆), 0.6mls/g (■)

The procedure chosen for the direct dye allowed both the accessible volume (V) and the apparent fibre carboxyl content [C] of the fibres to be established by model fitting. [14] The equilibrium isotherms at both 2g/l and 4g/l electrolyte concentrations are shown in figures 1 and 2. A plot of the bath and fibre log-activities combining both datasets is shown in figure 3, for different values for the accessible volume (V), with [C] set to zero. The correlation coefficient (r^2) describes a distinct maximum, allowing the volume (V) to be established within +/- 0.1mls/g. The use of data at two electrolyte concentrations greatly improved the reliability of the fitting exercise, with no clear maximum correlation being found with one dataset alone. After selecting (V) the data was replotted using equation (3), with the carboxyl content [C] adjusted to achieve a constant value for $(-\Delta G^{o})$ at across the range of dye solution activities (As), as shown in figure 4. The final values from the fitting exercise are summarized for Direct Blue 1 in table 1.

Single dyeings were carried out with the reactive dyes, applied to each of the selected fibre substrates. In this alternative approach the unknowns required for the Peters and Vickerstaff model were either supplied by direct analytical measurement or were deduced by the use of data from a control fibre sample [15]. The carboxyl contents for each sample were available for the model calculations. The accessible volume (V) for the factory-dried lyocell fibre was taken from the Direct Blue isotherm results. This was used initially to determine a free energy of dyeing $(-\Delta G^{o})$ for each of the reactive dyes applied to this fibre. With the free energies the accessible volumes could be established for the dyes applied to the other fibre substrates, by iterative adjustment using the model equations (3-7). The results for all reactive dyes are summarized in tables 2 and 3, with equilibrium dye uptake expressed as a partition ratio, $[D_f]/[D_s]$. The correlation between the average (V) from all dyes and the independently measured water retention is shown in figure 5, with rewetted lyocell excluded from the trend.

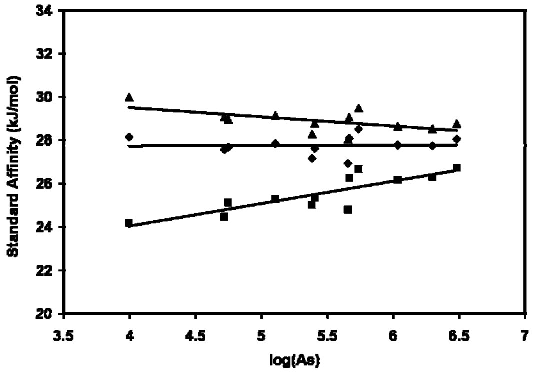


Figure 4 Variation in constancy of free energy of dyeing of lyocell from Peters and Vickerstaff model with adjustment of fibre carboxyl group content (C). 0 mequiv/kg (▲), 9 mequiv/kg (◆), 16mequiv/kg (■)

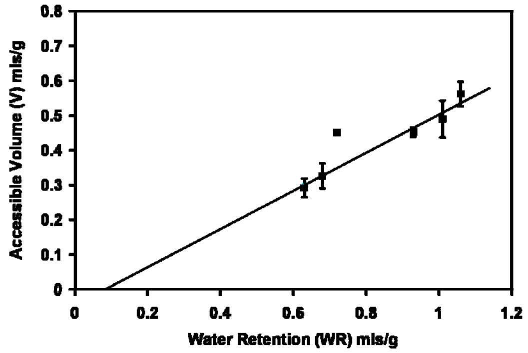


Figure 5 Relationship between model accessible volume (V) from dye adsorption, and experimental water retention (WR) from centrifugation, average from all dyes, error bars = 1 standard deviation.

The conditions for measurement of water retention by centrifugation were designed to remove all water between the fibres, with water in the small internal void spaces held against the centrifugal force by capillary action. The results obtained by gravimetry represent the total wet capacity of the fibres or their total pore volume, as summarized in tables 1 and 2.

Discussion

The results in table 1 indicate that the free energy of dyeing of direct blue 71 is of comparable magnitude for viscose and lyocell factory-dried fibres, around -28kJ/mol. This is suggests that the nature of the interaction is the same for both substrates and that at a molecular level the character of the internal surfaces are similar [13]. The direct dye and selected reactive dyes are all highly planar and show high substantivity towards cellulose. The chemical basis of the interaction is not fully understood but is likely to involve Van-der-Waals attractions between cellulose hydroxyl groups and the dye aromatic π-system. In addition, it is possible that the hydroxyl groups disrupt the water hydration layer around the dye reducing its solubility and bringing it closer to the cellulose surface [19].

Table 1: Dye isotherm fitted parameters and comparative experimental data for lyocell and viscose fibre, for Direct Blue 71 dye

3

Sample	WR, Water retention, (l/kg)	(V), Model fit (l/kg)	[C], Model fit (milliequiv/kg)	[C], Model fit (milliequiv/kg) predicted in total pore volume	(-ΔG°), Free energy of dyeing (kJ/mol)
As-received Lyocell	0.68	0.45 (r^2=0.991)	9	14	27.5
As-received Viscose	0.90	0.39 (r^2=0.991)	16	37	28.5
Causticised Lyocell	0.83	0.86 (r^2= 0.998)	3	3	23.5
Causticised lyocell, Forced ΔG° = 28kJ/mol	0.83	0.56 (r^2 =0.951)	9	-	28.0

Table 2: Equilibrium dye uptake, experimental carboxyl contents and total wet volumes of different cellulosic fibres, for reactive dye series

Dye	Partition ratio (P), (mmol/l / mmol/kg)					Carboxyl Content [C], (meq/g)	Centrifuged Water Retention (WR), (mls/g)
	Red 120	Red 141	Yellow 84	Orange 84	Blue 171		
never-dried lyocell	134	202	34	37	147	28	1.06
never-dried viscose	37	22	5	5	23	55	1.01
never-dried modal	19	9	3	2	12	39	0.68
factory-dried lyocell	49	91	19	14	71	29	0.72
factory-dried viscose	20	24	5	4	31	52	0.93
factory-dried modal	10	8	2	2	9	38	0.63

Table 3: Fibre accessible volume and free-energy of dyeing calculated from Peters and Vickerstaff Model, for reactive dye series

dye	Red 120	Red 141	Yellow 84	Orange 84	Navy 171	
free energy of dyeing (-ΔG°) (-kJ/mol)	29.0	36.8	29.3	27.1	30.3	
number of sulphonate groups (z)	6	8	8	8	6	
Purity (wt%)	55	52	46	51	55	
molecular weight	1338	1774	1658	1850	1419	
Fibre type	model accessible volume (V) mls/g					average
never-dried lyocell	0.60	0.53	0.54	0.61	0.55	0.56
never-dried viscose	0.57	0.44	0.48	0.52	0.45	0.49
never-dried modal	0.38	0.28	0.31	0.34	0.33	0.33
factory-dried lyocell	(0.45)	(0.45)	(0.45)	(0.45)	(0.45)	0.45
factory-dried viscose	0.45	0.43	0.47	0.46	0.47	0.45
Factory-dried modal	0.30	0.27	0.29	0.34	0.27	0.29

Causticisation raises both the water retention (WR) and the accessible volume (V) of lyocell. However, the model fitting led to a reduction in free-energy, which seems unreasonable. The reversible swelling action of sodium hydroxide is unlikely to seriously influence the character of the internal pore surfaces and is therefore not expected to disturb the dye-cellulose interaction. Causticisation is known to improve crystalline surface perfection so might be expected to lead to an enhanced interaction with the dye [20]. A forcing of the model using a free energy of -28kJ/mol resulted in a reduced accessible volume, without serious lowering of the correlation coefficient, as shown in table 1.

The assumption of a constant free-energy of dyeing implies that the strength of the interaction is dependent only on the molecular characteristics of the dye itself and therefore should be the same on any cellulose substrate. It is therefore reasonable to use the factory-dried lyocell as a standard, with its accessible volume assumed to be constant for all dyes applied in the study. This may not be universally true, but for this work the selected dyes all have similar molecular weight and planar character and therefore also similar cross-sectional dimensions. Their physical accessibilities within a given substrate would all be expected to be comparable, with each dye reporting in a similar way on the accessible volume of the different substrates according to the model, as summarized in table 3. The graph in figure 5 shows how the averaged accessible volume for all reactive dyes follows a trend with respect to water retention, for the series of rewetted and never-dried fibres, however with lyocell above the trend line.

All results suggest that the model accessible volume (V) is lower than the equivalent value for water retention (WR), which is reasonable given the large size of the dye molecules compared to water. The ratio of (WR) to (V) for both factory-dried and causticised lyocell is around 0.64 but for all other factory-dried and all neverdried fibres this ratio is around 0.48, although for neverdried lyocell this ratio is slightly higher at 0.53. After initial drying lyocell develops a highly ordered fibrillar structure, which exists in a less organized state in the nascent neverdried state. This is different from the fringed-micelle type structure exhibited by viscose and modal. Lyocell in contrast with these other fibres shows a large reduction in water retention between neverdried and factory-dried states, suggesting a high degree of structural consolidation. [21] The resulting lamellar interconnected pore structure of lyocell may be particularly accessible to planar dye molecules. [22] The response of lyocell to dyeing and possibly towards other aqueous treatment chemical may not be predicted reliably from its bulk water retention. Causticisation will increase the size of the crystalline domains that make up the fibrillar texture, leading to a corresponding expansion of interfibrillar void spaces. This would be expected to raise both the accessible volume and water retention.

The original work of Peters and Vickerstaff was carried out at electrolyte concentrations below those normally used for commercial dyeing. This gave rise to a greater distribution of dye between bath and fibre, leading to a wider and more useful range of isotherm points. The current work has extended this approach and has shown that model fitting is far more successful with two sets of data at different electrolyte level. In this study six data points were collected for each set, but in future work this might be reduced without compromising accuracy.

The model fitting is sensitive to adjustments of carboxyl content [C], which is especially the case at low electrolyte concentrations. The use of an extended isotherm dataset allows accurate fixing of this parameter, as shown in figure 4. The results obtained using the Direct Blue 71 dye show differences between the three fibres examined, in table 1, with viscose having a higher value than lyocell. Causticisation is known to remove low molecular weight polymer with a high proportion of carboxyl end-groups, which is consistent with the result of the fitting exercise for this fibre [13]. The experimental measurement of carboxyl concentration from methylene blue adsorption shows comparable differences between the various fibres, shown in table 2, although these values are higher than returned by the model fitting. Possibly the number carboxylate groups accessible to the small methylene blue molecule is greater than those influencing the adsorption of the larger direct or reactive dyes.

The experimentally determined carboxyl concentration found for viscose is almost twice that of lyocell, which partly explains the poorer dye uptake of this fibre under these low electrolyte conditions, despite its much higher water retention (WR). The model accounts for the effects of charge repulsion, through the use of Donnan equilibrium theory, with the accessible volume term representing only the physical volume within the fibre in which the dye and electrolyte ions are able to diffuse. As discussed, this volume is higher than expected for lyocell, from both isotherm and single dyeing results, which also helps to explain its higher than expected dye uptake. The isotherm results using direct blue 71 even suggest that the accessible volume for lyocell is above that of viscose, although this may be due to an under-valuing of the carboxyl corrections [C] in the model fitting.

The operation at low electrolyte levels and at low dye concentration allows the assumption that the adsorption of the dye is well below saturation, so there is no restriction in the availability of sites within the pores structure for surface interaction. However, the alternative Langmuir concept for surface adsorption implies that uptake is proportional to the number of available surface sites, even at low extent of saturation [6] The magnitude of the isotherm curve would be scaled according to the total surface capacity of the substrate for any given free-energy of dyeing. The Peters and Vickestaff model has been modified by including an additional term describing dye activity within the fibre (A_f), according to equation (9), where $[S_f]$ is the saturation capacity of the fibre internal surface [7].

$$A_f = \frac{[Na_f]^z [D_f]}{V^z([S_f]-[D_f])} \qquad (9)$$

This introduces another parameter [S$_f$], has a useful physical meaning in terms of the fibre internal structure and intuitively should have a bearing on the response of fibres to chemical treatment [23]. Figure 6 illustrates the influence of different fibre saturation values [S$_f$] on the theoretical isotherm, in comparison with the corresponding experimental data for factory-dried viscose, at 4g/l sodium chloride electrolyte concentration. An increase the fibre surface capacity leads to greater adsorption, with fixed values for accessible volume, free-energy and carboxyl content. In practice, a reduction of the free-energy term can be applied to compensate for the increasing surface capacity, resulting in a range of fitting solutions of equal merit. The Langmuir model expressed in Equation (9) leads to mathematical relationship between the surface capacity [S$_f$] and accessible volume (V). An evaluation of (V), which is established using the Peters and Vickerstaff model, will therefore allow a calculation of [S$_f$] under the same dyeing conditions. The assumption of a constant free-energy (-ΔG^o) means that (A$_f$) and (A$_s$) must always have the same relationship for a give dye, with (V) and [S$_f$] compensating for each other in the (A$_f$) term of the model for different fibre substrates. The surface and volume parameters for given fibre are therefore intrinsically linked in the Langmuir model and may be considered as alternative descriptions of the same fibre property.

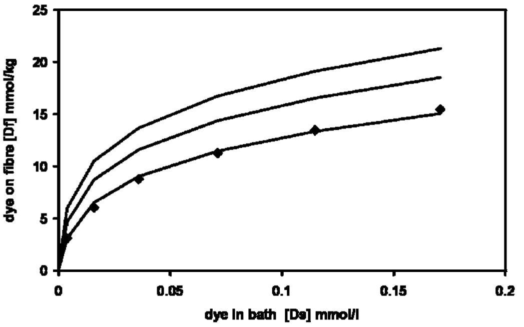


Figure 6 Model isotherm curves using Langmuir model, together with experimental data points for Direct Blue 71 applied to factory-dried viscose, at 4g/l NaCl, at 80°C. Model: (V) = 0.39, [C] = 16meq/g, [S$_f$] values: top curve = 500, middle = 300, lower = 150 mmol/kg

Conclusion

The use of classical dye adsorption techniques can provide information that relates quantitatively to fibre porosity. The modeling approach applied in this study allows the determination of a value for internal accessible volume, which can be used to interpret difference between fibres and the effects of fibre modification. The measurement of accessible volume will be of value in predicting the uptake behaviour of other textile process chemicals. In some cases the accessible volume correlates with the value for total pore volume determined by centrifugation. However, in this study it has been found that lyocell has a greater than predicted accessibility, consistent with its high dye uptake. This can be rationalized in terms of the known fibrillar structure of this fibre compared to other regenerated fibres manufactured using the alternative viscose process. The accessible volume represents the internal void space in which the dyebath species are able to diffuse. The assumption of the model is that adsorption for a given free energy of dyeing is related to the energy required to move the dye counterions against the concentration gradient between the external and internal volume, which is required to maintain electrical neutrality. An alternative model based on the Langmuir concept for adsorption at surfaces is intuitively reasonable, in that a higher surface capacity would be expected to promote greater dye uptake. However, the fitting this additional variable parameter is difficult without first fixing other fibre parameters. Although the volume and surface-capacity models are based on different concepts, the fibre properties derived from each are closely linked.

Acknowledgements

The authors would like to thank the Christian Doppler Society and Lenzing AG for financial support.

References

[1] T P Nevell in "The Dyeing of Cellulosic fibres" chapter 1, ed. C Preston, Dyers' Company Publications, Bradford, 1986.

[2] K Bredereck, A Blüher, Melliand Textilberichte, 8 (1992) 652.

[3] K Kasahara, H Sasaki, N Donkai, Textile Research Journal, 74(6) (2004) 509.

[4] K Bredereck, A Saafan, Die Angewandte Makromolekulare Chemie, 95 (1981) 13 (Nr. 1482)

[5] S Kaenthong, D A S Phillips, A H Renfrew, M A Wilding. Colouration Technology 121(1) (2005) 45.

[6] T Vickerstaff, in "The physical chemistry of dyeing" (Oliver and Boyd, London 1954)

[7] F Carillo, M J Lis. Dyes and Pigments 53 (2002),129.

[8] S R Sivaraja G. Srinivasan, N T Baddi, Textile Research Journal, July (1968) 693.

[9] H Gerber, Journal of the Society of Dyers and Colourists, 10, (1994) 375

[10] S-H Bae, H Motomura, Z. Morita, Dyes and Pigments, 34(1) (1997) 37.

[11] R H Peters, T. Vickerstaff, Proceedings of the Royal Society (London), A192 (1948) 292.

[12] L Peters, in "The Theory of Colouration of Textiles" chapter 4, ed. C L Bird and W S Boston, Dyers Company Publications, Bradford (1975)

[13] W J Marshall, R H Peters, Journal of the Society of Dyers and Colourists, 63 (1947) 446

[14] R N Ibbett, D A Phillips, S Kaenthong, Dyes and Pigments, 71 (2006) 168.

[15] R N Ibbett, D A Phillips, M A Wilding, S Kaenthong, Journal of Materials Science, in press.

[16] V Murtagh and J A Taylor, Dyes and Pigments 63 (2004), 17

[17] Morton and J W S Hearle, in "Physical Properties of Textile Fibres", chapter 10, 3rd edition, The Textile Institute (1993)

[18] G F Davidson, Journal of the Textile Institute, 39 (1948) T65.

[19] E H Daruwalla, A.P. D'Silva, Textile Research Journal, 59 (1993) 40.

[20] Dube, R H Blackwell, in TAPPI Proceedings of the International Conference on Dissolving and Speciality Pulps, Jan 1983.

[21] M E Vickers, N P Briggs, R N Ibbett, J Payne, S B Smith. Polymer, 42 (2000) 8241.

[22] K Bredereck, Rev. Prog. Colouration 35 (2005) 39.

[23] J J Porter, Textile Chemist and Colourist, February (1993) 27

Lenzinger Berichte, 85 (2006) 87-90

MASS COLORATION OF REGENERATED CELLULOSICS – A REVIEW

Avinash P. Manian [a], Hartmut Ruef [b], Thomas Bechtold [a,*]

[a] Christian Doppler Laboratory for Textile and Fiber Chemistry in Cellulosics, Institute of Textile Chemistry and Textile Physics, University of Innsbruck, Hoechsterstrasse 73, 6850 Dornbirn, Austria
[b] Textile Innovation, Lenzing AG, 4860 Lenzing, Austria
[*] Author for correspondence: textilchemie@uibk.ac.at, Phone: +43-5572-28533, Fax: +43-5572-2862

Abstract

Regenerated cellulosic fibers constitute a significant segment of the man-made fibers industry. This manuscript offers a critical review of the various methods available for their mass coloration; with 42 references.

Keywords: mass coloration, spun-dyeing, regenerated cellulosics.

Introduction

Regenerated cellulosic fibers are obtained from wood pulp by dissolution and reshaping of the cellulose via physico-chemical processes. Of the many methods available for producing regenerated cellulosics [1-3], the viscose, cuprammonium, and lyocell processes may be regarded as being most prevalent in commercial industrial-scale operations [3]. Brief descriptions of these processes, excerpted from more detailed information in literature, are given below:

Viscose Process [4]
Cellulose pulp is converted to alkali cellulose by immersion in alkali solution. The alkali cellulose is mixed with CS_2 to form cellulose xanthate, which is dissolved in a dilute solution of sodium hydroxide to form the 'viscose' dope, and wet-spun in a solution of sulfuric acid to form fibers.

Cuprammonium Process [5]
Cellulose pulp is dissolved in cuprammonium solution (prepared by dissolving copper hydroxide in a concentrated ammonia solution), and wet-spun in acidic aqueous solutions to form fibers.

Lyocell Process [6]
Cellulose pulp is shredded and wetted in an aqueous solution of amine oxide followed by removal of excess water, which results in the dissolution of cellulose. The resulting solution, which is very viscous, is extruded via an air-gap into a water/amine oxide bath to form fibers. The process is characterized by a near complete recovery of the amine oxide, N-methyl-morpholine-N-oxide (NMMO), after fiber production.

Mass coloration, spun-dyeing or dope dyeing may be defined as "a method of coloring manufactured fibers by incorporation of the colorant in the spinning composition before extrusion into filaments" [7]. One of the primary considerations in any mass coloration process is to ensure chemical and physical stability of the polymer-colorant mixture. This is especially important with regard to regenerated cellulosics as their manufacturing processes involve treatment of the cellulose with strong oxidizing/ reducing agents, which may militate against the stability of colorants. But, mass coloration of regenerated cellulosics has been found possible, and the different methods reported for its achievement are summarized below.

Mass Coloration of Viscose or Cuprammonium Rayon

Vat Dyes

Many of the techniques proposed for mass coloration of viscose or cuprammonium rayon involve the addition of vat dyes to spinning dopes, wherein the vat dye is reduced to its leuco form and oxidized back to its parent form in the course of manufacturing the substrate. Some techniques involve addition of reduced vat dye to the spinning dope [11, 12]. In others, it is proposed that the vat dye be reduced in spinning dope either by utilizing the chemical reagents already present in the system [8], or by addition of reducing agents such as sodium hydrosulphite [13]. Yet others involve dispersing the vat dye in spinning dope as a pigment, forming the regenerated substrate, and treating the formed substrate with reagents to reduce the vat dye within [9, 10, 14]. In all these techniques, the oxidation of the vat dye back to its parent form is achieved, in general, by treating the formed substrate with oxidizing agents.

There are limitations to these techniques. Adding reduced vat dyes to the spinning dope may result in stabilization of the spinning dope [9]. Proper aging and coagulation of the spinning dope is hindered, which affects the development of suitable viscosities for fiber/filament spinning. The reduced vat dyes are also susceptible to premature oxidation, which results in a non-uniform distribution of dye in the substrate [15]. Many vat dyes are not reduced under conditions that exist in the spinning dope [16], and the addition of reducing agents to the system renders the dope liable to gel formation [13]. The technique of dispersing vat dyes in the spinning dope and reducing them in the formed substrate is not without challenges; firstly because a uniform distribution of the dyestuff in substrate is difficult to achieve, and secondly because not all dyestuff in substrate may be reduced, causing visible specks of dyestuff particles to remain in the substrate [13].

In some techniques, vat acids or the ester derivatives of leuco compounds of vat dyes are added to the spinning dope [15, 16]. However, the leuco compounds are highly susceptible to oxidation, which may result in the formation of coarse dyestuff particles in dope thereby affecting the subsequent regeneration step [11].

Dissolved Colorants

Some of the proposed mass coloration techniques involve adding to spinning dopes colorants dissolved in polar water-miscible solvents, or dissolving colorants directly in the spinning dope [17-24]. The colorants used in these methods are selected dyes, dye derivatives, or pigments. The choice of dyestuffs available for this technique is limited by the fact that not all dyestuffs can withstand the strong alkaline conditions present in the spinning dope, or the strong acid treatments imparted to substrates during regeneration [15]. Moreover, the use of water soluble dyestuffs in mass coloration of regenerated cellulosics has been observed to result in poor water fastness of the formed products [13].

Dispersed Colorants

The dispersion of finely milled organic or inorganic pigments in spinning dopes has been suggested as a possible route for mass coloration [25-33], with additives being recommended in some cases to improve pigment dispersability [28-30, 34]. The process of milling pigments to obtain a suitable particle size is time intensive, and is accompanied by the risks of recrystallization and/or regrouping of dyestuff particles [35]. The possibility of poor pigment dispersion in spinning dope is an inherent risk in this technique, which may lead to problems both in the regeneration process and with the uniformity of color in formed substrates [28, 30]. The dispersing agents added to pigment formulations sometimes cause undesirable foaming in the spinning mass [32]. The colored substrates tend to be opaque [13], exhibit dull shades [9], and may also exhibit dichroism [29]. This technique of mass coloration may also exert a deleterious effect on substrate strength [22].

Other Methods

Other proposed techniques include the suspension of sulfur dye intermediates in spinning dopes [36], or utilizing waste cotton textiles dyed with reactive dyes by mixing them with fresh cellulose, subjecting the mixture to xanthation, and spinning colored filaments there from [37]. In what may be categorized as a quasi mass coloration method, it is proposed that naphthol dye grounders be dissolved or mixed in the alkaline spinning dope [38]. The color could then be developed by treating the fibers with coupling components, even when the fibers have been incorporated into yarns or fabrics.

Mass Coloration of Lyocell

Lyocell fibers are relatively new in comparison to the other regenerated cellulosics, with the first commercial samples being available in the mid-1980s and full-scale commercial production beginning in the early 1990s [6]. Hence, there are only a few methods reported for the mass coloration of lyocell.

In one of the first techniques reported [39], it is proposed that selected inorganic pigments, which contain small amounts of heavy metals and do not significantly decrease the decomposition temperature of the spinning mass, be mixed with the cellulose solution prior to fiber spinning. It has also been proposed that colorant or colorant precursors be mixed with the cellulose solution [40], with the caveat that the colorants be insoluble or sparingly soluble in amine oxide. In the most recent method reported [41], it has been suggested that cellulose pulp be dyed with a vat dye; and the dyed pulp optionally mixed with undyed pulp be used to spin lyocell fibers.

Summary

Like many other processes, every method for the mass coloration of regenerated cellulosic fibers has its advantages and limitations. Mass coloration processes in general offer the advantages of high color fastness in products and a high degree of colorant utilization which make the process more eco-friendly; but are usually cost efficient only in large-scale production [42]. There exist niche markets for such products, and mass colored regenerated cellulosic fibers are commonly used in technical textiles such as in medical applications, and outdoor textiles.

Acknowledgements

The authors gratefully acknowledge the financial support of the Christian Doppler Research Society (Vienna, Austria).

References

[1] Woodings, C., A brief history of regenerated cellulosic fibers, in *Regenerated Cellulose Fibers*, Ed. Woodings, C., Woodhead Publishing Ltd., Cambridge, England, 2001, pp 1-21.

[2] Turbak, A., Other processes, in *Regenerated Cellulose Fibers*, Ed. Woodings, C., Woodhead Publishing Ltd., Cambridge, England, 2001, pp 174-198.

[3] Bredereck, K., and Hermanutz, F., Man-made cellulosics, *Review of Progress in Coloration of Textiles*, 35, 59-75 (2005).

[4] Wilkes, A.G., The viscose process, in *Regenerated Cellulose Fibers*, Ed. Woodings, C., Woodhead Publishing Ltd., Cambridge, England, 2001, pp 37-61.

[5] Kamide, K., and Nishiyama, K., Cuprammonium processes, in *Regenerated Cellulose Fibers*, Ed. Woodings, C., Woodhead Publishing Ltd., Cambridge, England, 2001, pp 88-155.

[6] White, P., Lyocell: The production process and market development, in *Regenerated Cellulose Fibers*, Ed. Woodings, C., Woodhead Publishing Ltd., Cambridge, England, 2001, pp 62-87.

[7] A glossary of AATCC standard terminology, AATCC Technical Manual, 75, 399 (2000).

[8] Lockhart, G.R., Manufacture of rayon. US 1865701; Jul 5, 1932.

[9] Ruesch, R., and Schmidt, H. Preparation of dyed filaments and films. US 2043069; Jun 2, 1936.

[10] I. G. Farbenindustrie A.G. Process for the manufacture of dyed filaments and films. GB 448447; Jun 8, 1936.

[11] I. G. Farbenindustrie A.-G. The manufacture of dyed artificial masses from regenerated cellulose. GB 465606; May 10, 1937.

[12] Kline, H. B., and Helm, E.B. Manufacture of artificial silk. US 2143883; Jan 17, 1939.

[13] Batt, I. P., Process for producing colored pellicular gel structures of regenerated cellulose. US 3005723; Oct 24, 1961.

[14] Maloney, M. A. Mass coloring of regenerated cellulose with vat dyes. DE 1253864; Nov 9, 1967.

[15] Dosne, H. Colored cellulose material. US 2041907; May 26, 1936.

[16] Lutgerhorst, A. G. Spundyed rayon. US 2738252; Mar 13, 1956.

[17] Soc. pour l'ind. chim. a Bale. Pigment-containing spinning masses. CH 212386; Mar 3, 1941.

[18] Phrix-Werke A.-G. Spun-dyed regenerated cellulose. NL 6407087; Jan 18, 1965, vide Chemical Abstract No. 63:63815.

[19] Ciba Ltd. Dyeing of regenerated cellulosic fibers and films. FR 1417575; Nov 12, 1965, vide Chemical Abstract No. 65:57365.

[20] Ciba Ltd. Transparent colored regenerated cellulose. NL 6514672; May 13, 1966, vide Chemical Abstract No. 65:82924.

[21] Wegmann, J., and Booker, C. Colored viscose dope. DE 1220964; Jul 14, 1966.

[22] Ciba Ltd. Process for the preparation of transparent colored shaped articles of regenerated cellulose with the aid of organic dyestuffs of low solubility in water. GB 1128158; Sep 25, 1968.

[23] Riehen, W. M., and Reinach, F. S. Difficultly soluble organic dye compositions for dyeing transparent, shaped, regenerated cellulose bodies. DE 1806199; Apr 29, 1971.

[24] Riehen, W. M., and Reinach, F.S. Sparingly soluble organic dyestuffs. US 3620788; Nov 16, 1971.

[25] Novacel S. A. Colored regenerated cellulose sponges. FR 1025296; Apr 13, 1953, vide Chemical Abstract No. 52:3968.

[26] Manufactures de produits chimiques du Nord (establissment Kuhlmann). Coloring viscose fibers. FR 1114803; Apr 17, 1956, vide Chemical Abstract No. 53:102818.

[27] Jones, F. B. Glossy, spun-dyed threads from aqueous cellulose solutions. DE 1067173; Oct 15, 1959.

[28] Keil, A., Popp, P., and Krause, E. Process for the production of pigmented regenerated cellulosic fibers. GB 872207; Jul 5, 1961.

[29] Eskridge, B. E. Manufacture of pigmented viscose rayon. US 3033697; May 8, 1962.

[30] Gomm, A. S., Morgan, L. B., and Wood, L. Process of incorporating aqueous pigment composition in viscose. US 3156574; Nov 10, 1964.

[31] Heinrich, E. Spin-dyed regenerated cellulose products and process for their manufacture. GB 1046299; Oct 19, 1966.

[32] Schoenbach, V., Weissert, J., and Teige, W. Pigment dispersions for coloring viscose spinning masses. US 3337360; Aug 22, 1967.

[33] Hama, H., and Sakurai, H. Dope dyeing viscose rayon having a good black luster. JP 47051968; Dec 27, 1972, vide Chemical Abstract No. 80:28345.

[34] Ono, S., and Igase, T. Dope dyeing of rayon. JP 54038919; Mar 24, 1979, vide Chemical Abstract No. 91:40853.

[35] Whitehead, W. Colored organic derivatives of cellulose and method of making same. US 2128338; Aug 30, 1938.

[36] Cassella Farbwerke Mainkur A.G. Dyeing of regenerated cellulose in the spinning paste. BE 611323; Dec 29, 1961, vide Chemical Abstract No. 57:17664.

[37] von der Eltz, A. Recycling of dyed cellulosic wastes. EP 0717131; Jun 19, 1996.

[38] Kurahashi, I., Kudou, M, Tanibe, H, and Ando, K., Modified regenerated cellulose fiber and fiber product. EP 1270772; Jan 2, 2003.

[39] Bartsch, P., and Ruef, H., Method for producing cellulosic moulded bodies. WO 99/46434; Sep 16, 1999.

[40] Ruef, H., Colored cellulosic shaped bodies. WO 01/11121; Feb 15, 2001.

[41] Bechtold, T., Manian, A.P., and Ruef, H. Method for producing colored cellulosic shaped bodies. Appl. No. AT 2029/2005; Dec 19, 2005.

[42] Holme, I., Coloration of technical textiles, in *Handbook of Technical Textiles*, Ed. Horrocks, A.R., and Anand, S.C., Woodhead Publishing Ltd., Cambridge, England, 2004, pp 187-222.

Lenzinger Berichte, 85 (2006) 91-94

DIFFERENTIATED FABRIC OPPORTUNITIES FOR TENCEL® USING INNOVATIVE DYEING AND FINISHING PROCESSES

J M Taylor,

Lenzing Services Ltd., UK

Abstract

Since the market introduction some fourteen years ago, TENCEL® containing fabrics have become accepted and well known for their fibrillated aesthetic and soft touch character. However, this fibre type is capable of producing so much more. This paper will examine the various processing methods that have evolved over the past decade, and demonstrate the wide range of product types that can be produced. These range from the fully fibrillated, highly casual, garment processed jeanswear through to a classic formal piece processed product, and the whole host of opportunities that exist between the two extremes.

Introduction

TENCEL® is an extremely versatile fibre. The property of fibrillation allows a wide variety of fabric aesthetics and appearances to be achieved. These aesthetics range from a highly casual look, using a fully fibrillated fibre, to a clean, smooth, classical fabric achieved by suppressing fibrillation.
New and innovative dyeing and finishing techniques have been introduced into the market recently and development continues apace. These new methodologies, not only allow faster less complicated processes, but because in many cases times are reduced, garment styling can be introduced that previously has not been possible.

This paper will consider the range of aethetics possible and the dyeing and finishing techniques that can be used to generate them. It will also introduce a number of the innovative dyeing and finishing systems.

Product Possibilities

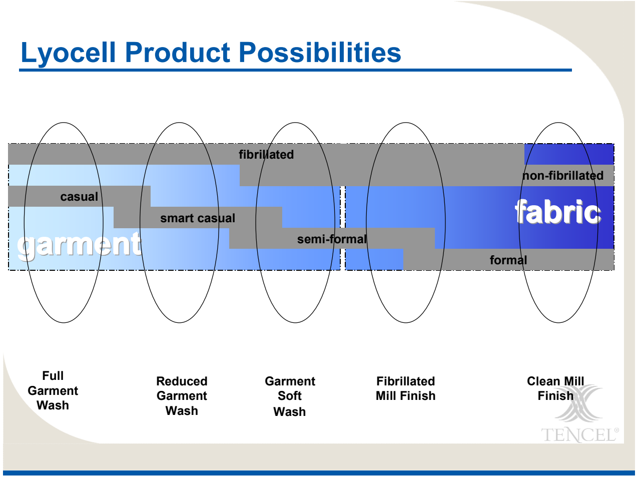


Figure 1 – TENCEL® Can Create a Wide Range of Fabric Aesthetics

TENCEL® fabrics can be processed in garment form or in the fabric piece. The finish can be either fibrillated or clean looking.

Depending on the method used and the fibrillation present this can give rise to very casual or formal appearances, or as is demonstrated in the figure above a number of possibilities between the extremes.

We will consider each of these sections independently

Full Garment Wash

This look is achieved by processing in a fully made up garment form. Abrasion and fibrillation on the seams creates a puckering and highlighting that gives a very casual aspect.

A typical manufacturing process will involve conventional open width dyeing of the fabric, followed by garment manufacture and carrying out an enzyme based washing process in a garment washing machine.

The time spent on the machine will be long because the TENCEL® process demands a three step system of fibrillate, enzyme and soften. This lengthy process as well as being relatively expensive means that garment styling needs to be simple as trims will break down in the long process. Also, the long abrasive process, naturally takes the garment to a very casual fibrillated aspect.

Figure 2 – Casual Garment Appearance

This look is achieved by processing in a fully made up garment form. Abrasion and fibrillation on the seams creates a puckering and highlighting that gives a very casual aspect.

A typical manufacturing process will involve conventional open width dyeing of the fabric, followed by garment manufacture and carrying out an enzyme based washing process in a garment washing machine.

The time spent on the machine will be long because the TENCEL® process demands a three step system of fibrillate, enzyme and soften. This lengthy process as well as being relatively expensive means that garment styling needs to be simple as trims will break down in the long process. Also, the long abrasive process, naturally takes the garment to a very casual fibrillated aspect.

Reduced Garment Wash

Recent innovations in dyeing and finishing have made it possible to significantly reduce the time needed in the washing process. By modifying the fabric preparation technique it is possible to greatly reduce or even eliminate the need for fibrillate and enzyme stages in the process.

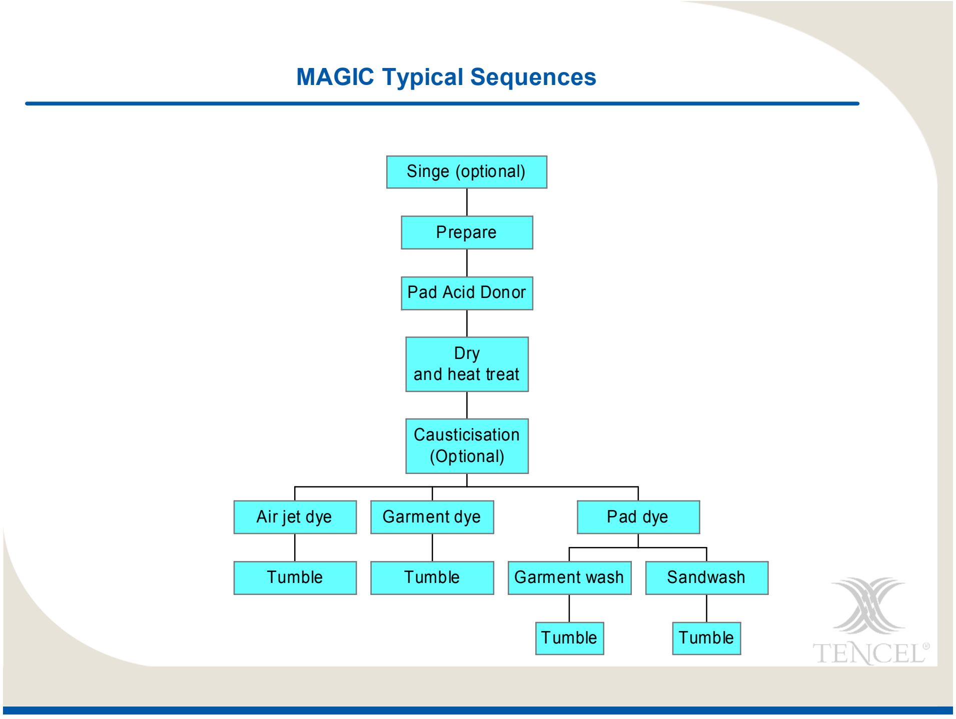
MAGIC technology involves the pre-treatment of fabric (prior to garment construction) in a solution of magnesium chloride followed by heat treatment in a stenter or similar. The controlled degradation brought about by this Lewis acid treatment greatly reduces the time needed in the subsequent garment washing steps. The time reduction has been shown to be 50% or even more.

The greatly reduced time in the washing process allows not just reduced time, but the introduction of more complex garment styling. More detailed pocket structures or trims and tapes can be introduced because now they will survive the garment wash process.

MAGIC has been developed by TENCEL® to simplify the process, but the treatment needed will vary depending on the fabric construction, weight and blend. A calculator has been developed that allows easy calculation of appropriate treatment conditions for fabrics of different weights and blend ratios.

MAGIC technology is wide reaching. It can be used to prepare fabric to speed the process through not just garment wash, but also garment dye, jet piece process or even sandwashing

Figure 3 – Innovative Fabric Preparation to Reduce Processing Cost



MAGIC Typical Sequences

Singe (optional)
Prepare
Pad Acid Donor
Dry and heat treat
Causticisation (Optional)
Air jet dye
Garment dye
Pad dye
Tumble
Tumble
Garment wash
Sandwash
Tumble
Tumble

Softener Only Garment Wash

This creates a semi formal garment look. It involves the straight forward production of open width dyed fabric. However, since the next steps are to involve a wash treatment in garment form it is important to consider the fibrillation. The aesthetic needed is fibrillation free, so the finisher must ensure that fibrillation is blocked before garment make up. This is achieved by simple resin finishing. Typically 2-3% fixed DMDHEU resin type is applied to achieve this. Too much and the fabric physical properties are adversely affected, too little and fibrillation will occur.

Once the fabric is open width dyed and resinated, the garment is cut and sewn. The garment is then given a simple cotton type “soft wash” to create little seam pucker, make the fabric softer and create a semi-formal or smart-casual look.

Because there is liitle washing, garment styles can be quite complex, and by virtue of the added resin, good easy care properties can be achieved

Figure 4 – Semi-formal Non-fibrillated Garment Appearance

Fibrillated Mill Finish

This more formal look is achieved by creating a fibrillated surface in the fabric piece. This is normally carried out on an air jet such as the Then AFS or Thies Airstream. Enzymes can be used much in the same way as in a garment process (the three stages), or the new MAGIC technology can be used to shorten the route and reduce cost.

Figure 5 –Formal Fibrillated Appearance

Non-fibrillated Mill Finish

A non-fibrillated aesthetic can be achieved either by avoiding fibrillation or removing it once it has formed.

The most simple way is to avoid the fibrillation forming. This can be done by dyeing without mechanical stress. This can be achieved by dyeing in open width by cold pad batch or fully continuous, by jig or beam dyeing or even dyeing in the yarn form on package or beam – anything that avoids a “rubbing” action on the fabric surface. A resin finish must be applied to avoid fibrillation occurring in consumer laundering.

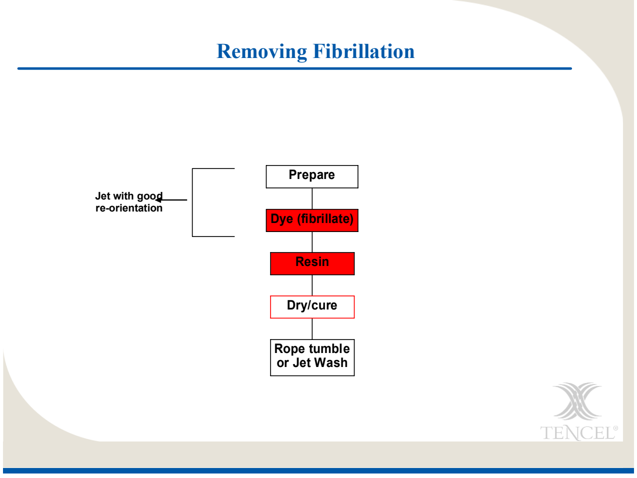
An alternative approach to avoiding fibrillation is to use a TENCEL® fibre that has been protected against fibrillation during manufacture, such as TENCEL® A100 or Lenzing TENCEL® LF. These fibres are fully cross linked as part of manufacture, which allows the processor to treat the fabric as if it was a conventional cellulosic material.

The final approach to a non-fibrillated look is to allow the fibrillation to develop during normal processing and then remove it. Fibrillation can be removed by enzymes, and in this case it would be important to use resin immediately after the enzyme step, before any further fibrillation is generated.

Fibrillation can also be removed by using the embrittling nature of resin finish applications.

The fibrillation is generated during the dyeing step.

The resin is applied, and the fibrillation subsequently removed by either tumbling in a machine such as the Biancalani Airo, or by washing. The washing can be on a continuous rope washer, or simply returning the resinated fabric back to the dyeing machine.



Removing Fibrillation

Jet with good re-orientation

Prepare

Dye (fibrillate)

Resin

Dry/cure

Rope tumble or Jet Wash

In conclusion

- •TENCEL® lyocell can produce a wide range of fabric aesthetics and appearance
- •Fibrillated looks are achieved by well known enzyme based routes in garment or piece
- •New processes allow more garment styling and more cost effective fabric manufacturing
- •Clean look fabrics achieved by avoiding fibrillation or removing fibrillation formed in the wet process
- •TENCEL ® A100 has been introduced to widen fabric scope

Lenzinger Berichte, 85 (2006) 95-97

FINISHING OF EASY-CARE, NON PILLING KNITWEAR OF LYOCELL FIBERS

Georg. Kling

Lenzing AG, Lenzing/Austria
Tel. +43 7672 701 2549, Fax +43 7672 701 3222

Lenzing Lyocell is made of cellulose - the main component of the cells of plants. The starting material for this is wood. A 100% cellulosic fiber, Lenzing Lyocell fulfils the requirements of the modern textile industry to perfection: it is environmentally friendly when it comes to its production, completely bio-degradable, ecological and economical when it comes to further processing and exceptionally versatile and innovative in terms of the surface design of finished textiles.

Ecology

In all the companies within the Lenzing group, utmost importance is attached to ecological considerations. For years, the staff at Lenzing AG have worked on new methods and processes to further reduce production-related environmental pollution - even in the viscose sector. For its efforts in this field the Lenzing group, primarily in Austria but also in Indonesia, has received numerous awards in recognition of the respectful way in which it treats nature and the environment at all of its sites. In December 2000 the lyocell production plant in Heiligenkreuz was selected amongst 85 European candidates for the "European Award for the Environment".

Specific finishing properties of lyocell

The fact that lyocell fibers fibrillate in wet conditions if exposed to sufficient stress as a result of their specific fiber morphology, is seen by the textile industry as an advantage and made use of to produce different surface effects. The classical finishing process contains the following process steps:

Fibrillation - d*efibrillation with enzymes (tumbling/optional) - crosslinking finish*

Due to the specifics of the machines used to finish knitwear (mostly in rope form) there is great difficulty obtaining reproducible results with this classical finishing method for knitwear of lyocell fibers when it comes to the color-visual appeal-hand and tenacity.
Yarn fibrillation, fiber fibrillation, enzyme biopolishing, all of these are processes which would require completely constant mechanical surface loads on the fabric to be treated from batch to batch in order for them to be 100% reproducible. From the point of view of the machinery this is not possible (different laying of ropes!).

In addition, a cross-linking of the knitwear is not permissible since fabrics of lyocell fibers then tend to show subsequent fibrillation in normal household washing conditions.
The surface fluffing connected with this, and fabric graying have a negative effect on the fabric appearance.

Even if it were possible to make these processes reproducible, the long process times lead to an unfavorable price/performance ratio. For this reason, Lenzing AG has developed a new finishing method which excludes the disadvantages named above.

New finishing method

The following finishing process method was carried out at the laboratory and industrial level.

1. *Batch preparation (Fig. 1)*

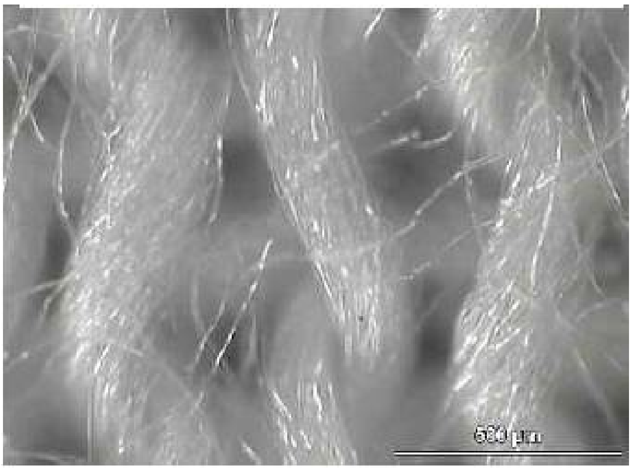


Fig. 1 Grey cloth Interlock 140 g/m² 100% Lenzing Lyocell 1.3 dtex Nm 70/1

In line with company-specific criteria.

2. Rope dyeing

The fabric can be dyed on all the rope dyeing machines suitable for regenerated cellulose, for example on a Jet, Overflow, Softflow, Airflow etc. In this respect it is only important that intensive "primary fibrillation" is obtained during the washing/bleaching and/or dyeing process (Fig. 2).

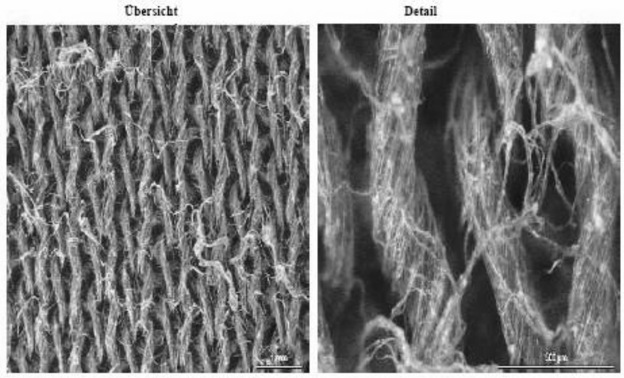


Fig. 2 Fibrillated surface after the dyeing process on Then Airflow AFS

Without this primary fiber fibrillation, the fabric has a propensity towards fluffing and fibrillation during subsequent household washes even when a fibrillation stop is performed using crosslinking agents.

For color matching purposes 'envelopes' have to be sewn, whereby the face side of the fabric represents the inner side of the envelopes. In this way the fabric can be matched without any problems since the inner side of these envelopes does not fibrillate (no mechanical influencing).

3. Extraction, opening, drying

After dyeing, water is as always extracted from the fabric (squeezed), followed by rope opening, tube cutting and drying on a belt drier or stenter frame.

4. Cross linking

Thereafter the fabric is impregnated with a cross-linking agent whereby, for reasons of expense and effect, shock curing is recommended. This takes advantage of the "negative effect" that when resin finishing regenerated cellulose, crosslinking agents tend to migrate to the surface of the fabric. This means that particularly in the fibrillated zone of the fabric an "excess concentration" of cross-linking agent occurs. As a result, the protruding fibrillated fiber ends and fluff packages become relatively rigid and brittle and break in the Airtumbler process which follows.

5. Air Tumbler:

Most common air tumblers are suitable for this process. The tumbler process is carried out warm (60-80 °C) - with a fabric speed of between 400-600 meters/ minute depending on the quality and tumbler make available. In this process the surface is mechanically cleaned, i.e. "mechanical polishing" instead of bio polishing (Fig. 3).

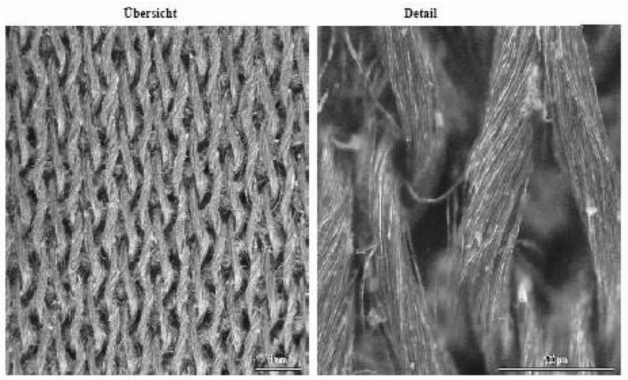


Fig. 3 After mechanical polishing on Then Airflow AFS Tumbler

6. Final finish

Then the fabric is given the final finish as requested (e.g. compacted, calendered, as a measure for corrections of the hand etc.). Other mechanical surface treatments such as emerizing, raising etc. can then no longer be performed.

The end-user obtains a washable, nonpilling, graying-free product of Lenzing Lyocell (Fig. 4).

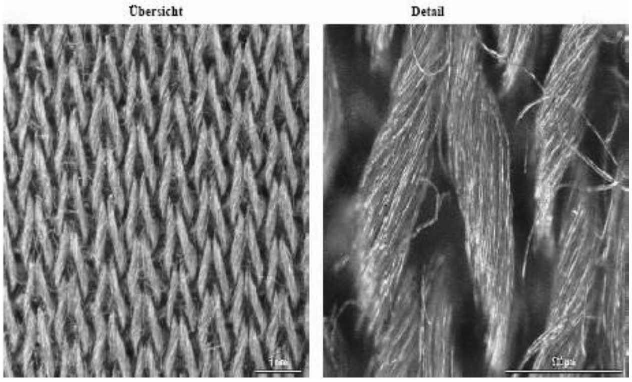


Fig. 4 Finished article after 10 household washes at 60 °C and tumble dry

Lenzing Lyocell = registered trademark

Lenzinger Berichte, 85 (2006) 98-106

HIGH DURABLE CELLULOSIC TEXTILES – STRATEGIES FOR HIGH RESISTANCE TO FIBRILLATION AND PILLING

HOCHBESTÄNDIGE ZELLULOSE TEXTILIEN – STRATEGIE FÜR WIDERSTANDSFÄHIGKEIT GEGEN PILLING UND FIBRILLATION

Satoko Okubayashi*, Wangsun Zhang, Thomas Bechtold

Christian-Doppler Laboratory of Textile and Fiber Chemistry of Cellulosics, Institute of Textile Chemistry and Textile Physics, University of Innsbruck, Hoechsterstrasse 73, A-6850 Dornbirn, Austria, Tel.: +43 5572 28533, Fax.: +43 5572 28629, e-Mail: textilchemie@uibk.ac.at
*Corresponding author: textilchemie@uibk.ac.at , Tel.: +43 5572 28533; fax: +43 5572 28629

Abstract

The mechanism of pill formation in lyocell fabric including fuzz formation and fibrillation in wet state was studied. The fuzz was mainly generated by mechanical abrasion in dry condition while the fibrillation was induced by mechanical abrasion in wet condition. The pilling was formed only on the fabric treated with wash and dry treatments. The fiber/fiber friction was measured as counts of twist to open the yarn until it starts to slip in dry and wet states. The pilling was promoted by lower fiber/fiber friction in dry state and higher fiber/fiber friction caused by higher fiber swelling in wet state. The influence of fiber swelling on fibrillation tendency of lyocell fiber was also investigated. The critical degree of swelling for lyocell fiber with no fibrillation was 0.45 cm^3/g in ethanol/water mixture. The fibrillation was retarded with alkali treatment in aqueous NaOH and KOH solutions at concentrations between 3.0 and 7.0 mol/l, and minimized at 5.0 mol/l where the uniform reorganization of macrofibrils was observed with scanning electron microscope. The fibril number of lyocell fiber treated in trimethylammonium hydroxide was enhanced with increasing concentration and weight loss. The fibrillation was retarded by crosslinking with 1,3-dimethylol-4,5-dihydroxyethylene urea and by treatment with aminofunctional polysiloxane accompanying decrease in water retention capacity.

Keywords: *alkali treatment, crosslinking, fibrillation, fuzz, pilling, swelling, weight loss*

1. Introduction

Man-made cellulosic fibers and natural fibers are comfortable to wear, and have a stable share of the fiber market. Currently, the lyocell is the most efficient large-scale alternative to the viscose process. The cellulose is dissolved in a tertiary amine oxide N-methylmorpholine-N-oxide (NMMO), spun into an aqueous spinning bath, and the filaments are run through several after-treatments, giving the desired textile features [1-3]. Fabrics produced from lyocell fibers are breathable, moisture absorbent [4] and have excellent dimensional stability. Lyocell fibers, alone or in blends, are used widely in apparel and other fashion articles [5].

In the swollen state lyocell has an extensive fibrillation tendency owing to linear high crystalline fibrillar morphology [6,7]. The fibrillation tendency of lyocell enables this fiber to be used in specific finishing effects such as peach skin, silk touch and soft denim. On the other hand, the fibrillations induce e.g. rope marking defect in hank finishing, graying of dyed fabrics and a change of handle of clothes that spoils garments features. Efforts to control the fibrillation tendency in lyocell fibers include dyeing with reactive dyestuffs and treating fabrics with crosslinking agents [8,9]. Some of the most important steps in fiber processing involve alkalis, such sodium hydroxide or sodium carbonate, and some fiber response to alkali treatments is an important criterion [10,11]. Many reports on the morphological structure of man-made cellulosic fibers and their treatment with crosslinking agents have been published [9,12]. However, few studies of the fibrillation tendency of man-made cellulosics have been conducted in alkali solution under different conditions.

Furthermore, fibrillation may lead to pilling and therefore spoil fabric appearance and touch [13]. Pill formation is a common problem mainly in knitted fabrics made not only from synthetic fibers but also from natural fibers, man-made cellulosics and their blends because no consumers accept the undesirably pilled garments. There have been many studies about pilling mechanism for knitted fabrics, which described influences of selected fiber properties e.g. tensile strength, elongation, bending rigidity, fiber count, shape of fiber cross-section and friction on the pilling phenomenon. Those models were, however, established for dry conditions but not for processes including wet condition e.g. laundry. Man-made cellulosic fibers are hygroscopic materials and their structures of fiber, yarn and fabric dramatically change by swelling with polar solvent such as water [14].

In the present study, a pilling mechanism including fibrillation and fuzz formation in dry and wet states is discussed and concepts to achieve high durable lyocell textiles against fibrillation and pilling are suggested.

2. Experimental

2.1. Materials

Modal, viscose and three varieties of lyocell (lyocell 1, lyocell 2, lyocell 3) fabrics (knit single jersey, woven fabric) were supplied from Lenzing AG, Austria and used for experiments. Five staple fibers of lyocell (lyocell 1, lyocell 2, lyocell 3), modal and viscose were also provided by Lenzing AG. The titer of the fibers was 1.3 dtex and the fiber length was 38 mm. The fibers lyocell 2 and lyocell 3 were wet-crosslinked with different agents while lyocell 1 was untreated. Analytical grade ethanol (EtOH, 96 %,), lithium hydroxide mono hydrate (LiOH; > 99 %), sodium hydroxide (NaOH; > 98 %), potassium hydroxide (KOH; > 99%), trimethylammonium hydroxide (TMAH; aqueous 25 % sol.) and other chemicals were purchased from Fluka. Plane woven fabrics of lyocell treated with crosslinker and softeners were supplied by BASF (Ludwigshafen, Germany). Crosslinking agent, catalyst, softening agent and wetting agent were also provided by BASF.

2.2. Treatments

Wash and dry treatments [13]

The knit fabric was cut into a square with area of 15 x 15 cm^2 and sewed on a cotton woven fabric. The sample fabric was washed with a domestic washing machine using the mixed detergent of fatty alcohol ethoxylate and secondary alkane sulfonate with liquor ratio of 1:20 at 40 °C for 30 min (W treatment). Then the wet fabric was dried with a tumble drier at 60 °C for 30 min (D treatment). The treatments of washing and drying (WD) were repeated 5, 10, 20 and 25 times. Pill rating of the fabric was assessed after the treatments according to a description.

Alkali treatment [15]

The lyocell fiber was treated with alkali as follows; 0.5 g fibers were immersed in the aqueous alkaline solution at certain concentration for 2 hrs at room temperature. After the fibers were rinsed with hot water at 60 °C for 5 minutes, neutralized with an acetate buffer containing 0.1 mol/l acetic acid and 0.1 mol/l sodium acetate (pH 5.0), and rinsed with water sufficiently, they were dried in an oven at 60 °C.

Crosslinking and softening treatments [16,17]

The lyocell woven fabric was immersed in a solution containing a given amount of crosslinking agent Fixapret® ECO which main component is 1,3-dimethylol-4,5-dihydroxyethylene urea, 15 g/l mixture of metal salts (Condensol® FB), 1 g/l wetting agent (Kieralon® TX 1563) and 0.5 g/l acetic acid (60 %w/w aq.). Excess solution was removed by passing through squeeze rolls to obtain wet pickups of 75 %w/w. After the fabric was dried at 110 °C, it was subsequently cured at 175 °C (air temperature) for 60 seconds.

For softening treatment, a solution containing a given amount of softener Siligen® SIN which component is aminofunctional polysiloxane and 1 g/l acetic acid (60 %w/w aq.) was used. After excess solution was removed by using a vacuum filter or a centrifuge to obtain wet pickups of 100 %w/w, the fibers were dried at 60 °C.

2.3. Measurements

Fiber/fiber friction [18]

For the determination of interfiber friction an apparatus to determine the number of count (Zweigle D315) was used. A defined length of 50 mm of yarn was fixed between two clamps of the apparatus at defined pretension 2 cN. The number of reverse turns T_r required to open the yarn twist to the point of slipping is obtained as experimental result. The slipping experiments were performed at 20 ºC and 65 % relative humidity. Each data point is the average from five measurements (T_{rdry}). After the yarn was set between two clamps, 1 ml of distilled water was dropped on the yarn and T_r in wet state (T_{rwet}) was measured by the same method for T_{rdry} .

Contraction force [18]

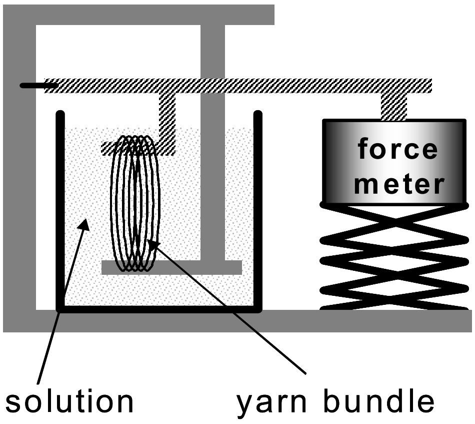


Figure 1. An apparatus for measurement of contraction force

The bundle of the yarn which length was 16 cm and consisting of 300 strings was mounted to the equipment shown in Figure 1 and the pretension of 300 g was given for 10 min. After the pretension was reduced to 50 g, the bundle was dipped into the distilled water solution for 15 min. The change of the contraction force was detected by a balance and recorded with a computer. The trials repeated four times to get a mean value.

Solvent retention capacity [19]

Fiber samples, 0.5 g in weight, were immersed in solution for 2 hrs at room temperature. The fibers were then centrifuged at 4000 G for 10 minutes and weighed (W_w). The fibers were dried in an oven at 105 °C for 2 hrs and the weight was measured (W_d). Solvent retention value in water (WRV) and in EtOH/water mixtures (ERV) were calculated by Equation 1.

$$WRV(ERV) = (W_w - W_d) / W_d \bullet D_{alk.} \qquad (1)$$

Here, $D_{alk.}$ is a density of the solution. The measurement was performed 4 times for each sample to obtain mean value.

Ball-bearings agitation [19]

A mass of fibers (0.5 g) was placed in a metal pot with 50 ml solution and 20 metal ball-bearings (0.5 cm diameter and 1 g weight). The pot was capped and tumbled end-over-end at 42 rpm and at fixed temperatures for 2 hrs. The fibers were then neutralized with a buffer solution containing 0.01 mol/l acetic acid and 0.01 mol/l sodium acetate (pH 5.0), rinsed with hot water at 50 °C and with cold water continuously. After the fibers were dried in an oven at 60°C for 1 hr, fibril numbers in fibers were counted on 0.38 mm segments using an optical microscope. Ten fibers from each sample were used to obtain mean values.

Weight loss [15]

Weight loss of the fiber during the alkali treatment was determined. 0.5 g of fibers was conditioned at 65 % relative humidity and 20 °C for 24 hrs and weighed (W_1). The fiber was treated with the aqueous alkaline solution at certain concentrations by the same method for the alkali treatment. After the fiber was dried at 105 °C for 2 hrs, the fiber was conditioned at 65 % relative humidity and 20 °C for 24 hrs again and weighed (W_2). The weight loss (WL) was calculated by Equation 2.

$$WL = 100 \times (W_1-W_2) / W_1 \qquad (2)$$

Scanning electron microscope [15]

Images of the fiber cross sections were obtained using a scanning electron microscope (SEM; HITACHI S-2600H). The sample fiber after the pretreatment without fibrillation test was frozen in liquid nitrogen and broken apart by bending with hands.

3. RESULTS AND DISCUSSION

3.1. Pilling mechanism

Fuzz was observed on the fabric treated with only D, indicating that fuzz mainly forms in dry state. There are some pills neither on the fabric treated with W nor D, but on the fabric treated with WD. The individual treatment of W and D causes no pill formation while the combined treatment WD induces the pilling in the condition used for this work.

Photo images of the surface of knit fabrics after 25 times of WD, D and W treatment are shown in Figure 2.

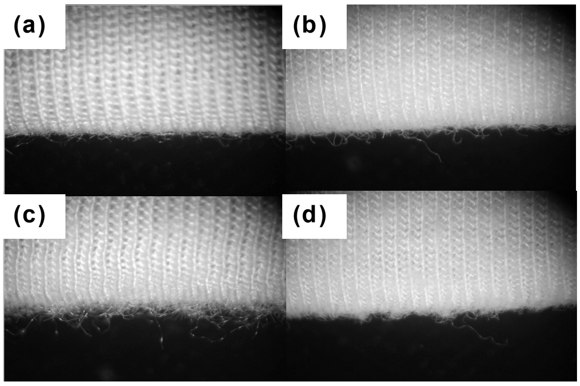


Figure 2 Photographic image of knitted fabric (a), after 25 times of W (b), after 25 times of D (c) and after 25 times of WD (d)

On the contrary of fuzz formation, fibrillation appears on the fabric treated with W and WD. For further comprehension, the relation between fuzz, pilling, fibrillation, wash and dry treatments are schematically drawn in Figure 3. The y-axis is relative degrees of fuzz, pilling and fibrillation evaluated from Figure 2 and x-axis indicates the relative cycles of wash and dry treatments.

The degree of fuzz is relatively high after D and low after W. Contrarily, the degree of fibrillation is low after D and high after W and WD. There is no pill formation after D or W, and the pills appear only after WD. The pill formation is related to fibrillation more strongly than to fuzz formation.

The critical number of count T_r where the fibers begin to slip in the yarn body and the applied force is sufficient to tear the yarn into two parts was obtained at F_R 50 cN and summarized in Table 1. As the fiber length is equal, the higher values of T_{rdry} indicate increased fiber/fiber friction [18]. As compared to lyocell 1, lyocell 3 shows larger T_r, indicating high fiber/fiber friction. It is presumed that high fiber/fiber friction in dry state suppresses fuzz formation and consequently pill formation.

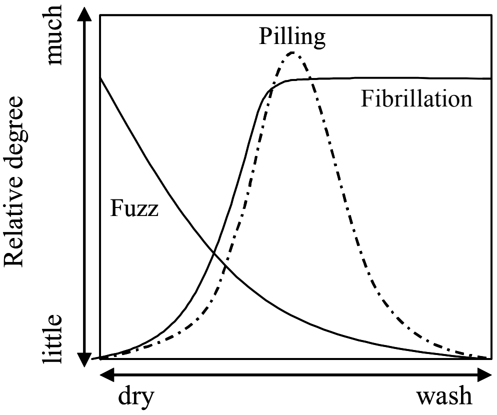


Figure 3. A schematic diagram of relationship among degrees of pilling, fuzz and fibrillation with wash and dry treatments.

Table 1 Relationship among fiber/fiber friction, water retention capacity, contraction force and pilling.

Material	T_{rdry} (counts)	T_{rwet} (counts)	T_{rwet}/T_{rdry}	WRV (g.g^{-1})	Contraction force (g)	Pill rating
lyocell 1	30.5	>>	>>	-	175	-
lyocell 2	27.1	37.3	1.38	0.816	250	3
lyocell 3	34.2	37.8	1.11	0.799	230	4
modal	33.9	42.7	1.26	0.692	180	1
viscose	31.8	39.0	1.23	0.966	110	2

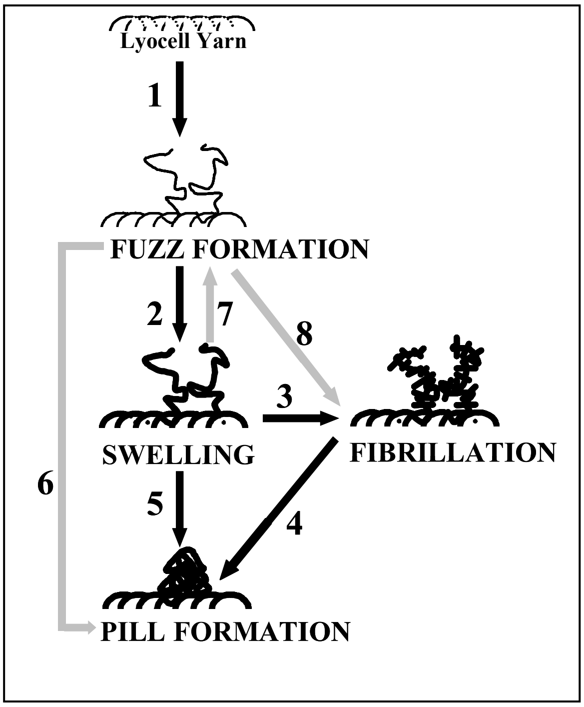


Figure 4. A schematic mechanism of pill formation during WD treatments. Arrows indicate the fuzz formation (1, 7), the swelling (2), the fibrillation (3, 8) and the pill formation (4, 5, 6)

The fiber/fiber friction in wet state and contraction force are specific parameters that are expected to indicate the change of fiber properties by water uptake. The results are given as well as the values of water retention obtained by centrifugal method in Table 1.

Considering the fiber properties in wet and dry states as shown in Figure 3 and Table 1, a mechanism of pill formation including the fibrillation step was detailed. An illustration of the mechanism is given in Figure 4.

Firstly a fiber end comes out from the inside of a yarn by a mechanical abrasion during D treatment, which induces the fuzz (1). The fuzz fiber is swollen with W treatment and gets softer as show in (2). The swollen soft fiber is easily fibrillated by mechanical abrasion during W and D treatments (3) and then tangled each other, which develops pilling (4). The fibrillation hardly occurs in dry state (9). Some swollen fuzz would lead to pilling without fibrillation as indicated in (5). The inducement of pill formation from fuzz is significantly hindered without wetting step as shown in Figure 2 (c) (6). Less degree of fuzz is formed when the fiber is swollen in wet state as shown in Figure 2 (b) (7). After a certain times of WD treatments, the fiber/fiber friction in dry gets higher which results suppress of fuzz formation in dry state. Increase in fiber/fiber friction in dry state, decrease in degree of swelling might lower tendency of pill formation as well as fibrillation.

3.2. Fibrillation mechanism

As shown in Figure 4, the fibrillation plays an important role in pill formation that is significantly affected by fiber swelling. In order to clarify the effect of fiber swelling on not only pilling but also fibrillation, the fibrillation tendency in different degree of swelling was investigated. Figure 5 exhibits the plots of fibril numbers against the solvent retention values of fibre lyocell 1 in different solutions at room temperature.

The fibrillation of lyocell fiber occurs when the solvent retention value in EtOH/water mixture is higher than 0.45 cm^3/g, and the fibril number is increased with increase in the retention value. The value 0.45 cm^3/g characterizes a critical degree of swelling to obtain no fibrillation. The result implies that a lyocell fiber showing less than 0.45 cm^3/g of water retention capacity should exhibit no fibrillation in water.

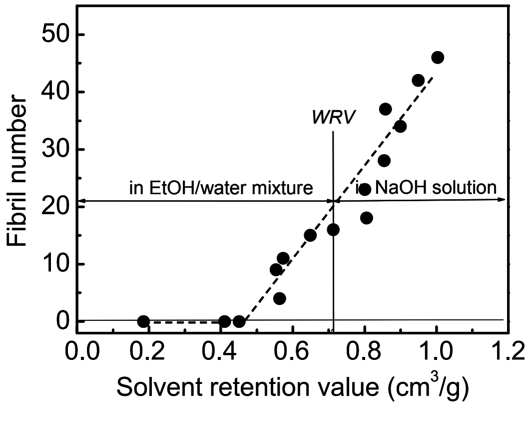


Figure 5. Fibril number as a function of solvent retention value of lyocell 1 at room temperature.

Alkali treatments are conventional process applied to textile such as mercerization, dyeing and resin-finishing. It is of great interests to study influence of alkali treatment on fibrillation tendency of lyocell fibers. The influence of the alkaline concentration in the alkali treatment of the

The influence of the alkaline concentration in the alkali treatment of the lyocell on the fibril number (FN_{pre}) was investigated. The results are shown in Figure 6. The lyocell fiber was treated with an alkali at a given concentration and then the fibrillation was induced in water by the method using metal balls with tumbling.

The FN_{pre} at 0 mol/l of alkaline concentration is the fibril number of the lyocell treated with water. As the fiber was treated with TMAH and LiOH, fibril number is increased with increasing the alkaline concentration. The FN_{pre} of the lyocell treated in NaOH sol. decreases, increases and decreases to 7 counts continuously with increasing the alkaline concentration to 5.0 mol/l. Further, the FN_{pre} increases again and reaches constant value at 7.0 mol/l. The curve of the FN_{pre} with KOH is comparable to that with NaOH.

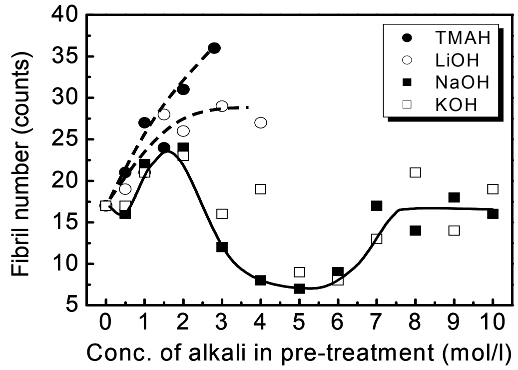


Figure 6 Plots of fibril number of lyocell fiber treated in alkaline solution against concentration of TMAH (■), LiOH (●), NaOH (▲) and KOH (▼)

The WRV in lyocell fiber treated with alkalis (WRV_{pre}) was measured and plotted against the alkaline concentration in Figure 7. The WRV_{pre} with TMAH and LiOH increase up to approximately 0.70 cm^3/g with increasing concentration of alkaline solution in the range of concentration between 0.5 and 4.0 mol/l. The WRV_{pre} in fiber treated with NaOH solution increases to 0.66 cm^3/g, the value is unchanged at the concentration between 3.0 and 7.0 mol/l, and then increases again. For the pretreatment with KOH solution the WRV_{pre} increases to 0.66 cm^3/g at the concentration of 5.0 mol/l and the value is constant until the concentration increases to 10.0 mol/l. At concentration of 5.0 mol/l where the minimal FN^{pre} is obtained the WRV^{pre} with both NaOH and KOH is the equal value of 0.66 cm^3/g though alkali retention value in NaOH is larger than that in KOH [19]. The WRV^{pre} with NaOH at concentration between 3.0 and 7.0 mol/l where the FN_{pre} decreases is unchanged at 0.66 cm^3/g. These results suggest a consecutive structural change of the fibrils in NaOH solution at concentration between 3.0 and 7.0 mol/l. The change of fibril structure improves the fibrillation tendency of the lyocell fiber.

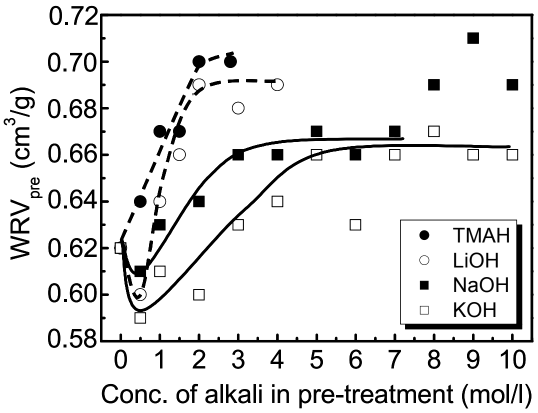


Figure 7 Plots of water retention value of lyocell fiber treated in alkaline solution against concentration of TMAH (■), LiOH (●), NaOH (▲) and KOH (▼)

The weight loss is one of the important factors affecting the fiber property The FN_{pre} and WRV_{pre} are plotted against weight loss in Figures 8 and 9.

Both the FN_{pre} and the WRV_{pre} increase up to the weight loss of 15 %w/w and reach at constant value of 35 counts and 0.70 cm^3/g, respectively, regardless of the type of alkalis. Consequently, WRV_{pre} and weight loss of lyocell fiber treated with alkali are increased with increasing alkali concentration except in FN_{pre}, though the degrees of the increases are different among the alkali. The FN_{pre} of fiber treated with TMAH and LiOH increases with increasing alkaline concentration. Contrarily, the FN_{pre} is minimized in 5.0 mol/l NaOH and KOH solutions. The similarities in the relation of alkaline concentration, FN_{pre} and WRV_{pre} between in NaOH and in KOH solutions as shown in Figure 6 and 7 indicate that the mechanism of fibrillation after pretreatments in NaOH and KOH is similar but different from those in TMAH and LiOH.

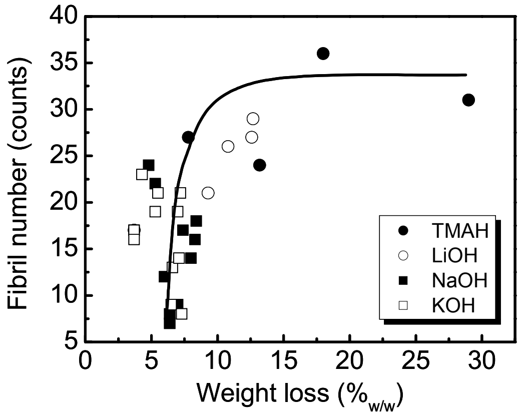


Figure 8. Plots of fibril number of lyocell fiber treated in alkaline solution against weight loss of lyocell fiber treated with TMAH (■), LiOH (●), NaOH (▲) and KOH (▼)

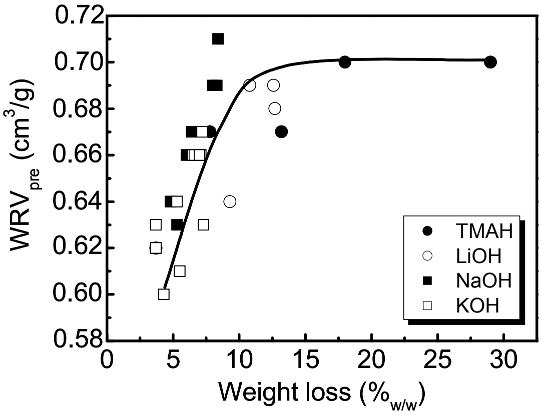


Figure 9. Plots of water retention value of lyocell fiber treated in alkaline solution against weight loss of lyocell fiber treated with TMAH (■), LiOH (●), NaOH (▲) and KOH (▼)

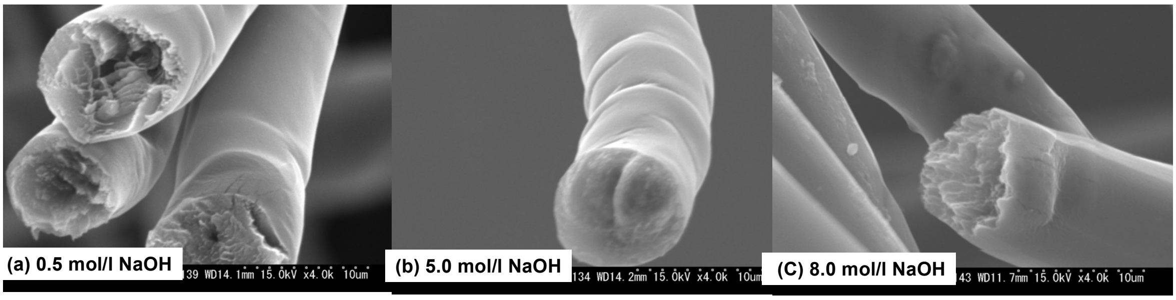


Figure 10. SEM images of lyocell fiber treated with 0.5 mol/l (a), 5.0 mol/l (b) and 8.0 mol/l of NaOH (c)

In order to clarify the structural change during alkaline treatments, image analysis was performed using SEM. Figure 10 gives the images of cross section of fiber treated in NaOH solution.

The large bundles or layers of macrofibrils are clearly observed on the cross section of the fibers treated in 0.5 mol/l and 8 mol/l NaOH solutions. The fiber treated with aqueous solution containing 5.0 mol/l of NaOH shows a smooth cross section without any bundle and layer of macrofibrils. The fiber surface treated with 0.5 mol/l of NaOH is less rough than that treated with 8.0 mol/l of NaOH.

The less fibrillation was observed on the fiber with the smooth cross section without the bundle or the layers of macrofibrils. The formation of the bundle and the layers of the macrofibrils clearly elevate the fibrillation.

These results suggest that the treatments with alkalis cause the re-orientation of fibril structure and the fibrillation tendency is related to re-orientated microfibril structure. When the macrofibrils are re-orientated unequally, the bundles or the layers of the macrofibrils generate and the fiber shows high fibrillation tendency. Contrarily, the fibrillation is retarded if the uniform re-orientation of fibrils is induced by the treatments. In this study, the uniform reorganization of the macrofibrils was obtained by the alkaline treatment with 5.0 mol/l NaOH and KOH.

The chemical modification of fibrillar structure using crosslinking agent and additive polymers are of great interest regarding change in fibrillation resistance. Figure 11 and Figure 12 show the effect of concentration of crosslinking agent and softener on FN and WRV of lyocell fabric.

The FN and WRV considerably decrease by crosslinking with 10 g/l agent. The fibrils are crosslinked and the force among fibrils is increased, resulting in lower degree of fibrillation.

The FN is strikingly decreased from 16 counts to 8 counts by adding 2 g/l softener. The result indicates that the fibrillation resistance is enhanced by the addition of aminofunctional polysiloxane and the addition of small amount of softener decreases 50 % fibrillation. The reduction in fibrillation is caused by coverage of fiber surface with the polymer, resulting in the decrement in fiber/fiber friction.

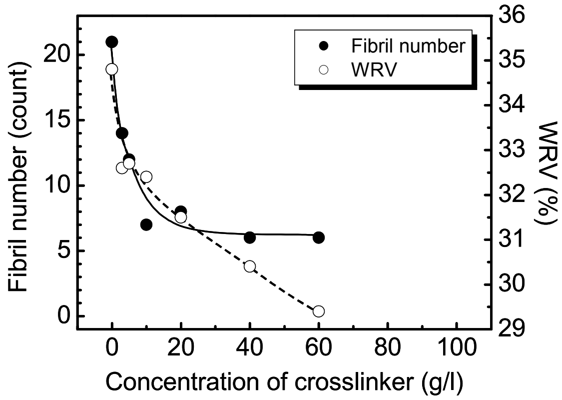


Figure 11. Plots of fibril number (●) and water retention value (○) of lyocell fabric treated with crosslinking agent against concentration of crosslinking agent

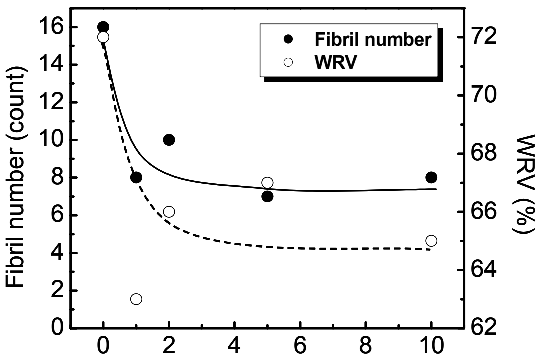


Figure 12. Plots of fibril number (●) and water retention value (○) of lyocell fiber treated with softener against concentration of softener

4. CONCLUSIONS

The mechanism of pill formation including fibrillation process was proposed taking into account the effects of consecutive wash and dry treatments, T_r corresponding to the fiber/fiber friction in dry and wet, the water retention capacity and contraction force indicating softness of the swollen fibers on degree of fibrillation, fuzz formation and pilling. The model suggests that the fibers come out from yarn by mechanical abrasion due to low fiber/fiber friction, they are fibrillated and tangled owing to the softness and high fiber/fiber friction in wet condition. The pilling was greatly accelerated by a combination of fuzz formation caused in dry state and fibrillation in wet state.

The fibrillation tendency is directly related to degree of swelling of fibers. The critical degree of swelling, that is the maximum retention capacity of fibers in the solution with no fibrillation, is 0.45 cm^3/g in ethanol/water mixture. The fibrillation is retarded by alkali treatment in 3.0-7.0 mol/l NaOH or KOH solution and minimized at 5.0 mol/l where SEM images shows smooth cross section with small and uniform macrofibrils of fiber. The weigh loss of lyocell fiber enhanced fibrillation. The fibrillation resistance was enhanced by crosslinking with 1,3-dimethylol-4,5-dihydroxyethylene urea and by treatment with small amount of aminofunctional polysiloxane accompanying the decrement in water retention capacity of fibers. The fibrillation is inhibited by not only prevention of fibril separation but also modification of fiber surface, resulting in decrease in surface friction and water accessibility.

Consequently, the pilling of lyocell fabric maybe retarded by high fiber/fiber friction in dry state but low in wet state, low degree of fiber swelling and less extent of fibrillation caused by re-orientation of fibril structure, decrease in weight loss, enhancement of inter-fibril force and reduction in fiber surface friction.

ACKNOWLEDGMENT

The authors gratefully acknowledge the Christian-Doppler Research Society and Lenzing AG in Austria to the financial and material support, and Prof. Dr. Teruo Hori, Department of Applied Chemistry and Biotechnology of Fukui University in Japan for SEM measurements. We also appreciate BASF in Germany for providing the correspondingfinishing products and carrying out finishing trials.

REFERENCES

[1] Nechwatal A., Nicolai M. and Mieck, K.-P. 1996. Crosslinking reactions of spun-wet NMMO fibers and their influence on fibrillability. Textile Chemist and Colorist 28 (5): 24-27.

[2] Lenz J. Schurz J. and Wrentschur E. 1992. Comparative characterization of solvent spun cellulose and high wet modulus viscose fibres by their long periods. Acta Polymer 43: 307.

[3] Fink. H.-P., Weigel P., Purz H. J. and Ganster J. 2001. Structure formation of regenerated cellulose materials from NMMO-solutions. Prog. Polym. Sci. 26: 1473-1524.

[4] Okubayashi S., Griesser U. and Bechtold T. 2004. A kinetic study of moisture sorption and desorption on lyocell fibers. Carbohydrate Polymers 58(3): 293-299.

[5] Brauneis F. and Eibl M. 1998. Fnishing of knit goods produced from Lenzing Lyocell. Melliand Textilberichte 79(3): 155-156.

[6] Rohrer C. Retzl P. and Firgo H. 2001. Lyocell LF – profile of a fibrillation-free fibre from Lenzing. Lenzinger Berichte 80: 75-81.

[7] Nemec H. 1994. Fibrillation of cellulosic materials – Can previous literature offer a solution? Lenzinger Berichte 74: 69-72.

[8] Nechwatal A., Nicolai M. and Mieck K.-P. 1996. Textile crosslinking reactions to reduce the fibrillation tendency of lyocell fibers. Textile Res. J. 66(9): 575-580.

[9] Nicolai M., Nechwatal A. and Mieck K.-P. 1998. Modified fibrillation behavior of solvent-spuncellulose fibers by the reaction with reactive dyes. Angew. Makromol. Chem. 256: 21-27.

[10] Bredereck K., Stefani H.-W., Beringer J. and Schulz F. 2003. Alkali- und Fluessigammoniak-Behandlung von Lyocellfasern. Melliand Textilberichte 12: 58-64.

[11] Toth T., Borsa J., Reicher J., Sally P., Sajo I. And Tanczos I. et al. 2003. Mercerization of cotton with tetramethylammonium hydroxide. Textile Res. J. 73(3): 273-278.

[12] Chae D. W., Choi K. R. and Kim B. C. 2003. Effect of cellulose pulp type on the mercerizing behavior and physical properties of lyocell fibers. Textile Res. J. 73(6): 541-545.12.

[13] Okubayashi S. and Bechtold T. 2004. A Pilling Mechanism of Man-Made Cellulosic Fabrics – Effects of Fibrillation. Textile Res. J., 75 (4), 288-292, 2005.

[14] Ibbett R. N., and Hsieh Y. L. 2001. Effect of Fiber Swelling on the Structure of Lyocell Fabrics. Textile Res. J. 71(2): 164-173.

[15] Zhang W., Okubayashi S. and Bechtold T. 2005. Fibrillation tendency of cellulosic fibers – Part 3. Effects of alkali pretreatment of lyocell fiber. Carbohydrate Polymers 59(2): 173-179, 2005.

Lenzinger Berichte, 85 (2006) 107-112

TECHNICAL ASPECTS IN ENZYMATIC HYDROLYSIS OF CELLULOSICS

Christian B. Schimper, Constanta Ibanescu[+], Thomas Bechtold

Christian Doppler-Laboratory "Chemistry of Cellulosic Fibres and Yarns",
Institute of Textile Chemistry and Physics, University of Innsbruck,
Hoechsterstrasse 73, A-6850 Dornbirn, Austria, E-mail: textilchemie@uibk.ac.at

Abstract

Fabrics of viscose, modal, lyocell and cotton were subjected to enzymatic hydrolysis with a view to determine the influence of fibre type on degradation rate and weight loss in substrates. The influence of enzyme concentration on substrate hydrolysis was examined by subjecting selected substrates to treatments at two different enzyme concentrations. The influence of pre-treatments such as desizing, washing, bleaching, and heat treatments (dry and steam) on the hydrolysis of cellulosics was also studied. The influence of process variables such as machine type, liquor ratio on the hydrolysis of substrates were investigated. The enzyme used in all experiments was a total crude cellulase preparation.

Introduction

Hydrolytic treatment of cellulosic fabrics and garments with cellulases has become a common treatment step in textile processing [1]. Cellulase preparations consist of several different cellulolytic enzymes which act synergistically in hydrolysing cellulose to glucose [2]. This effect is used in finishing processes to improve the handle and drape, prevention of fuzz and pilling, removal of fibrils, and in colour protection and increase in lustre and brightness of fabrics or garments [3]. In denim finishing cellulases are introduced to replace pumice stones and/or aggressive chlorine chemistry [4]. The variables in textile processing or finishing operations include: fibre and fabric types; enzyme formulations and their dosage; and machinery types with different loading capacities. All of these factors, combined with the pre-treatment history of the fabric, lead to unique properties in all processed fabrics, which may strongly influence the degradation rates observed in substrates.

In this manuscript, we present an overview of select factors that are influent in the enzymatic hydrolysis of cellulosic fibres and fabrics. Three different man-made cellulosic fibres and natural cotton fibre were hydrolysed with a commercial enzyme mixture to compare the degradation behaviour of substrates [5]. The enzyme dosage chosen was higher than what is normally used in technical-scale processes to highlight all the differences. As pre-treatments are known to change hydrolysis rates, experimental substrates were subjected to laboratory-scale treatments of such technical processes as heat pre-treatments and conventional desizing and washing steps, and their impact on enzymatic hydrolysis was determined [6]. In addition, the influence of machine type (and level of agitation), garment load and washing/bleaching steps were also studied.

Material and Methods

The substrates used in experiments were woven fabrics of man-made cellulosic fibres (fiber length 38 mm) Viscose (CV), Modal (CMD), and lyocell (CLY) provided by Lenzing AG, Austria; along with Cotton (Co). The fabric parameters are listed in Table 1. The enzyme used was a total crude acid cellulase preparation, provided by Genencor (USA), with 32 $mg.mL^{-1}$ protein content and a specific activity of 3.1 carboxymethylcellulose units per mL.

Unless otherwise mentioned, the hydrolysis experiments were carried out on a Pretema Multicolor Laboratory dying unit Type MC360 (Caromatic, Switzerland) for 8 h at 55°C with a liquor ratio of 1:25, using an enzyme formulation consisting of 24 mg protein per gram of fabric (30 $mL.L^{-1}$ solution) in a

---

[+] Permanent Address: Department of Macromolecules, Faculty of Industrial Chemistry, "Gh. Asachi", Technical University, Iasi, Romania

50 mM Na-acetic buffered system. A detailed description of the enzymatic treatment is available elsewhere [5].

To determine the influence of pre-treatments on enzymatic hydrolysis, a 100% cotton fabric (plain-woven, of basis weight 60 g.m^{-2}) was desized, washed and bleached under typical conditions. After each step a specimen was used for enzymatic hydrolysis. Dry and steam heat pre-treatments were carried out at 130 and 190°C in a laboratory steamer from Mathis (Switzerland) for 45 seconds and the substrates were subsequently subjected to enzymatic hydrolysis treatments [5].

Soda wash after 4 or 8 hours of hydrolysis time was performed with a sodium carbonate solution (pH 10) at 75°C for 10 minutes. Bleaching experiments after 4 and 8 hours of hydrolysis was performed for 1 hour at 95°C with a mixture of the following reagents: 0.2 g.L^{-1} $MgCl_2$, 1 g.L^{-1} Periquest BSD (Textilchemie Dr. Petry GmbH), 1 mL.L^{-1} Sandozin MRN and 5 mL.L^{-1} Stabilisator 2000 (Clariant), 4.5 mL.L^{-1} NaOH 50% technical grade and 20 mL.L^{-1} Peroxide 35% technical grade. To study the influence of machine type, hydrolysis treatments were conducted on an Atlas Launder-Ometer (Atlas Electric Devices Co., USA), at 40 rpm with the same hydrolysis conditions described above.

The amount of soluble reducing sugars released was determined with the neocuproine method [7], in terms of mg glucose per mL of solution [mg.mL^{-1}]. Weight loss in fabrics was calculated from the difference between the initial and hydrolysed fabric weights [8]. All laboratory chemicals employed were of analytical grade supplied by Fluka Chemie, Switzerland.

Results

The weight loss in Co, CV, CMD and CLY after 8 hours of hydrolysis is shown in Figure 1. Owing to different production methods for the man made fibres it appears reasonable that each fibre type exhibits different behaviour during cellulase degradation. A weight loss of 50% after 8 h hydrolysis was found in viscose, which has a high proportion of amorphous regions. The weight loss in modal and lyocell were 13% and 5% respectively, reflecting the decreasing proportion of amorphous regions in these fibre types; and the weight loss in the natural fibre, cotton, was about 22%. These results indicate that in industrial scale enzymatic hydrolysis treatments, more care is needed with fabrics of viscose as compared to those of lyocell. An approximate basis of comparison is that the weight loss observed after 10 min of hydrolysis in lyocell is similar to that observed in viscose after 1 min of treatment. Hence, special attention may be needed when processing blends of viscose and lyocell, as excessive hydrolysis may lead to strength loss in fabrics.

Normally, an enzyme dosage of up to 3% on weight of garment is recommended for industrial-scale processing, but the actual dosages used may vary. We used enzyme dosages of 75% and 250% on weight of garment (30 and 100 mL.L^{-1} enzyme solution) to detect the influence of the enzyme concentration on CV samples. The extent of degradation in substrates was determined by measurement of reducing sugars in solution with the neocuproine method, and is shown in Figure 2. The amounts of reducing sugars expected in solutions as estimated from the weight loss observed in substrates were calculated, and are also shown in the figure.

Table 1. Fabric parameters

Fabric	Texture	Mass [g.m^{-2}]	Yarns warp [y.cm^{-1}]	Yarns fill [y.cm^{-1}]	Linear density of warp [tex]	Linear density of fill [tex]	Yarn twist warp [cm^{-1}]	Yarn twist fill [cm^{-1}]
Viscose	plain	143	36.6	28.8	20.2	24.0	7.3	7.5
Modal	plain	142	34.9	29.1	21.5	23.0	7.6	7.4
Lyocell	poplin	145	37.9	29.1	20.6	23.0	7.5	7.7
Cotton	satin	118	51.3	30.8	14.0	14.9	8.2	9.1

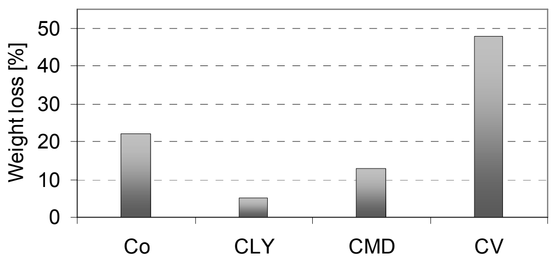


Figure 1. Weight loss in Co, CLY, CMD and CV after 8 hours of hydrolysis in the Pretema Unit.

A near linear increase in the extent of degradation with time was observed through the 8 h period. This may be caused by the high enzyme concentration in this experiment. An increase of 3.3 fold in enzyme dosage resulted only in a 1.5 fold increase in the amount of reducing sugars produced, which may be indicative of that fact that the range of enzyme dosages used were at or near saturation levels of enzyme-substrate complex. The amount of reducing sugars expected in solutions as calculated from weight loss in substrates were higher than those actually determined with the neocuproine method, and is attributed to the release from substrates of insoluble pieces of cellulose that were not degraded to glucose. In industrial processing, such non-degraded cellulosic material may be visible as particulates in treatment solutions. In the range of enzyme dosages studied, the influence of enzyme dosage on substrate degradation rate was found to be marginal but significant.

In cotton processing, fabrics are commonly desized, washed and sometimes bleached before subsequent manufacturing. The influence of individual pre-treatment steps on the overall degradation rates in a bleached fabric is shown in figure 3. From the results obtained, it was observed that the degradation rate in raw materials was ca. 40% of that in bleached samples; the degradation rate in desized samples was ca. 60% of that in bleached samples; and the degradation rate in samples washed after desizing was 90% of that in bleached samples. These values reflect the influence of increasing degrees of purification of substrates. The degradation rate is increased 250% with a “clean” fabric. The presence of residues of size and waxes in substrates decrease degradation rate. Such influences are also evident in man-made cellulosics fibres, in that a desizing step has a measurable effect on the degradation rate of warp.

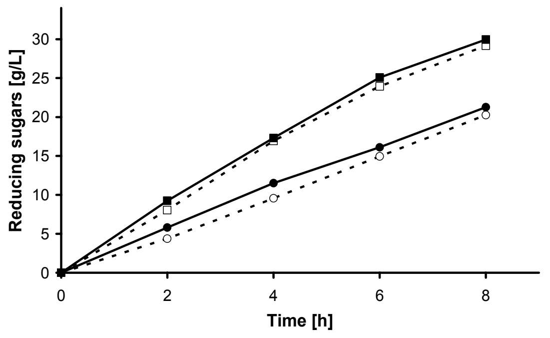


Figure 2. Production of reducing sugars as function of time during enzymatic hydrolysis of CV fabrics with enzyme dosages of: (□,■) 100 mL.L^{-1} and (○,●) 30 mL.L^{-1}; from: (□, ○) measurements of glucose with the neocuprine method, and (■, ●) estimations of glucose amounts from the degree of weight loss in substrates.

Figure 3. Relative increase in degradation rate of cotton samples with progressive pre-treatments: desizing, washing and bleaching.

In textile processing, fabrics are treated with solutions in various steps, and hence the fabrics are subjected to numerous wetting and drying steps. The drying operations involve subjecting fabrics to temperatures of ca. 130-190°C in drying and curing operations. In our experiments, we subjected samples to 45 s of drying or steaming to investigate the effect on enzymatic hydrolysis, and the results are shown in Table 2. An increase in degradation rate as compared to control was found with treatments at 130°C: with steam heat in viscose, lyocell, and modal; and with dry heat in cotton. For all samples, except lyocell, an equal or decreased degradation rate as compared to the control was found upon treatments at 190° with steam or dry heat, which indicates that: (1) there is an advent of hornification in fibres, and (2) at 190°C, dry or steam heat processes have the same impact on fibres. Heat pre-treatment of lyocell fibres results in increased degradation

Table 2. Formation of reducing sugars after 8 hours of enzyme treatment depending on the pre-treatment temperature in [g.L^{-1}h^{-1}].

		Dry heat [°C]		Steam heat [°C]	
	Control	130	190	130	190
Viscose	2.19	1.82	1.83	2.73	1.71
Modal	0.88	1.15	1.03	1.68	0.97
Lyocell	0.42	0.6	0.56	0.72	0.69
Cotton	1.82	2.19	1.45	1.78	1.24

rate. Heat pre-treatment has a visible impact on degradation rate, but this effect is small in comparison to those of other factors.

In textile processing many different machine types can be used. Efficient cellulase treatments require a reasonable amount of agitation. To measure the impact of agitation on degradation rate, two different machine types were tested: (1) a Launder-Ometer system, where the fabric is rotated in canisters, and (2) a Pretema multicolour system, where the fabric is mounted on a perforated tube and the liquor is squeezed through the ensemble. Both systems provide a high agitation level. No clear difference could be found between the two systems (Figure 4). Therefore, at high levels of agitation the machine type has only a subordinate impact. No conclusions could be reached with this type of measurement on fabric damage due to agitation. A homogenous degradation in substrates is likely in treatments with the Pretema system, but the filtration of particulate matter onto fabrics may influence the results obtained. Launder-Ometer type systems may lead to uneven degradation in fabric, which may be beneficial especially in denim finishing.

The following experiment was performed to examine the influence liquor ratio (LR) on the amounts of reducing sugars in solution and weight loss in fabrics. An LR of 1:25 indicates 1 kg fabric in 25 L solution. At LR below 1:10 the amounts of reducing sugars released in solution reached a plateau and low degrees of weight loss were observed (Figure 5). This point indicates the near attainment of v_{max} (maximum velocity in formation of reducing sugars). Above an LR of 1:50, weight loss reached a maximum, which may result from the fact that the amount of enzyme exceeded that of available surface in substrate i.e. a maximum in the enzyme-substrate complex was reached. In this region, the amounts of treatment solution and the concomitant process costs increase to an exorbitant level. Therefore a LR between 1:10 and 1:50 maybe regarded as an optimal working range. Within this range, the LR was observed to exert a medium impact on degradation rate.

After hydrolysis, the enzyme has to be inactivated by means of a soda wash at a pH of above 10 for 10-15 minutes [9]. In Figure 6, the weight loss is shown depending on the inactivation method. A peroxide-bleach instead of soda wash increases the weight loss to 135%. This can be explained by removal of the filtered particulates inside the fabric. An additional soda wash in the middle of the experiment leads to an increase of 24% over that observed in samples washed with soda at the end of the process, but no increase was found for the bleached sample. No significant difference can be found when new treatment solution is used after a soda wash. A washing step in between treatment has a medium impact on the degradation rate, but the influence of removal of particulates from the fabric is clearly detectable when the fabric is bleached at the end of the process.

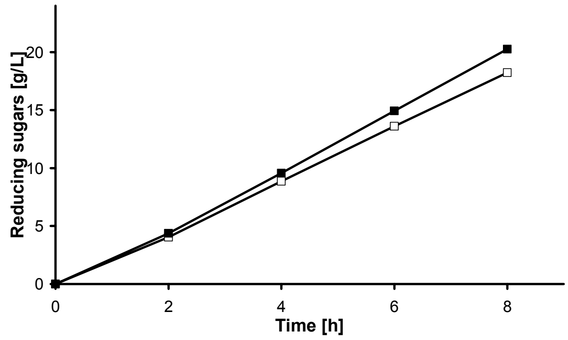


Figure 4. Produced reducing sugars during a degradation process of CV in a ■ Launder-ometer and a □ Pretema multicolor system.

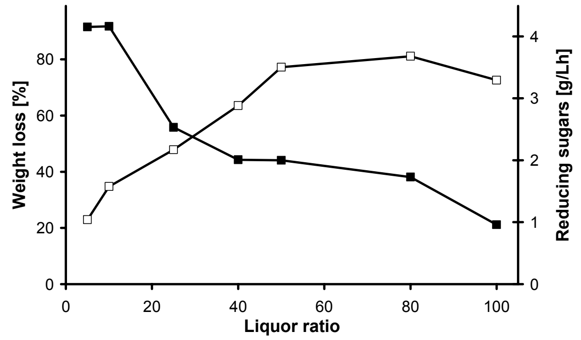


Figure 5. Influence of liquor ratio on degradation of CV: ■ Produced reducing sugars [g.L^{-1}h^{-1}], □ Weight loss [%].

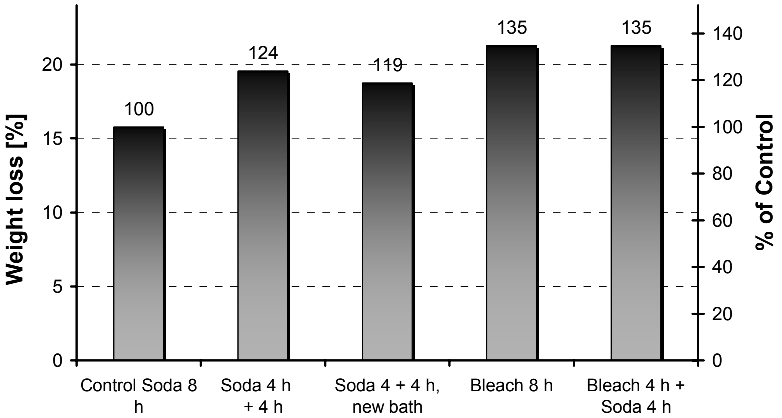


Figure 6. Effect of soda wash and bleaching in the middle and at the end of hydrolysis of CV

Discussion

Cellulase treatment is widely used in textile industry now. Some selected parameters and their influence on degradation behaviour of cellulases are presented.

The fibre type has a strong influence on the degradation rate. Viscose was shown to be more degradable than modal, cotton or lyocell. More time is required for lyocell as compared to viscose to achieve similar levels of weight loss by enzymatic hydrolysis.

With high enzyme concentration, enzyme dosage did not influence hydrolysis rates to large extents. By doubling the enzyme concentration the degradation rate only can be increased by 15%. This may be caused due to the high enzyme concentration in this experiment.

A clean fabric is prerequisite for an increased degradation rate. While raw cotton exhibited only 40% degradation rate of bleached cotton; desizing, washing and bleaching procedures resulted in increments of 20%, 30% and 10% increase in degradation rates as compared to that of the bleached cotton. Steam heat pre-treatments at 130°C exerted an impact on man-made cellulosics. At 190°C dry and steam heat yielded the same results.

When strong agitation was applied, no significant differences in degradation rate were found between a stationary and a moving fabric treatment. The optimal liquor ratio was found to be in the range between 1:10 and 1:50. The results indicated that below this range, v_{max} is reached. Above this level, the total enzyme amount exceeded the available substrate surface, i.e. a maximum in the enzyme-substrate complex was reached. Higher liquor ratios may only lead to an increase in wastage and concomitant process costs. Instead of a soda wash for enzyme inactivation, bleaching leads to increased weight loss ascribed to the removal of particulate matter from inside the fabric.

Acknowledgement

The authors wish to thank the CD-Research Society for financial support of the research project and R. Wohlgemuth and R. Schüpbach from Fluka Chemie GmbH, Switzerland, for supporting laboratory chemicals. The assistance of Avinash Manian with the preparation of this manuscript is also acknowledged.

References

[1] Gübitz, G. M., Cavaco-Paulo, A., (2001), Journal of Biotechnology 89: 89-90.

[2] Wood, T. M. (1991), Fungual Cellulases. Biosynthesis and Biodegradation of Cellulose. P. J. Weimer, Haigler, Candace H.,. New York, Marcel Dekker: 491-533 (694)

[3] Kumar, A., Purtell, C., Lepola, M., (1994), Textile Chemist and Colorist 26(10): 25-28.

[4] Heinkinheimo, L., Buchert, L., Miettinen-Oinonen, A., Suominen, P., (2000). Textile Research Journal 70(11): 969-973.

[5] Schimper, C. B., Keckeis, R., Ibanescu, C., Burtscher, E., Manian, A. P., Bechtold, T., (2004), Biocatalysis and Biotransformation 22(5/6): 383-389.

[6] Schimper, C., Campos, R., Ibanescu, C., Bechtold, T., (2003), 3rd AUTEX Conference, 25. 06. – 27. 06. 2003, Gdansk, Poland.

[7] Cavaco-Paulo, A., Almeida, Luis, Bishop, David, (1996), Textile Chemist and Colorist 28(6): 28-32.

[8] C. Schimper, R. Campos, C. Ibanescu, T. Bechtold, (2003), Book of Proceedings, 3rd Central European Conference, Fibre Grade Polymers, Chemical Fibres and Special Textiles, 10. 09. – 12. 09. 2003, Portorose, Slovenia.

[9] Harnden, A., Donelly, M.J., York, J., (2001), Coloration Technology 117: 217-224.

Lenzinger Berichte, 85 (2006), 113-123

MECHANISM OF CROSS-LINKING OF TENCEL WOVEN FABRIC FOR SUPERIOR EASY-CARE PROPERTIES AND ANALYSIS USING FLUORESCENCE MICROSCOPY

Richard S. Blackburn [a,*], Iram Abdullah [a], Stephen J. Russell [a], Jim Taylor [b]

[a]Centre for Technical Textiles, University of Leeds, Leeds, UK; [b]Lenzing Fibers Ltd., Derby, UK;
[*]Author for Correspondence:r.s.blackburn@leeds.ac.uk , phone: +44-113-343-3757; fax: +44-113-343-3704

Abstract

A cross-linking treatment to impart easy-care properties to Tencel fabric has been investigated, using dimethyloldihydroxyethylene urea (*Reactant DH*) as cross-linking agent and magnesium chloride hexahydrate as catalyst. Non-conventional treatment techniques such as 'flash curing', 'moist curing', 'pad-batch-cure' and 'pad-dry-dry steam cure' are used to facilitate better penetration of cross-linking monomer into the fibre interior. Easy-care properties of Tencel fabrics using these techniques are evaluated and compared to those treated with resin monomer using conventional pad-dry-cure process. Analysis of treated fabric using a fluorescent labelling technique and image analysis shows that non-conventional techniques significantly improve the penetration of cross-linking agent. The results further suggest that these techniques can be used to improve abrasion resistance and fabric handle of Tencel woven fabric.

Keywords: *microstructure, adsorption, cross-linking, curing of polymers, resins*

Introduction

Tencel is a regenerated cellulosic fibre, which within a few years has already developed its own market profile. In addition to its characteristic physical properties and value in the textile and clothing industry, the manufacturing process offers a much greener, ecological alternative to traditional viscose and cotton [1-3].

Longitudinal fibrillation of Tencel induced by the introduction of wet abrasion or mechanical energy is a characteristic feature of the fibre. Fibrillation affects both the physical and aesthetic properties of apparel fabrics making it more difficult to meet retail quality requirements and affects the serviceability of garments in use, particularly in respect to washing. The appearance of fibrils after domestic washing causes greying and creasing of fabrics [4-7], and is generally considered to be objectionable. Many attempts have been made to control the propensity of Tencel to fibrillate by controlling production parameters during fibre formation [8-12] as well as during fabric processing [5-7,10,13]. It has been found that resins used for textile finishing, particularly those used to control crease resistance can be a practical method of controlling this problem.

From initial investigations, it has been found that reducing the degree of fibrillation by cross-linking resins gives a parallel reduction in dry abrasion resistance. Possible contributing factors are the degradation caused by the acid catalyst, and the restriction of stress distribution within the fibres due to their rigid cross-linking by monomeric resins [14,15]. Pad-dry-cure procedures to impart easy-care properties to other cellulosic fabrics have shown that rayon loses little or no tensile strength and suffers no acid damage under the same conditions, where cotton not only loses strength but sometimes suffers irreversible acid damage. Nuessle, Fineman and Heiges [15] employed 10% (dissolved solids) of highly efficient cyclic urea formaldehyde, together with either ammonium chloride or an amine hydrochloride catalyst, at a cure of 10 minutes at 149 °C. On the removal of resin with organic amine catalyst, the loss was recoverable, indicating no acid damage, but with ammonium chloride the loss was partially recoverable [15]. This is because cotton tensile strength is dependant upon a high degree of polymerisation of the molecular chains, hence, breaking of chains by acid hydrolysis results in strength loss. In viscose rayon, by contrast, the fibre strength is dependent on the orientation and inter-tangling of chains during the drawing process, thus acid hydrolysis is less likely and less destructive if it does occur. The deterioration in the physical properties of viscose rayon fabrics on treatment with resin is due to altered stress-strain characteristics of the fibres [15,16]; it is noted that the main change resulting from resin finishing is an increase in the elastic recovery, an increase in modulus, but a decrease in fibre extensibility. Both cotton and viscose rayon demonstrate reduced fibre extensibility as a result of resin treatment, which is alone responsible for the loss in abrasion resistance [17].

Numerous studies of chemical modification of cellulosic fabrics have been conducted for the purpose of improving strength and abrasion resistance. Varying degrees of success have been achieved with variations in processes, but it is understood that conventional pad-dry-cure processes do not result in significant morphological changes in the fibres, mainly because of poor penetration of the resin monomer into the fibre structure; the success of non-conventional processes highly depends on the diffusion of the resin monomer into the fibre interior and the covalent cross-linking or anchoring of resin to the fibres [16]. The objective of this preliminary study is to investigate the efficacy of non-conventional resin treatment techniques to facilitate satisfactory penetration and to investigate the effect of these treatments on fabric performance properties.

Experimental

The non-conventional techniques used in this study were ‘pad-batch-cure’, ‘flash cure’, ‘moist cure’, and ‘pad-dry-dry steam’ processes [18]. The treatment parameters of catalyst type, concentration of resin and catalyst, and drying and curing conditions were kept constant throughout the study to observe the effect of each process on fabric performance. The physical properties of treated fabric of dry crease recovery angle, abrasion resistance and fabric appearance after domestic washes were evaluated. A fluorescent labelling technique [19] and image analysis were preformed to locate the resin in the treated samples and also to confirm the changes in fibre structure.

Materials

The white and dyed 100% Tencel 3/1 twill fabrics of 30 x 30/44 x 35 quality, obtained from Lenzing Ltd., was used throughout this study; the fabrics had been singed and desized. *Reaktant DH*, the crosslinking agent, was obtained from TextilColor AG Ltd. *Reaktant DH* is dimethyloldihydroxyethylene urea, the dissolved solids contents was 41%. All other chemicals were of general laboratory grade supplied by Aldrich.

Fabric Treatments

The fabric samples were scoured and neutralised before use and treated in an aqueous bath containing 50 g dm^{-3} *Reaktant DH* and 10 g dm^{-3} catalyst (magnesium chloride hexahydrate). The following five different treatment processes were used:

1. Pad-dry-Cure (PDC) Process

The fabric samples (30 x 42 cm) were impregnated in the pad bath containing resin and catalyst for 10 min. The samples were padded through the squeeze rollers at a pressure of 15 kg cm^{-2} to obtain 80-85% pick-up, then dried in Werner Mathis stenter for 3 min at 130 °C, and finally cured for 3 min at 160 °C.

2. Pad-batch-cure (PBC) Process

This process is similar to PDC process, except that after padding, samples were fixed by being individually sealed in polyethylene sheet and placed at a specific temperature for a specific time. Three different conditions were used; one sample was kept at room temperature for 24 hr, another sample kept in an oven at 65 ºC for 30 min, and one more sample kept in an oven at 85 ºC for 15 min. After this fixation step samples were dried and cured as described in PDC process.

3. Flash Cure (FC) Process

The flash cure process is identical to PDC process, except that the drying and curing were performed in one step. The fabric samples were padded using the same padding conditions and then were cured at 160 ºC for 3 min.

4. Moist Cure (MC) Process

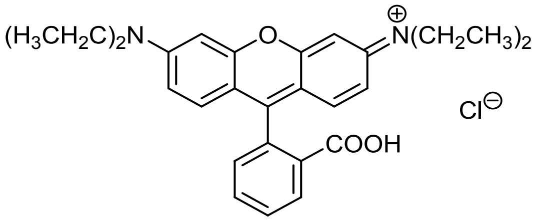
In this process, fabric samples were cured in a moist, partially swollen state. The fabric samples were padded with resin liquor then subsequently dried at 130 °C for 1 min to residual moisture of 6-12%. Because no cross-linker or strong acidic catalyst was added, after being batched for 24 hr at room temperature, the fabric samples were cured at 160 °C for 3 min.

5. Pad-dry-dry steam (PDDS) Process

Pad-dry-dry steam process is also identical to PDC process except that a steam and hot air mixture was used for curing. At 160 °C curing temperature, steam content was 125 g m^{-3} and moisture content was 26%. Two fabric samples were prepared; one sample was padded, dried and dry steamed, the other was padded, batched for 24 hr at room temperature and then dried and dry steamed.

Fabric Evaluation and Analysis

Fluorescent labeling was used to obtain information concerning the location of resin in the treated samples. The fabric samples were dyed with 10^{-3} M Rhodamine B (C.I. Basic Violet 10; **1**) solution for 1 hr at room temperature, twice washed in a pH 9.3 buffer solution (NH_4Cl/NH_3) for 20 minutes, then dried at room temperature for at least 24 hr.



1

The resin embedded fabric samples were prepared using JB-4 embedding kit; the embedding resin was based on glycolmethacrylate (GMA). The cured blocks of resin embedded samples were trimmed and 4 µm sections were cut using a base sledge microtome with a wedge knife. Four sections of each fabric samples were mounted on slides and studied using and Olympus BX51 optical microscope with mercury burner lamp, monochromatic Rhodamine/Texas red filter, and a digital Evolution MP Colour camera at 545-580 nm excitation. The images were captured using Image Pro Plus version 4.5. Subsequently, the percentage of resin penetrated into the fabric interior was determined by performing image analysis of captured images using the same Image Pro Plus analysing system. Due to differences in fabric thickness, thickness of the resin layer and thickness of the fabric, samples were measured at 8 different places and presented as % of each sample thickness.

Prior to testing, all fabric samples were conditioned at 50% RH and 20 °C. The percentage of resin solids on the fabric was determined by determining the bone dry weight of fabric before and after resin application. The 10 cm x 10 cm fabric samples were placed in clean weighing bottles and conditioned for 48 hrs. The conditioned samples were placed in a drying oven at 105 ± 5 ºC for 18 hours. After 18 hours the samples were placed immediately inside a desiccator containing silica gel and allowed to cool for an hour. The cooled samples were then weighed by means of the same electronic balance. The % solid add-on was determined by using equation 1:

$$\% \text{ Solids Add-on} = [\,(W_1 - W_0) / W_0] \times 100\% + (a)\,\% \qquad (1)$$

where W_1 is the bone-dry weight of the fabric after resin finishing, W_0 is the bone-dry weight of the fabric before resin finishing (control sample), and (a) is the correction factor. Some small loss of the fibres occurred during padding of fabric; therefore a correction factor was used to determine the actual solid add-on on the bone dried fabric.

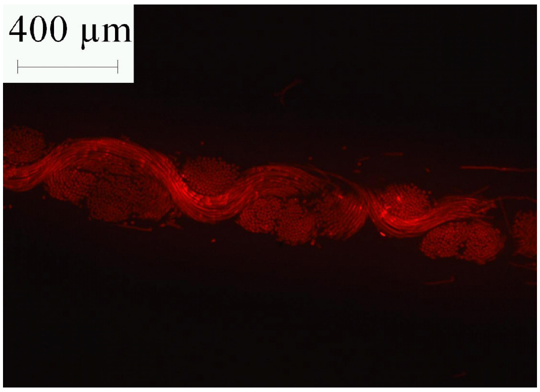
The easy care properties of unwashed and 5-times-washed treated samples were evaluated using standard procedures including dry crease recovery angle (DCRA; BS EN ISO 2213) and Martindale abrasion resistance (BS EN ISO 12947-2) using standard worsted abradant fabric and constant pressure of 9 kPa.

The treated samples were washed using standard procedure BS EN ISO 15487 at 40 ºC for 100 min with an additional load of 1 kg. After washing fabric samples were tumble dried for 15-20 min, to achieve a reduction in moisture level to 15-20 % and then air-dried.

Results and Discussion

Diffusion of monomer

On non-treated Tencel fabric the Rhodamine B did not dye intensively, but was able to penetrate the surface and weak fluorescence is seen through the cross-section (Figure 1). It was expected that the treatment conditions provided by PBC, MC and PDDS processes would facilitate better penetration of monomer into the fabric interior with respect to the PDC and FC processes.



(1)

Figure 1 Typical optical microscopic image of untreated Tencel fabric sample, Exposure time 55 ms, magnification 40x.

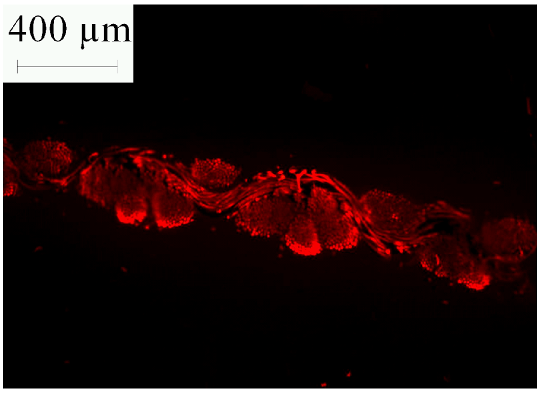


Figure 2 Typical optical microscopic image of resin finished fabric sample using PDC process, Exposure time 55 ms, magnification 40x.

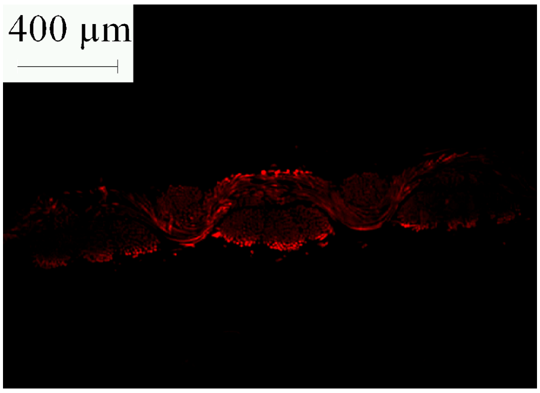


Figure 3 Typical optical microscopic image of resin finished fabric sample using FC process, exposure time 55 ms, magnification 40x.

Figures 2 and 3 show the cross-sections of resin treated fabric samples using the PDC and FC process. The presence of resin on the surface of fabric is clearly visible indicating that treatment conditions provided by PDC and FC processes are not effective in facilitating the penetration of resin throughout the fabric thickness. Using PDC process, the penetration of resin was 11% of the sample thickness, furthermore, resin distribution was not uniform. In the FC process, performing drying and curing in one step reduced the diffusion time, the rate of cross-linking was greater than the rate of diffusion, thus resin penetration was only 7.8% of the sample thickness

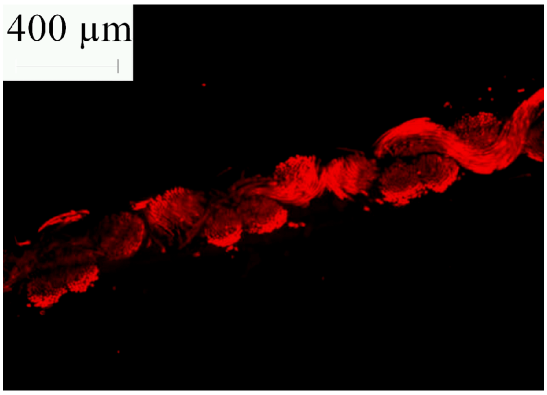


Figure 4 Typical optical microscopic image of resin finished fabric sample using room temperature, 24 hr PBC process, Exposure time 55 ms, magnification 40x.

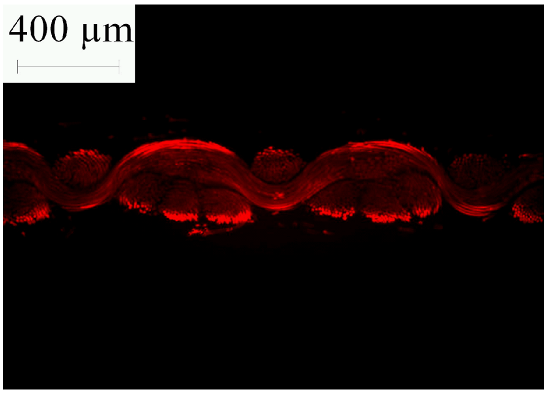


Figure 5 Typical optical microscopic image of resin finished fabric sample using 65 ºC, 30 min PBC process, exposure time 55 ms, magnification 40x.

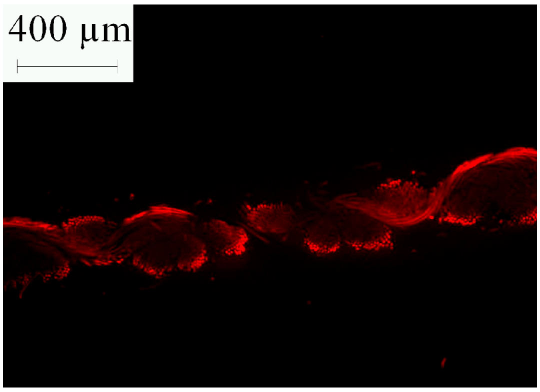


Figure 6 Typical optical microscopic image of resin finished fabric sample using 85 ºC, 15 min PBC process, exposure time 55 ms, magnification 40x.

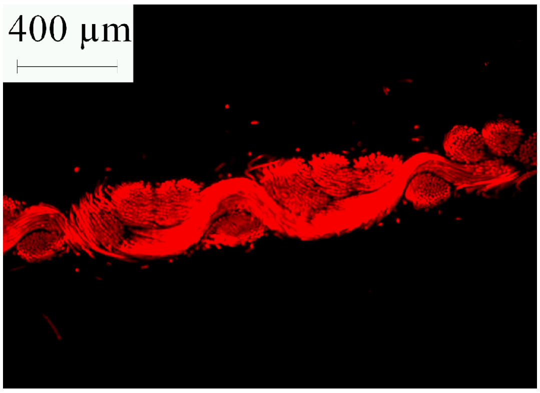


Figure 7 Typical optical microscopic image of resin finished fabric sample using MC process, exposure time 55 ms, magnification 40x.

The microscopic images of the PBC processes (Figures 4 to 6) show that the diffusion time given to the resin monomer before drying is important to achieve maximum diffusion of resin, however, temperature is important to achieve uniform distribution of cross-links. Using the PBC process, in which samples are batched for 24hr at room temperature, the distribution of resin is not uniform, the migration of resin can be clearly seen; at some points resin had penetrated through the cross-section of fabric, while at others the penetration was only 16% of the thickness of the treated sample. The samples which were batched at 65 ºC for 30 min and at 85 ºC for 15 min form a significant uniform resin layer on the fabric surface.

Using the 65 ºC, 30 min PBC process resin penetration was 10%; however, using the 85 ºC, 15 min PBC process resin penetration was slightly higher, 12% of sample thickness.

Figure 7 shows the cross-section of MC treated fabric sample in which the penetration of resin is 100%. It is also observed that the fibres have a fuller structure than other differently treated fabrics. With this process, the diffusion and cross-linking process can be completely separated. Monomers diffused into the fibre interior during 24 hr batching process and cross-linking occurred during the subsequent curing process. This greater extent of diffusion of resin monomer has also given the fabric uniform distribution and soft handle.

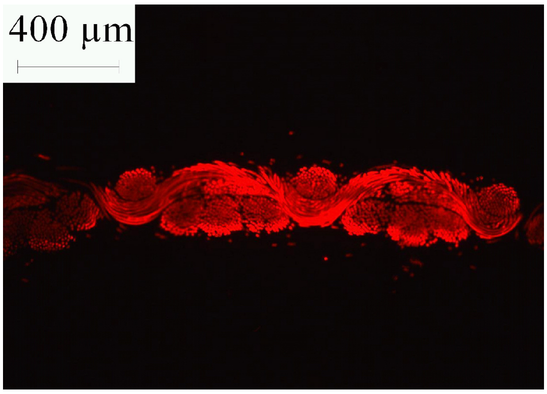


Figure 8 Typical optical microscopic image of resin finished fabric sample using PDDS process, exposure time 55 ms, magnification 40x.

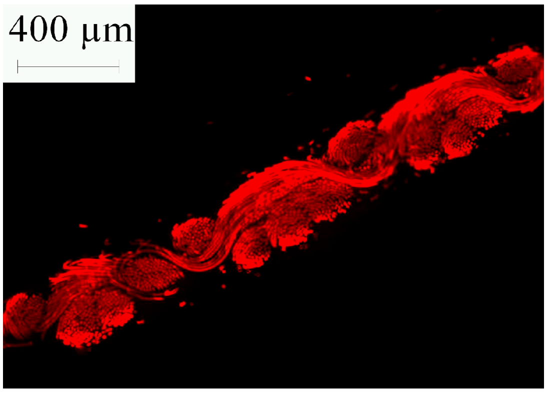


Figure 9 Typical optical microscopic image of resin finished fabric sample using pad-batch (24 hr)-dry-dry steam process, exposure time 55 ms, magnification 40x.

Considering PDDS treated samples, the penetration of resin was 12%, which is higher than PDC treated samples (Figure 8), but it was also observed that the fibres in the resin layer had fuller structure than the fibres in the fabric interior. This suggests that dry steaming not only gives better penetration of resin monomer but also helps monomer to diffuse into the fibre interior. However batching for 24 hr had given better penetration of resin monomer than subsequent drying-dry steaming (Figure 9). Again better diffusion of resin had given the fabric softer handle.

Effect of different curing processes on easy-care properties

Table 1 shows the effect of different curing processes on DCRA values of fabric. The fabric samples treated using PDC process had better DCRA values compared with those treated using MC and PDS processes, which, in turn, were better than those treated using the FC and PBC processes. The DCRA values of FC and PBC processes are even less than the DCRA values of original Tencel fabric. The better DCRA values of PDC samples are due to the formation of a more extensive and stronger hydrogen bonding system established at the junction points because of high temperature cross-linking. The combination of normal hydrogen bonds, heat-generated hydrogen bonds and resin entanglements provides an elastic network which imparts recovery from creasing [15,20,21].

In PBC and FC samples resin is deposited as surface resin at the fabric surface and at or near the fibre surface in case of PBC samples. This surface resin welded the fibres together inside the yarns and produced a stiff three-dimensional structure. The resin links are inextensible, so when dry fabric was creased high localized stresses were produced in the strain areas; the non-recoverable strain in these areas accounts for the poor dry crease recovery. These processes enhanced the abrasion resistance due to deposition of surface resin but failed to aid crease recovery.

Table I. Effect of Various Treatments on the Mechanical Properties of Tencel Fabric

Curing processes	Resin Solids Add-on (%)	Recovery in Warp Direction		Recovery in Weft Direction		DCRA (degree)		Abrasion Resistance (no of cycles)
		1 min	5 min	1 min	5 min	1 min	5 min	
Original		82.5	91.5	90.3	99.2	172.8 ± 4.4	190.7 ± 4.2	10250
PDC	1.54	97.3	107.3	104.7	113.7	202 ± 5.3	221 ± 5.1	5480
PB(24hr)C	1.76	76.8	85.5	83	93.2	159.8 ± 5.3	178.7± 4.9	9567
PB(65º)C	1.61	75.5	85.2	79	89.5	154.5 ± 7.0	174.7± 7.1	9000
PB(85º)C	1.55	79.3	90.3	79.5	91.5	158.8 ± 6.6	181.8 ± 6.2	10567
FC	1.63	82.8	92.5	83	95.5	165.8 ± 6.7	188 ± 6.8	11433
MC	1.73	83.2	96.3	99.2	107.5	182.4 ± 6.1	203.8 ± 5.4	14000
PD-Dry Steam	1.11	89.5	99.2	90.2	101.7	179.7 ± 5.8	200.9 ± 5.6	7433
PBD-Dry Steam	1.23	88.7	99.5	90.5	100	179.2 ± 5.5	199.5 ± 5	9600

Table II. Effect of Five Domestic Washes on Mechanical Properties of Variously Treated Tencel Fabric

Curing processes	Recovery in Warp Direction		Recovery in Weft Direction		DCRA (degree)		Abrasion Resistance (no of cycles)
	1 min	5 min	1 min	5 min	1 min	5 min	
PDC	111.2	121.8	105.7	115.3	216.9 ± 5.3	237.1 ± 4.6	11000
PB(24hr)C	92.8	105	93.8	104.2	186.6 ± 6.0	209.2 ± 5.9	7500
PB(65º)C	92.7	103.7	92.7	104.8	185.4 ± 4.5	208.5 ± 4.2	6433
PB(85º)C	84.7	95.8	87.5	99.2	172.2 ± 5.5	195 ± 5.2	7500
FC	82.3	93.5	93.8	105	176.1 ± 9.0	198.5 ± 8.8	11133
MC	90	101.3	98.7	109.2	188.7 ± 7.3	210.5 ± 6.6	9833
PD-Dry Steam	79.7	92.2	89.3	101.2	169 ± 8.7	193.4 ± 8.6	7420
PBD-Dry Steam	85.7	98	89.3	102.3	175 ± 7.5	200.3 ± 7.2	8110

Table III. Effect of Various Treatments on the Mechanical Properties of Tencel Fabric

Curing processes	Resin Solids Add-on (%)	Recovery in Warp Direction		Recovery in Weft Direction		DCRA (degree)		Abrasion Resistance (no of cycles)
		1 min	5 min	1 min	5 min	1 min	5 min	
Original		82.5	91.5	90.3	99.2	172.8 ± 4.4	190.7 ± 4.2	10250
PDC	1.54	97.3	107.3	104.7	113.7	202 ± 5.3	221 ± 5.1	5480
PB(24hr)C	1.76	76.8	85.5	83	93.2	159.8 ± 5.3	178.7± 4.9	9567
PB(65º)C	1.61	75.5	85.2	79	89.5	154.5 ± 7.0	174.7± 7.1	9000
PB(85º)C	1.55	79.3	90.3	79.5	91.5	158.8 ± 6.6	181.8 ± 6.2	10567
FC	1.63	82.8	92.5	83	95.5	165.8 ± 6.7	188 ± 6.8	11433
MC	1.73	83.2	96.3	99.2	107.5	182.4 ± 6.1	203.8 ± 5.4	14000
PD-Dry Steam	1.11	89.5	99.2	90.2	101.7	179.7 ± 5.8	200.9 ± 5.6	7433
PBD-Dry Steam	1.23	88.7	99.5	90.5	100	179.2 ± 5.5	199.5 ± 5	9600

Table IV. Effect of Five Domestic Washes on Mechanical Properties of Variously Treated Tencel Fabric

Curing processes	Recovery in Warp Direction		Recovery in Weft Direction		DCRA (degree)		Abrasion Resistance (no of cycles)
	1 min	5 min	1 min	5 min	1 min	5 min	
PDC	111.2	121.8	105.7	115.3	216.9 ± 5.3	237.1 ± 4.6	11000
PB(24hr)C	92.8	105	93.8	104.2	186.6 ± 6.0	209.2 ± 5.9	7500
PB(65º)C	92.7	103.7	92.7	104.8	185.4 ± 4.5	208.5 ± 4.2	6433
PB(85º)C	84.7	95.8	87.5	99.2	172.2 ± 5.5	195 ± 5.2	7500
FC	82.3	93.5	93.8	105	176.1 ± 9.0	198.5 ± 8.8	11133
MC	90	101.3	98.7	109.2	188.7 ± 7.3	210.5 ± 6.6	9833
PD-Dry Steam	79.7	92.2	89.3	101.2	169 ± 8.7	193.4 ± 8.6	7420
PBD-Dry Steam	85.7	98	89.3	102.3	175 ± 7.5	200.3 ± 7.2	8110

Table V. Effect of Various Treatments on the Mechanical Properties of Tencel Fabric

Curing processes	Resin Solids Add-on (%)	Recovery in Warp Direction		Recovery in Weft Direction		DCRA (degree)		Abrasion Resistance (no of cycles)
		1 min	5 min	1 min	5 min	1 min	5 min	
Original		82.5	91.5	90.3	99.2	172.8 ± 4.4	190.7 ± 4.2	10250
PDC	1.54	97.3	107.3	104.7	113.7	202 ± 5.3	221 ± 5.1	5480
PB(24hr)C	1.76	76.8	85.5	83	93.2	159.8 ± 5.3	178.7± 4.9	9567
PB(65º)C	1.61	75.5	85.2	79	89.5	154.5 ± 7.0	174.7± 7.1	9000
PB(85º)C	1.55	79.3	90.3	79.5	91.5	158.8 ± 6.6	181.8 ± 6.2	10567
FC	1.63	82.8	92.5	83	95.5	165.8 ± 6.7	188 ± 6.8	11433
MC	1.73	83.2	96.3	99.2	107.5	182.4 ± 6.1	203.8 ± 5.4	14000
PD-Dry Steam	1.11	89.5	99.2	90.2	101.7	179.7 ± 5.8	200.9 ± 5.6	7433
PBD-Dry Steam	1.23	88.7	99.5	90.5	100	179.2 ± 5.5	199.5 ± 5	9600

Table VI Effect of Five Domestic Washes on Mechanical Properties of Variously Treated Tencel Fabric

Curing processes	Recovery in Warp Direction		Recovery in Weft Direction		DCRA (degree)		Abrasion Resistance (no of cycles)
	1 min	5 min	1 min	5 min	1 min	5 min	
PDC	111.2	121.8	105.7	115.3	216.9 ± 5.3	237.1 ± 4.6	11000
PB(24hr)C	92.8	105	93.8	104.2	186.6 ± 6.0	209.2 ± 5.9	7500
PB(65º)C	92.7	103.7	92.7	104.8	185.4 ± 4.5	208.5 ± 4.2	6433
PB(85º)C	84.7	95.8	87.5	99.2	172.2 ± 5.5	195 ± 5.2	7500
FC	82.3	93.5	93.8	105	176.1 ± 9.0	198.5 ± 8.8	11133
MC	90	101.3	98.7	109.2	188.7 ± 7.3	210.5 ± 6.6	9833
PD-Dry Steam	79.7	92.2	89.3	101.2	169 ± 8.7	193.4 ± 8.6	7420
PBD-Dry Steam	85.7	98	89.3	102.3	175 ± 7.5	200.3 ± 7.2	8110

The performance results of MC and PDDS samples show the importance of diffusibility of resin into the fibre interior. Diffusion of resin into the fibre interior has improved the DCRA values and also the abrasion resistance values are better than the abrasion resistance value of conventionally cured (PDC) sample. Notably the MC process gave the fabric significantly increased abrasion resistance; this suggests that MC may have resulted in a significant modification of fibre structure, probably due to the greater extent of penetration and diffusion of resin monomer into the fabric interior.

Effect of domestic washing

The easy-care properties of differently treated samples after five domestic washes are shown in Table II. The DCRA values of five times washed fabric samples increased in all cases, except for PDDS cured samples, which were unchanged (Figure 10). Comparison of abrasion resistance before and after five domestic washes (Figure 11) shows that abrasion resistance of PDC treated samples significantly increased. The abrasion resistance of PBC, MC and PBDS treated samples slightly decreased, while abrasion resistance values of PDS and FC remained almost the same.

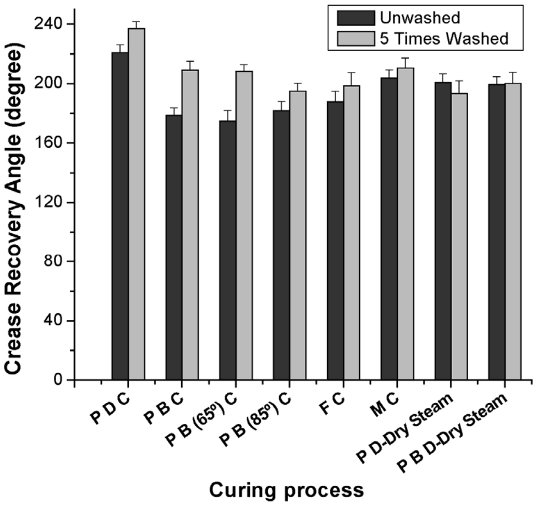


Figure 10 Crease recovery angle values (degree) of unwashed and five times washed; differently treated fabric samples.

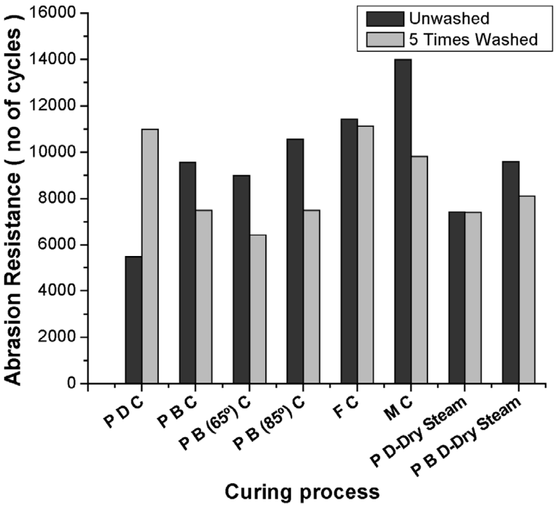


Figure 11 Abrasion resistance values (no of cycles) of unwashed and five times washed; differently treated fabric samples.

It was observed that, apart from minimising the formation of fibrils during domestic washing, resin finish also leads to dehairing of fabric. The brittle fibrils and hairs break off easily during laundering, leaving fabric surface clean and smooth; this gives the advantage of pill-free fabric, but also causes significant loss in abrasion resistance.

The visual analysis of differently treated fabric samples shows that all resin treated samples have clean, pill-free surface, except FC treated samples. Deposition of resin on the surface did not prevent fabric fibrillation; appearance of mild fibrillation caused entanglement of hairs on the surface, causing light scattering and an associated visually paler appearance. Appearance of fibrillation also accounts for the unchanged abrasion resistance of the fabric sample.

Conclusions

This work has resulted in significant findings about the mechanism of easy-care finishing and imparted properties of Tencel woven fabric. The critical feature of Tencel fabric crosslinked by pad-batch process at 65 °C and 85 °C is the uniform distribution of cross-links throughout the fabric surface as compared to pad-dry-cure process. Unwashed samples have better abrasion resistance (in comparison with pad-dry-cure treated samples) presumably due to the deposition of surface resin, but dehairiness caused by the presence of the resin furnishes a 30 % reduction in abrasion resistance after domestic washing.

Though flash cured samples have slightly better DCRA values than pad-batch-cured samples and better abrasion resistance values compared to PBC, PDC and PD-Dry steamed treated samples, fabric appearance after domestic washes is compromised due to fibrillation.

From the properties of the fabric samples shown in Tables I and II in can be concluded that the MC process provides the most superior performance overall in comparison with other differently treated samples. This process yields a high level of diffusion of resin monomer into the fibre interior in conjunction with a high abrasion resistance value and soft handle. After five domestic washes the abrasion resistance has decreased by 30 %, but is still higher than the abrasion resistance values of other differently treated samples. The DCRA values of MC samples are less than the DCRA values of PDC treated samples, but are better than untreated, PBC, FC and dry steamed samples.

From a continuous processing perspective, dry-steam curing is an attractive option; better abrasion resistance values are obtained with respect to fabric treated with a conventional pad-dry-cure process because fibres were cross-linked in a partially swollen state, but the treatment is not as effective as MC. The DCRA values are also not as high as obtained in pad-dry-cure processes, which could be because the steam curing time is too short. Furthermore, laundering does not have any adverse effects on performance properties. A 160 °C curing temperature and 3 minutes curing time has been used in order to compare this process with other non-conventional processes, but optimization of experimental parameters such as moisture content, curing time and temperature can further improve performance properties of fabric, however, this is beyond the scope of the research discussed here due to its comparative nature, but this work is ongoing.

Acknowledgements

The authors wish to thank Lenzing Fibers Ltd and the Engineering and Physical Sciences Research Council (EPSRC) for the provision of a TechniTex Faraday Partnership Industrial Case Training Grant (Quota 03301969) to Ms. Abdullah.

References

[1] Woodings, C. R. Int J Biol Macromol 1995, 17(6), 305.

[2] Woodings, C. Text Techno Int, 1996, 29.

[3] Albrecht, W.; Reintjes, M.; Wulfhorst, B. Chem fibres Int 1997, 47, 298.

[4] Zhang, J.; Shi, M.; Zhu, H.; Lai, K. Chem Fibres Int 1999, 49, 494.

[5] Hohberg, T.; Thumm, S. Melliand English 1998, 79 (5), E85.

[6] Hohberg, T.; Thumm, S. Melliand English 1998, 79 (6), E124.

[7] Mieck, K.-P.; Nicolal, M.; Nechwatal, A. Melliand English 1997, 78 (5), E69.

[8] Mortimer, S. A.; Peguy, A. A. J Appl Polym Sci 1996, 30, 117.

[9] Chanzy, H.; Paillet, M.; Hagege, R. Polymer 1990, 31, 400.

[10] Nicoliai, M.; Nechwatal, A.; Mieck, K. P. Text Res J 1996, 66 (9), 575.

[11] Nechwatal, A.; Nicolai, M.; Mieck, K. P. Text Chem Col 1996, 28 (5), 24.

[12] Nechwatal, A.; Mieck K. P.; Langner, H. Melliand English 1993, 74 (10), E333 (945).

[13] Taylor, J.; Fairbrother, A. J. Soc Dyers Col 2000, 116, 381.

[14] Gagliardi, D. D.; Nuessle, A. C. Amer Dyestuff Rep 1950, 39, 12.

[15] Nuessle, A. C.; Fineman, M. N.; Heiges, E. O. J. Text Res J 1955, 25 (1), 24.

[16] Gagliardi, D. D; Gruntfest, I. J. Text Res J 1950, 20 (3), 180.

[17] Humburger, W. J. Text Res J 1945, 15 (5), 169.

[18] Parikh, D. V.; Frick J. G.; Reid J. D. Amer Dyestuff Rep 1971, (2), 48.

[19] Kokot, S.; Matsuoka, M.; Meyer, U.; Zurcher, J. Textileveredlung 1975, 10, 127.

[20] Reeves, W. A.; Perkins, R. M.; Chance, L. H. Text Res J 1960, 30 (3), 178.

[21] Marsh, J. T. Self Smoothing Fabrics, Chapman and Hall, London, 1962.

Lenzinger Berichte, 85 (2006) 124-130

CHITOSANS FOR PERMANENT ANTIMICROBIAL FINISH ON TEXTILES

Dierk Knittel, Eckhard Schollmeyer

Deutsches Textilforschungszentrum Nord-West e.V. (DTNW), Adlerstr. 1, D-47798 Krefeld,
Tel. +49-2151-843-0, Fax: +49-2151-843-143, E-Mail: info@dtnw.de knittel@dtnw.de

Zusammenfassung

Eine neuartige Modifizierungsstrategie für textile Oberflächen besteht darin, funktionalisierte Bio-Moleküle wie Chitosan(e) permanent auf Polymeroberflächen zu fixieren. Vor allem gilt es, Moleküle aus der Klasse biokompatibler, kohlenhydratischer Polymere anzuwenden, die aus nachwachsenden Quellen gewonnen werden können.

Anwendungsziele für chitosan-ausgerüstete Textilwaren werden erwartet bei:

- Bioaktivem Fasermaterial für den Medizinbereich,
- der Schaffung von Substraten für Wundheilung,
- bei Textilien für sensible Haut (Allergiker, Neurodermitiker),
- bei Textilien mit Depotwirkung von Pharmaka,
- bei Textilien mit antimikrobiellen (bakteriostatischen/fungistatischen) Funktionen.

Es wird über Strategien zur permanenten Ausrüstung von Fasermaterial mit Chitosan berichtet und die Wirkung als antimikrobielle Beschichtung dargestellt. Methoden zur Bestimmung der antimikrobiellen Wirkung von Chitosan und der ausgerüsteten Textilien werden beschrieben (Laser-Nephelometrie, Tetrazolium Redoxsystem).

Der Aufbau funktionalisierter Schichten, auch in Mehrschichtanordnung auf Werkstoffen erscheint möglich (z.B. durch Schichtbildung zwischen polykationischem Chitosan und polyanionischen Alginaten etc.), wobei Biokompatibilität erhaltbar bzw. erreichbar ist.

Abstract

Surface chemistry and structure determines most uses of textiles (adhesion, skin contact, handle ...) whereas the fibre core has to give strength. Thus, new strategies have to be developed for imparting permanent functionality to textile surfaces. This aim can be reached by using e.g. biocompatible polymers like carrageenans, chitosans from the carbohydrate family or some of their derivatives for permanent finish.

- Chitosan: film forming, polyelectrolyte, antibacterial effects,

Anchoring of biopolymers like chitosan(s) follows the chemical strategy of introducing anchoring chemicals like cyanuric chloride or hydroxydichlorotriazine.

Following fields for application of biopolymer treated textiles may be seen:

- Bioactive fibres for medicine,
- Creation of textiles with improved properties for wound dressing,
- Textiles for sensitive skin (allergies, neurodermitis),
- Textiles with ion-binding capacities (i.e. for Ag^+-Ions),
- Polymers on textile surfaces with depot characteristics for Pharmaka.

Results on the permanent fixation of chitosan on cotton surfaces and on synthetic fibres using different chemical bond formation are presented. The antimicrobial activity of those finished textiles has been determined using laser nephelometry and tetrazolium compounds against some selected bacteria and fungi

Keywords: *Textile finishing, Surface modification, Biopolymers, Chitosan, Antimicrobials*

Introduction

An increasing demand develops for imparting active agents to textile materials (fabrics and non-wovens) by chemical ways in order to create additional properties ('functional textiles'). With synthetic fibres this may create a better hydrophilic behaviour (water retention, sweat transport ...). On natural fibres this could mean the anchoring of bacteriostatic or odour binding agents and similar. An advantageous strategy is to rely on existing fibre types and to modify only the surface thus retaining the well known mechanical properties of the bulk fibre. In addition such a strategy imparts more flexibility to the textile finishing industry [1].

This aim can be reached by using e.g. biocompatible polymers like carrageenans, chitosans from the carbohydrate family or some of their derivatives for permanent finish.

So an important task for research and development lies in the evaluation of methods how to anchor such biopolymers permanently onto fibre surfaces in a way that the biopolymers retain their bulk beneficial properties of action [2, 3].

The physicochemical interactions used for permanent fibre surface modification are summarized in Tab. 1.

Table 1. Interactions of (derivatisized) biopolymers for permanent fixation on fibre surfaces (Co, cotton; CV, regenerate cellulose; Wo, wool; PA, polyamide; PET, poly(ethylene terephthalate); PAN, polyacrylnitrile); + possible interaction; 1*) possible after pretreatment; - weak/no interaction.

Anchoring types	**Fibre type**				
	Co/CV	**Wo**	**PA**	**PET**	**PAN**
Crosslinker (durable press resins)	+	-	-	-	-
Ionic Interaction	-	+	+	-	+
Covalent Bonding	+	+	+	± 1*)	-
van der Waal's interaction	-	-	+	+	+

An important functionalization of fibre surfaces lies in the development of durable antimicrobial or at least biostatic finishes for the hygienic sector. Known antimicrobial finishes often are based on the use of quaternary ammonium salts or organometallic or halogenated compounds with often unsatisfactory fastnesses or even undesirable side effects for the human skin [4].

Chitosan (CTS) is a polycationic carbohydrate polymer (depending on pH-value of aqueous solutions) derived from natural resources having interesting properties. It shows bacteriostatic and fungi static effects in solution. Chitosan is processed from crabs or shrimp waste from chitin (a N-acetylglucosamine-polymer) by alkaline treatment and split-off of acetyl groups [5, 6]. Other natural sources are insect and fungal cuticula but currently they are not used. The chemical structure resembles that of cellulose bearing amino groups at carbon 2 of the glucan ring (Fig. 1).

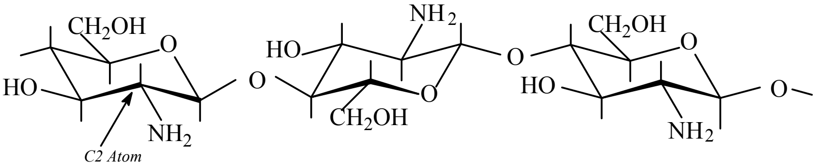


Figure 1. Structure of chitosan

The antimicrobial activity of chitosan against different groups of microorganisms, such as bacteria and fungi, has received considerable attention in recent years. Due to the variability of chitosan preparations some of the antimicrobial tests performed up to now seem to be not conclusive due to the use of poorly characterized CTS preparations or by the use of incorrect, non-physiological pH-values. Therefore new testing methods have to be introduced.

According to research at DTNW chitosan can be permanently fixed on textile materials.
In this work chemical bond formation via different anchor groups is compared regarding to add-on achieved and the antimicrobial activity of modified textiles was exemplarily investigated.

Together some new testing methods for the antimicrobial effect of CTS-treated textile surfaces are given. Whereas CTS-fixation on natural fibres using chlorotriazine based anchor chemicals has been described previously [7], strategies for the permanent finish of synthetics are presented as novel results.

Preparation and finishing of polyester with chitosan (derivatives)

For permanent anchoring of CTS or other polymeric carbohydrates on synthetic fibres two strategies can be followed which are schematically given in fig. 2 and 3. Firstly PET can be surface-modified with i.e. dodecylamine using disperse dyeing technique. Thus amino functions are created which in a second step are treated with CTS solutions using anchor chemicals like hydroxydichlorotriazine. The second way is to modify the biopolymer (i.e. CTS) with a certain amount of long alkyl chains and fixing this derivative again by disperse dyeing techniques on PET (Fig. 3).

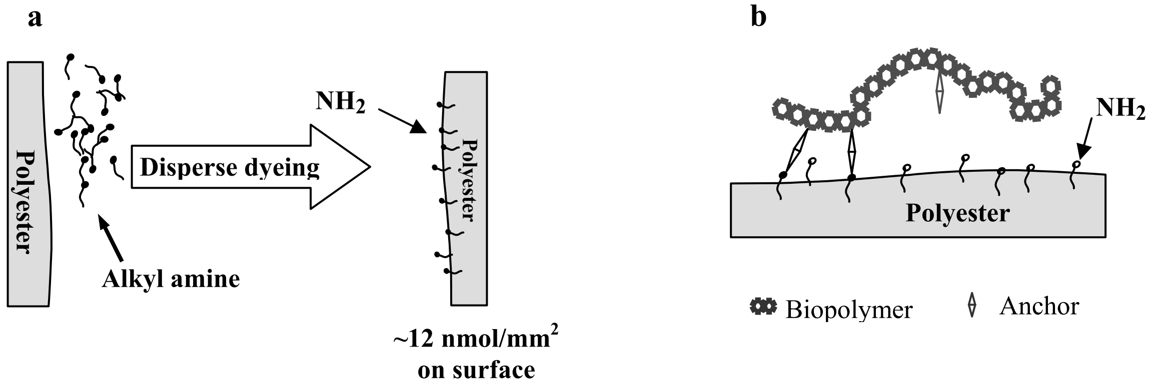


Figure 2. Finishing strategy for synthetic fibres by fibre surface modification (a) followed by chemical bonding of biopolymer (i.e. CTS) (b)

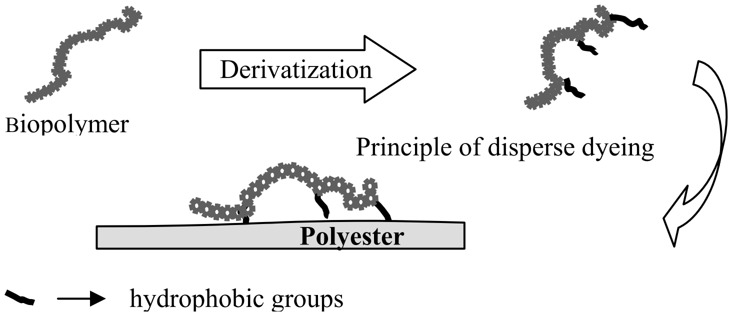


Figure 3. Finishing strategy for synthetic fibres using derivatization of the biopolymer (i.e. CTS) followed by fixation according to disperse dyeing recipes.

Material and Methods

Chitosan with degree of deacetylation of 85 % and mean molecular weight of 136 kDa was used (code of supplier: p 85/60 /A1, Heppe GmbH, Queis). Plain woven cotton fabric of 102 g.m^{-2} and polyester test fabric (same weight) were used for textile treatment.

Preparation and finishing of cellulosics with chitosan:

For permanent finishing of Co chitosan was dissolved in 1 wt.-% solution using acetic acid, followed by pH-adjustment with Na-carbonate to the final desired value (pH 5 to 6.5) and anchoring chemical added. The textile was impregnated for 5 – 10 min and squeezed between rollers to a liquor uptake of ~100 %. Fixation was done at 170 °C for 3 min after pre-drying at 80 °C (5 min). Washing was done using a buffer solution of pH 4.66 at 40 °C.

Anchoring chemicals:

Cyanuric chloride (with addition of co solvent dioxane), butane-1,2,3,4-tetracarbonic acid and propane 1,2,3-tricarbonic acid. The amount of anchoring chemical used has been 5 to 8.10^{-4} mol.g^{-1} fibre. Reactions with carbonic acids were catalyzed by 0.6 mol sodium acetate relative to polycarbonic acid.

Pretreatment of PET:

Surface functionalization of PET was done in solution of 2-10 g/l n-docecylamine in isopropanol/water (1:1) at various temperatures according to procedures of disperse dyeing. Surface concentration of amino groups has been determined using trinitrobenzene sulfonic acid [8].

Derivatization of CTS:

CTS was reductively aminated with n-hexanal according to [6] and used in PET finishing as 5 % solution at pH 5 – 6 according to disperse dyeing procedures at 130 °C.

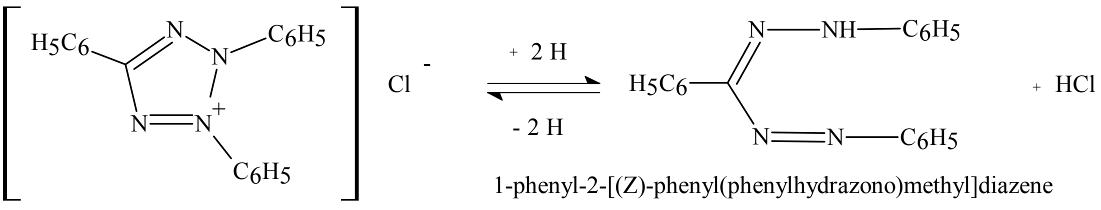
Determination of antimicrobial efficiency of chitosan on cotton or PET:

Bacterial counts in solution were done either with agar dilution method and suspension measurements or by the tetrazolium test (see below). Determination of the growth of fungi was done with a turbidimetric method using Lasernephelometers NEPHELOstar Galaxy® (BMG LABTECH GmbH). Both types of microbes were subject to CTS-solutions of pH value of 6.

Other materials and methods are described in detail in [7, 8, 9]. Only specials are given here.

The redox couple of tetrazolium/formazane, acting as proton acceptor or as oxidans, is a well established indicating system for the determination of the viability of microorganisms (Scheme 1) [10]. Especially the TTC-system is suited for the investigation on surfaces.

Testing on textile surfaces was done by incubation of the textile samples to be evaluated for antimicrobial efficiency at 37 °C for 3 – 4 h with 10 µl of an *E. coli* (10^8 cfu.ml^{-1}) culture containing 100 µl TTC (0.5 % solution). The red formazane formed was twice separated by centrifugation, dissolved in ethanol and photometrical determined at 480 nm. The reduction of microbe viability can be seen from the decrease of the absorbance value.



2,3,5-triphenyl-2H-tetrazol-3-ium

1-phenyl-2-[(Z)-phenyl(phenylhydrazono)methyl]diazene (triphenylformazane)

Scheme 1. TTC- Testing method

Results and Discussion

Fig. 4 shows antimicrobial results of dissolved CTS at pH 6 (FIG. 4, left side vs. control). These experimental parameters have been chosen since some work in the literature probably only determined the effect of acetic acid which had been used for dissolution of CTS. The inhibitory effect of chitosan on *E. coli* thus is proven even for almost neutral conditions when CTS is only protonated to an extent of around 50 % of maximum.

Fig. 5 gives the antimycotic effect of dissolved CTS as determined by lasernephelometry. Compared to a quick cell growth of the control sample, even medium concentrations of CTS reveal a distinct inhibition of the fungal cells.

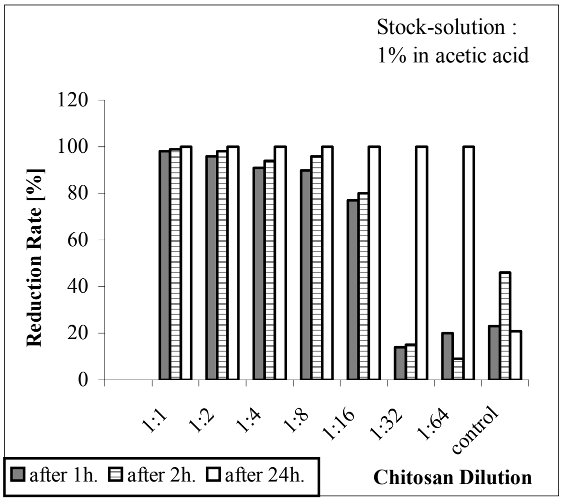


Figure 4. Time dependence of the influence of dissolved CTS with various dilution on the reduction rate of *E. coli* (pH adjusted to 6; 25 °C)

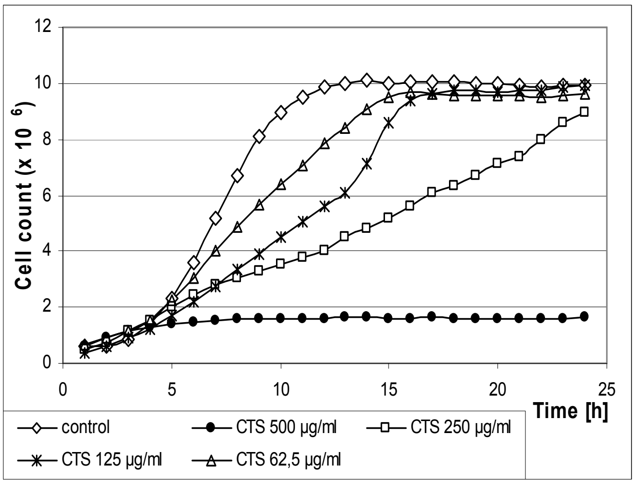


Figure 5. Influence of chitosan on the viability of *Candida krusei* (nephelometric determination).

Following studies dealt with the permanent fixation of chitosan onto cotton using different anchor molecules for chemical bond formation. Anchoring amount varies since it is expected that only few anchoring points are tolerable in order to have high activity of the chitosan polymer chain. But fixation points enough for giving permanent treatment have to be created. The reactive triazines were expected to give high fixation rates, the cyanuric chloride possibly leading to more cross linking than the hydroxy compound. Polycarbonic acids bind via intermediate anhydride formation [11]. Though much more expensive they have been chosen because of their low toxicity. Figures 6 and 7 show the percent add-on achieved using two distinctly different anchoring chemicals, chlorotriazine based and polycarbonic acid based. The amount of anchoring chemical used is always calculated as being equivalent to only a part of reactive amino groups of chitosan (<< 50 % of stoichiometry).

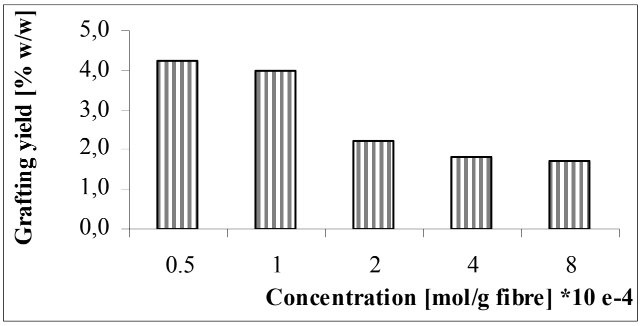


Figure 6. Grafting yield of chitosan on cotton with cyanuric chloride anchoring

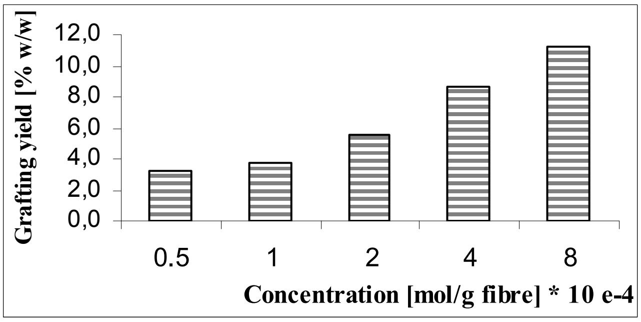


Figure 7. Effect of butane-1,2,3,4 tetracarboxylic acid as an anchor group on the grafting yield of chitosan on cotton

As it becomes evident a higher amount of anchoring chemicals in all cases results in a higher weight-gain. The loss of finish during the first washing is very high (~50 %) when using cyanuric chloride under the conditions used but with other anchoring systems a sufficient add-on remains. Add-on of chitosan using propane 1,2,3-propane tricarboxylic acid as an anchor group gives similar results. One has to note that a finish of > 5 % (which is obtainable when using CTS of high molecular weight) looses its textile character becoming a rather stiff material.

For the covalent binding towards dodecylamine pretreated PET, figure 8 shows the amount of free amino groups ready for binding of CTS using anchoring chemicals like hydroxydichlorotriazine.

Figures 9 and 10 exemplarily show results of antibacterial effect of the CTS-treated surface acc. to the TTC-test. The lower the formazane absorption the more bacteria have ceased life. So at least a bacteriostatic, permanent textile finish is achievable.

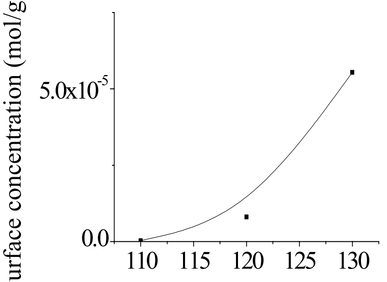


Figure 8. Surface concentration of aminogroups on amine pretreated PET (5 g.l^{-1} dodecylamine) in dependence of treatment temperature

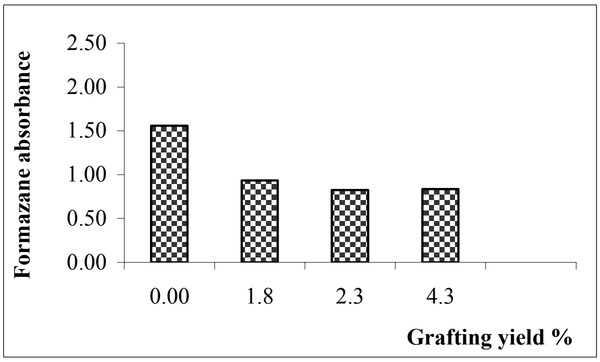


Figure 9. Effect of grafting yield [% w/w] of chitosan on the reduction of *E. coli* after washing using the TTC test method. Anchor: Cyanuric chloride

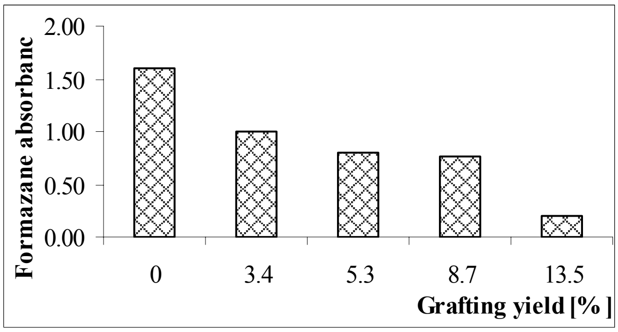


Figure 10. Effect of grafting yield [% w/w] of chitosan on the reduction of *E. coli* after washing using the TTC test method, Anchor: Butane 1,2,3,4 tetracarboxylic acid

Even if there is a distinct difference in grafting yield on cotton using the different anchors the antimicrobial suppression seems to be similar. As far as textile properties have to be retained add-ons of less than 5 % seem to be reasonable. Fig. 11 shows results on the reduction of bacterial counts using chitosan treated PET-fabrics.

The sample finished with hexylchitosan having about 4 % add-on, the sample with CTS anchored by polycarbonic acid about 1.3 % add-on.

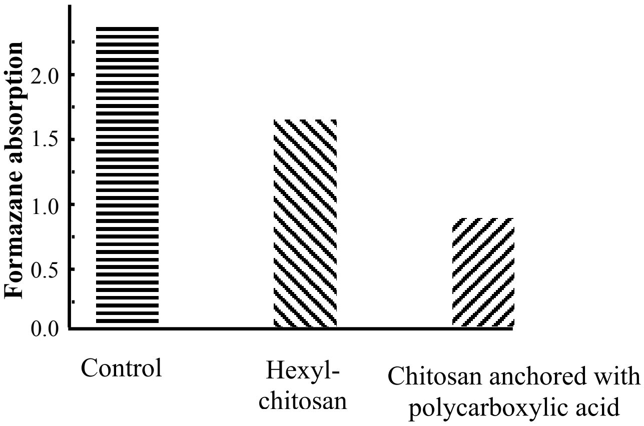


Figure 11. Bacteriostatic effect of PET with permanent CTS-finish

It could thus be shown that chitosan imparts antimicrobial activity to cotton fabrics even when tested under nearly neutral pH-conditions (more details on finishing PET can be found in [8]). The finish will be durable because of chemical bonding. Future tasks will be aimed to test against more microbe types and in introducing chitosans of different molecular mass, the lower ones preferred because of processing behaviour and to the treatment of other fibre types.

Acknowledgement
We would like to thank the Forschungskuratorium Textil e.V. for funding these research projects (AiF-Nos.11652N, 13519). These projects were funded with financial resources of the Bundesministerium für Wirtschaft und Arbeit (BMWA) with a grant of the Arbeitsgemeinschaft industrieller Forschungsvereinigungen "Otto-von-Guericke" e.V., AiF).

References

[1] Knittel, D.; Schollmeyer, E.: Technologies for a New Century. Surface Modification of Fibres, J. Text. Inst. **91** (2000) 151–165.
[2] Knittel, D.; Stehr, R.; Schollmeyer, E.: Verfahren zur Modifizierung der Faseroberfläche eines textilen Fasermaterials, P 196 24 170.7, 23.06.96 (1996).
[3] Knittel, D.; Schollmeyer, E.: Permanent finishing of cotton with ionic carbohydrates and analysis of thin layers obtained, Melliand Textilber. **83** (2002) E15-E16.
[4] Vigo, T.L.: Protection of Textiles from Biological Attack. Handbook of Fiber Science and Technology, Chemical Processing of Fibers and Fabrics, Functional Finishes, Part A; Lewin, M.; Sello, S.B. (Eds.), Marcel Dekker, New York, 1983, II, 367-426.
[5] Goosen, M.F.A.: Application of Chitin and Chitosan, Technomic Publ. Co., Lancaster, PA, 1977.
[6] Muzzarelli, R.A.A.: Chitin, Pergamon Press, Oxford, UK, 1977.
[7] Knittel, D.; Schollmeyer, E.; Zimehl, R.; Zorjanovic, J.: Verankerung von Biopolymeren auf Synthesefasermaterial, DTNW-Mitt. **47** (2005) ISSN 1430-1954.
[8] Fouda, M., Knittel, D.; Zimehl, R.; Hipler, C.; Elsner, P., Nickisch-Hartfiel, A.; Schollmeyer, E.: Melliand Textilber., (in preparation).
[9] Fouda, M.; Use of Natural Polysaccharides in Medical Textile Applications, Thesis, University Duisburg-Essen, 2005.
[10] Seidler, E.: The Tetrazolium-Formazan System: Design and Histochemistry, G. Fischer Verlag, Stuttgart, 1991, 1-86.
[11] Choi, H.; Welch, C.M.; Morris, N.M.: Nonphosphorous Catalysts for Formaldehyde-Free DP Finishing of Cotton with 1,2,3,4- Butanetetracarboxylic Acid, Part II: Sodium Salts of Fumaric, Maleic, and Itaconic Acids, Text. Res. J. **64** (1994) 501-506.

Lenzinger Berichte, 85 (2006) 131-136

ALCERU®silver – A NEW ALCERU® FIBRE WITH VERSATILE APPLICATION POTENTIAL

Reiner Büttner, Hardy Markwitz, Carmen Knobelsdorf

Thuringian Institute for Textile and Plastics Research (TITK), Breitscheidstraße 97, D-07407
Rudolstadt, Germany, E-mail: Markwitz@titk.de

Abstract

The broad-spectrum bactericide silver went into focus of interest as active component in antimicrobial fibres recently. In the TITK a technique has been developed, which allows to bring high concentrations of silver into a cellulosic fibre. The well known ALCERU® process has been modified: By incorporation of pulverized special ion exchange materials it is possible to immobilise large amounts of antimicrobial active silver on the fibre. In the textile application field ALCERU®silver fibres are manufactured in mixtures with other fibres to yield yarns. Normally, mixing with small amounts of ALCERU®silver is sufficient to achieve an antimicrobial effect. Other cellulosic fibres like cotton or viscose are the preferred mixing components. The dyeing techniques for such blended yarns are adjusted to the predominant carrier fibre. Yarns with ALCERU®silver fibres find their application field in textiles with direct skin contact, for example in socks, underwear, sportswear and the lining of shoes. Odours caused by bacteria will be reduced. Further application fields are textiles with durable disinfectant properties, for example diabetic socks, neurodermatitis wear, hospital textiles and wound dressings. Apart from the textile applications close-cropped ALCERU®silver fibres, embedded in a paper matrix, can be used as component in air filter systems.

Keywords: *Cellulosic fibre, ion exchange, silver, antimicrobial activity*

Introduction

Antimicrobial active fibres are gaining increasing economic importance, because they protect both, customer and materials against dangerous germs. Such fibres have numerous applications where area-measured materials need to have durable hygienic properties, for example in wound dressings, in air filter systems and in many textile applications with high contamination risks. Recently, the broad-spectrum bactericide silver went into focus of interest as active component in antimicrobial fibres. Different types of antimicrobial active fibres containing silver are commercially available. There are two types of fibres basing on melt spun polymers: Fibres of polyester, polypropylene or polyamide with incorporated silver containing particles (ceramics, zeolithes, etc.) and polyamide fibres coated with metallic silver by galvanisation. In both cases hydrophobic fibres are resulting, in which the active components are accessible on the fibre surface only. The textile processing of electrosilvered fibres has to be classified as difficult. Up to now cellulosic fibres were available with very limited silver contents. In TITK the incorporation of high silver loads into a cellulosic fibre succeeded for the first time.

Fibre Production

Under the trademark ALCERU® process the Thuringian Institute for Textile and Plastics Research developed a technology that allows spinning cellulosic fibres directly from the solution of cellulose in N-Methylmorpholine-N-oxide (NMMNO) [1-5]. This spinning technology is especially suitable to functionalize the fibres in favour of commercial product demands [6-8]. By incorporation of super-ground special ion exchange materials (particle sizes < 10 µm) into the spinning solution ion exchange fibres are available. Cellulose, NMMNO-solution and ion exchange materials are mixed to get the pre-dope. After distilling off a pre-set amount of water and homogenizing a spinning solution results, which is extruded through a spinning nozzle into an aqueous spinning bath. The precipitated cellulose filaments are washed and cut to staple fibres. These fibres are able to immobilize heavy metal ions from aqueous solutions [9]. The adsorption capacity depends on the amount of ion exchange material physically incorporated in the cellulose matrix. These ion exchange fibres can be loaded with silver ions. Loads up to 80.000 mg silver per kg fibres are possible without any difficulties and without losing the fibres textile character. In aqueous media these fibres release silver ions and a distinctive antimicrobial effect on many bacterial strains is shown.

Properties of ALCERU®silver Fibres

ALCERU®silver owns the typical properties of cellulosic fibres like hydrophilicity and swellability. The silver content of the fibres is exactly adjustable by type and filling grade of the incorporated ion exchange material. Therewith the fibre can be adapted to the corresponding application. Silver is released in small but antimicrobial active doses over a long period of time. Because of the swellability of the cellulosic fibre even the silver depots in the interior are accessible and remain effective. Currently, TITK produces fibres with a fineness of 0.4 – 0.7 tex, providing the option to decrease the fibre fineness further. Previous experiences have shown that the textile physical parameters allow textile processing without any problems. Figure 1 shows an electron-scanning microscopic image of ALCERU®silver. Some adhering ion exchange particles and a relatively smooth fibre surface are identifiable.

Application in Paper Industry

Special antimicrobial filter papers with 0,5; 2,0 and 10 mass-% of close cropped ALCERU®silver fibres have been developed for application in air filter systems for clean-rooms, hospitals and other air conditioning plants. The antimicrobial efficiency has been investigated in dependence on the silver content. For each of the three silver concentrations tests with four different strains of microorganisms have been carried out: *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Bacillus subtilis* spores and *Fusarium solani* spores.

The filter papers were cut into stripes with 20,7 cm in length and 3 cm in width. Each stripe was transferred into a test tube filled with 10 ml of 0,9% NaCl solution. Thereafter the 12 prepared test tubes were inoculated with the bacterial strains. The inoculum was about 10^5 CFU (colony forming units) per test tube. One control was performed for each of the four test

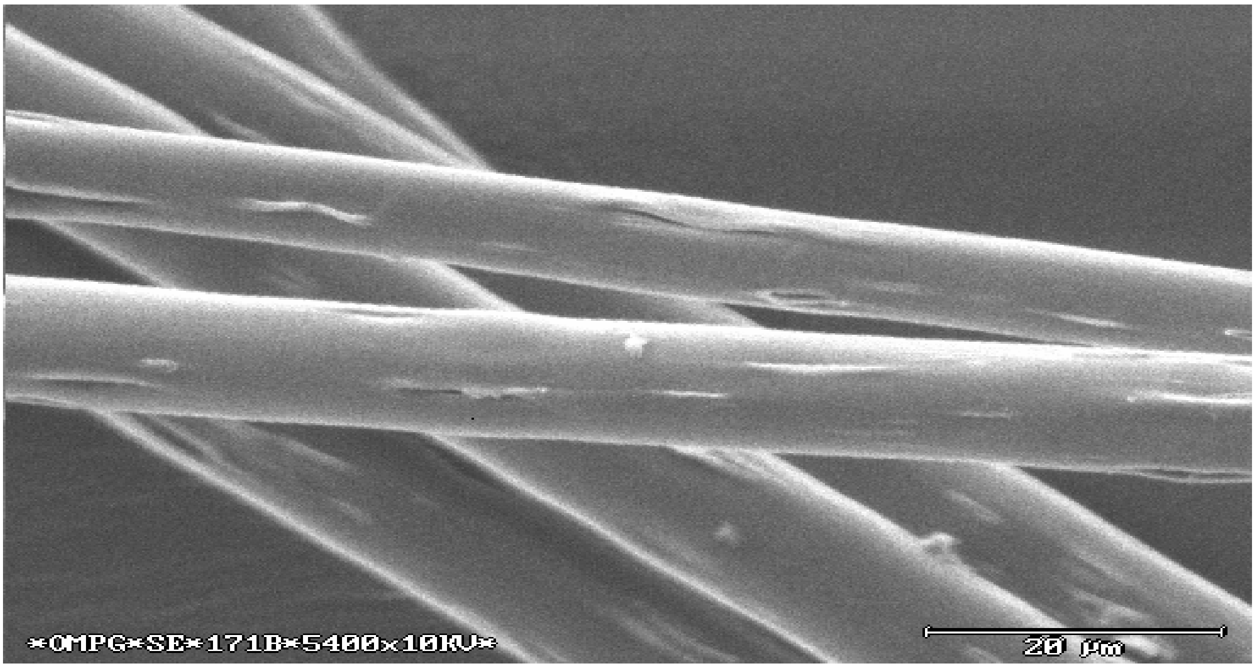


Figure 1. : Electron-scanning microscopic image of ALCERU®silver (magnification: 5400x)

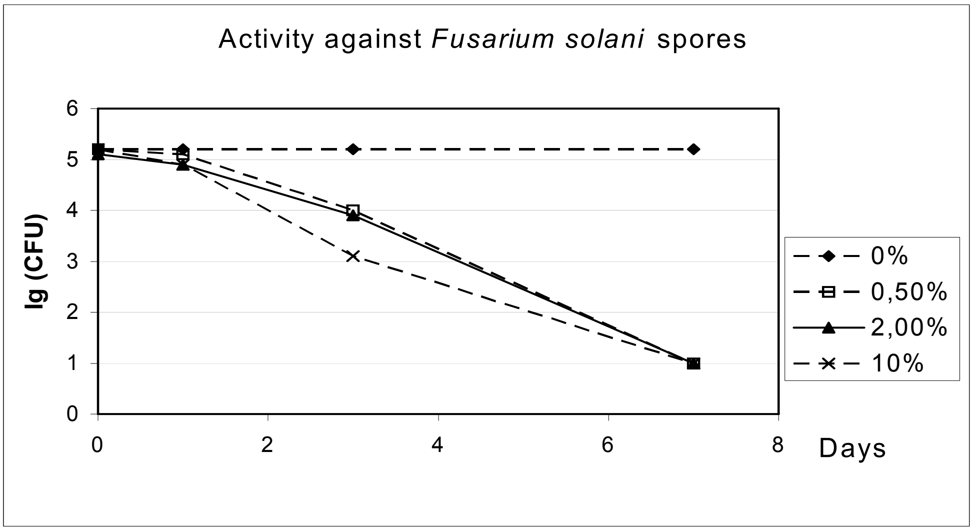


Figure 2. Filter papers with different amounts of ALCERU®silver; activity against *Fusarium solani* spores.

organisms. Four tubes without stripes were filled with NaCl solution and inoculated with the respective test organisms. All tubes were stored at 20 – 25°C for seven days. During this storage time the number of CFU was determined immediately at the beginning (= 0 min) and after 1, 3 and 7 days. The results of these microbiological examinations are shown in figures 2 – 5.

The activity against Fusarium solani spores is easy to recognize. After 3 days the number of germs is reduced strongly with all filter papers and after 7 days nearly all germs are destroyed. A coherence between the rate of germ reduction and the silver concentration is less distinctive.

Pseudomonas aeruginosa reacts more sensitive to the antimicrobial filter papers than *Fusarium solani* spores. Within one day the germs were destroyed almost completely. The higher sensitivity is also expressed by the more distinctive dependence of the rate of activity on the silver content.

The activity against *Staphylococcus aureus* is compareable to that against *Fusarium solani* spores. *Bacillus subtilis* spores are relatively resistant to the applied silver concentrations, and will be attacked not before one week of contact.

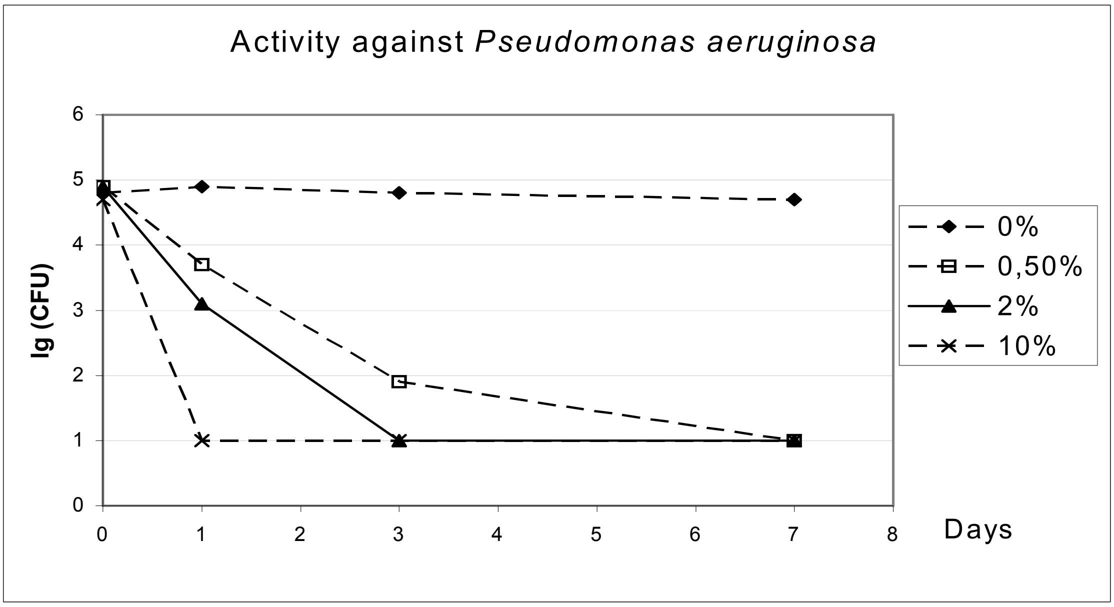


Figure 3. Filter papers with different amounts of ALCERU®silver; activity against *Pseudomonas aeruginosa.*

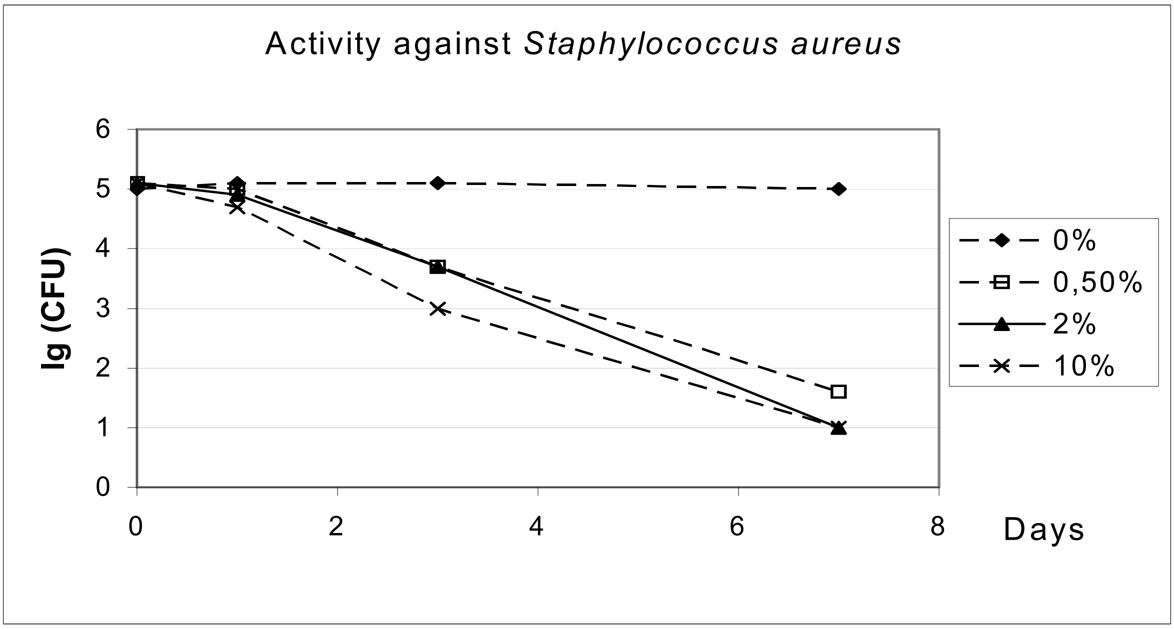


Figure 4. Filter papers with different amounts of ALCERU®silver; activity against *Staphylococcus aureus.*

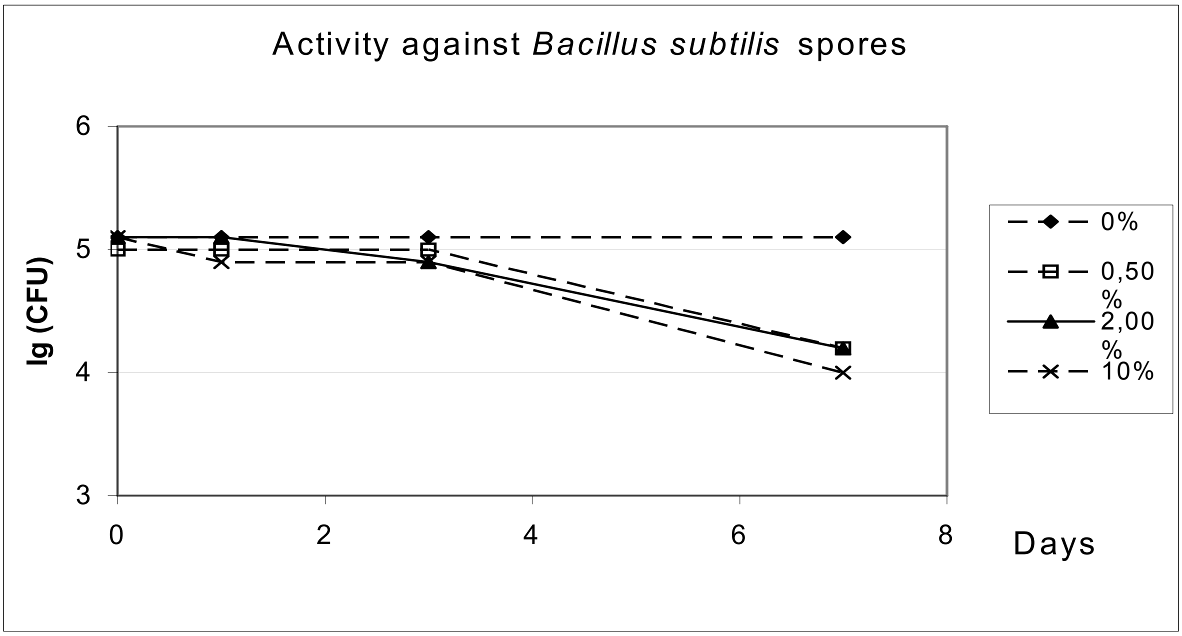


Figure 5. Filter papers with different amounts of ALCERU®silver; activity against *Bacillus subtilis* spores

Application as Textile Fibre in Fibre Mixtures

ALCERU®silver fibres have some outstanding properties which predestinate them for different textile application fields. The fibre has both cellulosic character and a very high silver content. Moreover, the fibre is miscible with common fibres like cotton, wool, viscose, modal or unmodified Lyocell without any difficulties. The yielded fibre mixtures can easily be processed to get yarn. Another very important aspect for textile applications is the good dyeability of ALCERU®silver containing yarns.

Because of their cellulosic character the ALCERU®silver fibre is hydrophilic and swellable. In combination with its breathability these properties are responsible for a pleasant wear comfort. The textile processing corresponds to common cellulosic fibres like cotton or viscose. The previous experiences have shown very good processing properties of ALCERU®silver on all applied textile machines. The high silver content of the fibres in combination with their miscibility offers economic advantages. That's why ALCERU®silver is preferably processed to the yarn in mixture with a common carrier fibre. Small amounts of a relatively expensive special fibre are blended with larger amounts of low-cost standard fibres. Because of the high silver content of the fibres the antimicrobial effect can be achieved with relatively small loads of ALCERU®silver and that allows to offer a cost-effective material. Moreover, the principle of blending allows an exact determination of the silver content in the yarn and therewith an adaptation to the corresponding application. Dyeing the manufactured knitting yarns is possible with common dyeing methods and commercial types of dyestuffs. Normally the knitting yarns are dyed with reactive dyestuffs and finished on dye bobbins. The fastnesses obtained are corresponding to the level of standard Lyocell yarns or standard cotton yarns. The antimicrobial effect is not affected by the dyeing process.

Textile Application Fields

An important application field for ALCERU®silver are textiles with desodouring finish. It is well known that microorganisms on the skin, like Lactobacillus brevis, subsist on substances that are secreated by human sweat. The decomposition of these substances evokes the typical unpleasant smell of perspiration. In the course of wearing ALCERU®silver containing textiles silver ions are eluated and their antimicrobial effect becomes active in the fabric and also on the skin. The growth of sweat decomposing bacteria is inhibited and the formation of unpleasant odours is reduced. Application fields are shoe linings, socks, underwear and sportswear.

Another extensive group of applications can be summarized under the headline „Textiles with durable antimicrobial properties“. The colonization of the skin with microorganisms may have negative influences on the severity of some diseases like neurodermatitis and diabetes. In the case of neurodermatitis *Staphylococcus aureus* is in the focus of interest. The germs are reaching deeper skin layers via open scratched skin areas and promote the severity of the pathogenesis. The application of ALCERU®silver in special neurodermatitis wear may inhibit the growth of bacteria and a faster restoration of the affected skin areas may be reached. A further application field are diabetic socks. The diabetic foot syndrome causes perceptive disorder of the foot, so that smaller dermal injuries cannot be noticed punctual. Infections are likely to follow and in the consequence foot abscesses come into being that heal up very badly. In much cases an amputation of the affected extremity is the final consequence. Infections of the dermal injuries could be prevented by socks from antimicrobial functionalized fabrics. In hospitals patients with weakened immune system are endangered by hospital-acquired infections. By finishing hospital textiles with ALCERU®silver one potential source of transmission may be defused.

The applications in men's socks and diabetic socks have been realized in cooperation with the Strumpfwerk LINDNER GmbH, Hohenstein-Ernstthal. Both products were introduced into the market successfully.

The antimicrobial effect of ALCERU®silver containing fabrics have been tested by the institute FRESENIUS. The sample presented in figure 6 contains 10 % ALCERU®silver and has been dyed and washed several times before examination. The textile has been inoculated at the moment t=0 with a defined number of colony forming units (CFU) of *Lactobacillus brevis* as test germ. After an incubation period of 24 hours the number of CFU's was determined. For comparison a control sample without ALCERU®silver has been examined simultaneously. While the lg(CFU)-value of the control sample increases from 5,2 up to 9,3 the lg(CFU)-value of the ALCERU®silver fabric decreases from 5,4 down to 3,0.

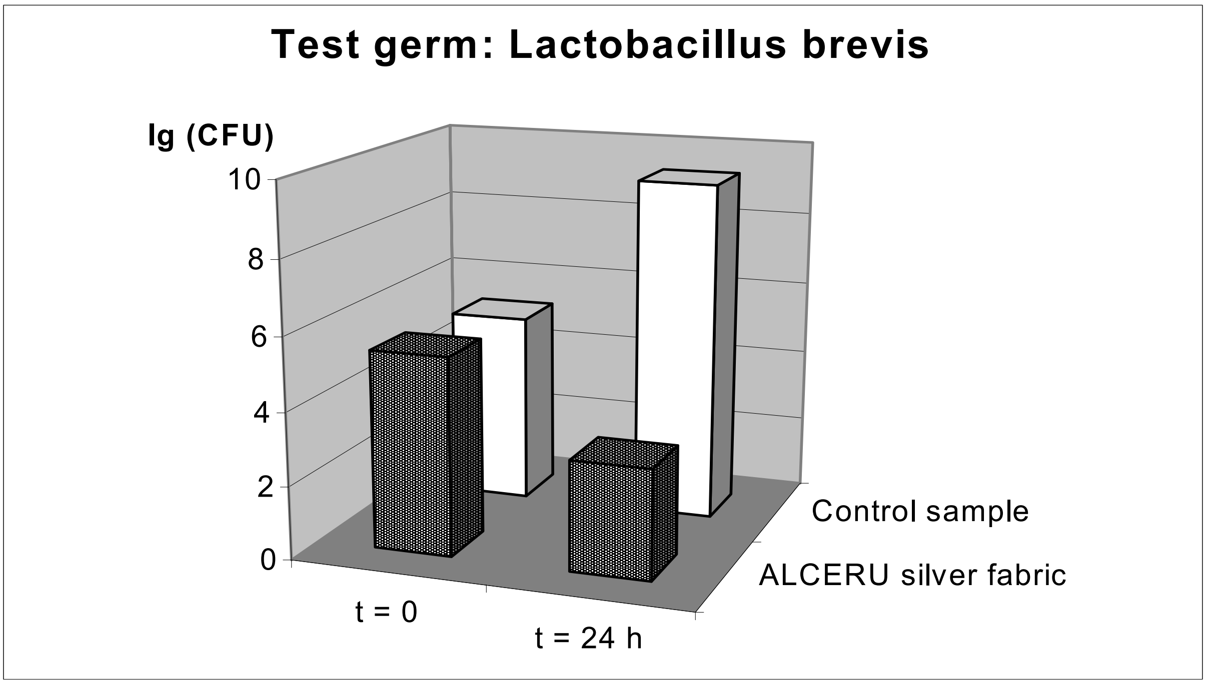


Figure 6. ALCERU®silver containing fabrics; activity against *Lactobacillus brevis* [3]

Conclusion

With ALCERU®silver the development of a new type of cellulose based antimicrobial fibre is succeeded. This fibre has a large number of application fields in paper and textile industries. Further possible applications are expected in the field of medical products (wound dressings, etc.). The silver concentration in the final product is exactly adjustable in a wide range by the parameters degree of filling of the fibre and ALCERU®silver amount. Therewith an adaptation to the corresponding application is possible. The principle of blending with other fibres for textile applications is very economic.

Acknowledgement

Financial support was provided by the German Federal Ministry of Economics and Technology and by Schoeller & Hoesch GmbH & Co KG, Gernsbach. We also express our gratitude to Strumpfwerk Lindner GmbH, Hohenstein-Ernstthal and Kulmbacher Spinnerei GmbH, Mainleus.

References

[1] H. Chanzy; M. Pailet; R. Hagege, *Polymer 3*1 (1990) 400-405.
[2] E. Taeger; H. Franz; H. Mertel, *Formeln, Faserstoffe, Fertigware 4* (1985), 14-22.
[3] B. Phillip, Pure *Appl. Chem. A30* (1993), 703-714.
[4] D. Loubinoux; S. Chaunix, *Textile Research Journal 2* (1987, 61-65.
[5] E. Taeger, Ch. Michels, A. Nechwatal, *Das Papier 12* (1991), 784-788.
[6] J. Schurz, *Lenz. Berichte 9* (1994), 37-40.
[7] D. Vorbach, E. Taeger, DE 44 26 966 C2.
[8] E. Taeger et. al., *Lenz. Ber. 76* (1997), 126-131.
[9] Pat. EP 1175520.

Lecture held at the 43rd International Man-Made Fibres Congress, September 15th – 17th 2004 in Dornbirn, Austria.