Functionalized Cellulose Based Microcomposites

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Summary: A technique has been developed that allows the production of cellulosic micro composites by immobilizing super-ground functionalised materials in the cellulose matrix. For this purpose, the well-established ALCERU® process has been a subject of technological modification. Depending on the degree of filling, several types of composites are accessible. At lower concentrations, the fibres maintain their textile-physical parameters and may be used in applications, where a textile appearance is required. The increasing concentration of the functional additives influences increasingly the overall properties of the composite and leads to composites with special functions such as water retention, electric conductivity, and specific absorption ability for organics or heat storage functions. In addition, loads exceeding the cellulose portion are useful as green shapes for ceramics.

Keywords: ALCERU; cellulose; composite; function

Introduction

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 (NMMO).[1–5] This spinning technology is especially suitable to functionalize the fibres in favour of commercial product demands.[6–9] That means that homogeneously dispersed particles are introducing the desired functionality into the cellulosic matrix by forming micro composites. The course of production mainly follows the Lyocell process and involves basic processing steps such as dope preparation, spinning and after-treatment, but is faced with some special features that will be subject of the present paper.

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Technological Aspects

The basic Lyocell process or the process variant ALCERU® as well, belong to the class of dry-wet spinning techniques. Generally, the starting materials aqueous NMMO, pulp, stabilisers and additives are mixed to form the pre-dope. The pre-dope is converted into a spinnable solution by evaporating water until the real solvent, the NMMO monohydrate, is formed. Insoluble additives are homogeneously distributed in the dope, will pass through all subsequent processing steps and will finally be embedded in the cellulose matrix.

In order to bring the dope into a defined shape, it is extruded through spinnerets and coagulates immediately in contact with the aqueous spinning bath after passing a small air gap. The final product is formed after removing adherent residual solvent by aqueous washing and drying.

Preparing a spinnable dope does not only require a homogeneous particle distribution, but also particles with a size not exceeding 10 μm. Because most of the commercially available polymers are supplied as coarse powders, the application of special grinding techniques is indispensable in order to produce the desired functionalised micro particle/cellulose composites. Therefore, the additives have been subjected to several preliminary treatments in order to adapt them to the spinning process. Whether or not the fibre formation proceeds without deterioration, mainly depends on the grain size and its distribution. On the other hand, the additive load has a significant impact on the dope viscosity, and hence attainable fibre fineness.

However, many of the organic additives provide an additional positive effect on spinning stability and process safety. As they are able to absorb ions, they may additionally act as dope stabilisers, making storage, conveying and spinning more reliable.

Results and Presentation of Brands

Cellulose micro composites can roughly be classified into several classes according to their content of functionalised additives. Because any foreign particle entering the void between cellulose chains will weaken the structure-forming hydrogen bonds, the textile- physical properties of final fibres may significantly become deteriorated. It is thus self-evident that processing conditions and textile make-up will strongly be determined by the total content of additives.

Low-filled Cellulose Microcomposites - Smartbioclean® fibres (Brand of Smart Fibres AG, Rudolstadt)

In general, any cellulosic Lyocell fibre will retain its textile processability as long as the content of additive does not exceed about 10% (w/w). This class of fibres is produced by incorporating special super-ground ion exchangers (particle sizes $<10\ \mu m$) into the cellulosic matrix. Fibres carrying about 10% (w/w) ion exchange resin will accept silver loads of up to 80 g silver per kg fibre and maintain its textile character. In aqueous media these fibres release silver ions and a distinctive antimicrobial effect on many bacterial strains is achieved.

Smartbioclean® fibres show the typical properties of cellulosic fibres; they are hydrophilic and swell. The silver content of the fibres is precisely adjustable by type and degree of filling of the incorporated ion exchange material. Consequently, the fibre can be adapted to the corresponding application.

Silver is released in small but antimicrobially active doses over a long period of time. Caused by the swellability, the silver depots in the interior still remain accessible and active. Currently, Smart fibre AG, a subsidiary of TITK produces fibres with a fineness of 0.4–0.7 tex, providing the option to further decrease the fibre fineness. Previous experiences have shown that the textile-physical parameters allow textile processing without significant problems. Figure 1 shows a scanning electron microscopic image of Smartbioclean®. Some adhering ion exchange particles and a relatively smooth fibre surface are visible.

An important 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 Smartbioclean® in special neurodermatitis wear may inhibit the growth of bacteria and a faster restoration of the affected skin areas may be reached.

Further application fields 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. Even an amputation of the affected extremity may be the consequence. Infections of the dermal injuries could be prevented by socks from antimicrobial functionalized fabrics.

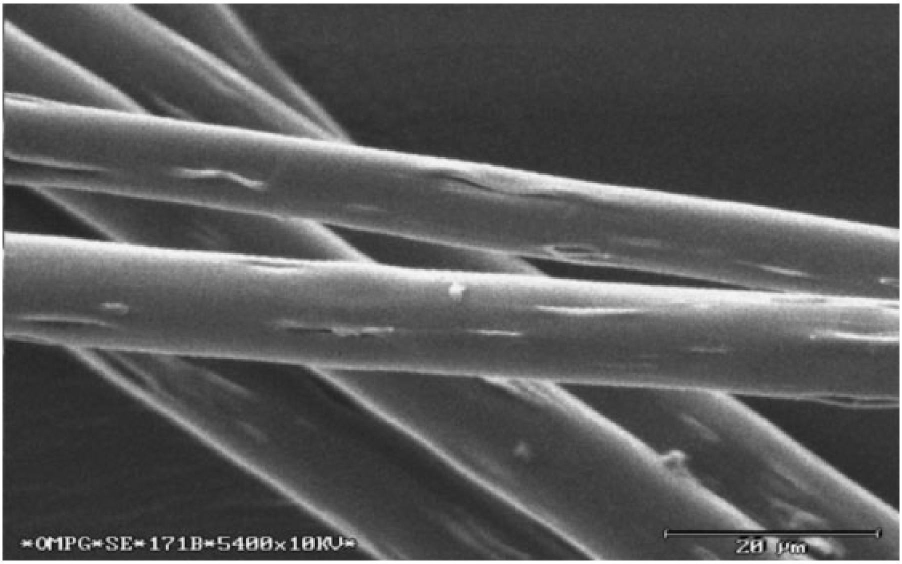

Figure 1.
Scanning electron microscopic image of Smartbioclean® (magnification: 5400×).

In hospitals, patients with weakened immune system are endangered by hospital-acquired infections. By finishing hospital textiles with Smartbioclean® 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,

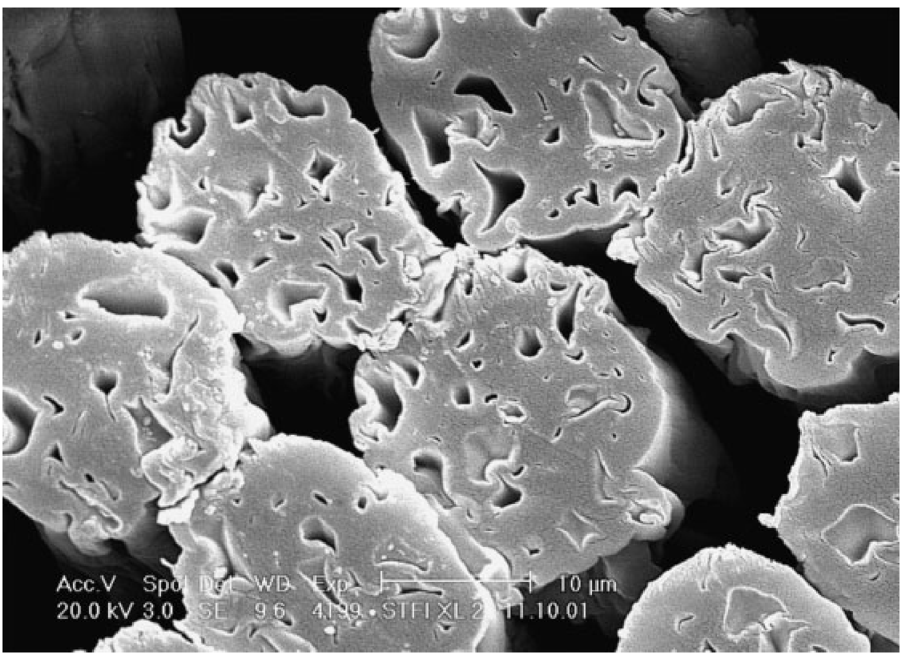

Figure 2.
Scanning electron microscopic image of Smartsupersorb® in cross-section.

Hohenstein-Ernstthal. Both products were successfully introduced into the market.

The antimicrobial effect of ALCERU® silver containing fabrics have been tested by the institute FRESENIUS. The sample contains 10% ALCERU®silver and has been dyed and washed several times before examination. The textile has been inoculated at t = 0 with a defined number of colony forming units (CFU) of *Lactobacillus brevis* as test germ. After an incubation period of 24 h 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 to 3.0.

Smartbioclean® is also admitted to the Öko-Tex list of "Accepted Active Chemical Products", i.e., all Smartbioclean® containing products are compatible to Öko-Tex-Standard-100 in principle.

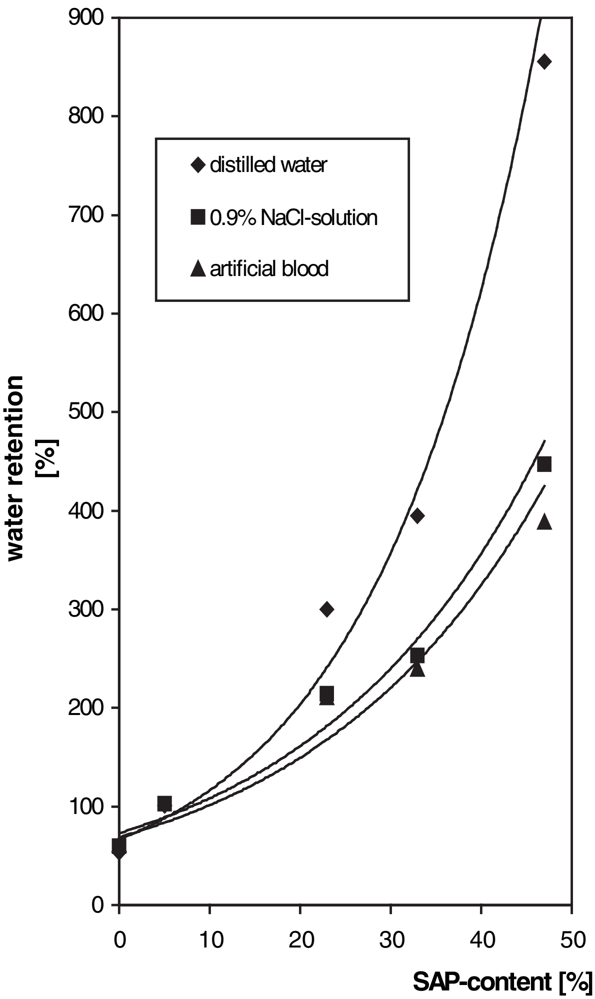

Figure 3.
Correlation between water retention and superabsorbing polymer content of Smartsupersorb® in water, 0.9% NaCl solution and in artificial blood.

Medium-filled Cellulose Micro Composites-Smartsupersorb Fibres

When increasing the additive load to an extent that does not allow continuous extrusion, the filled dopes may still be shaped into short fibres or fibrides. Causing faulty spinning is not assignable to a specified additive load, whereas an average value between 20–50% (w/w) was found for substances with high volume filling properties or low density, respectively. Some typical examples of this type of fibrous products are: activated charcoal and synthetic resins for neutral adsorbers[10], saturated hydrocarbons for phase change materials[11], carbon black for generating electric conductivity[12] or super absorbing material possessing high water retention.

Absorbing fibres represent another class of loaded Lyocell products. These fibres commercialised under the brand name Smartsupersorb® fibres are able to absorb large quantities of water or body fluids. Despite its high water retention ability of up to 800% (w/w) these materials do not loose their textile characteristics. Figure 2 shows a scanning electron microscopic image of Smartsupersorb® in cross-section. Some cavities with included superabsorbing polymer (SAP) particles are identifiable. A correlation between the content of SAP and water retention ability is depicted in Figure 3.

Smartsupersorb® fibres have advanced properties compared with other cellulosic fibres regarding hydrophilicity and swellability. The water retention ability is adjustable for different applications, like wound management or female care. The fibre does not release water under load. This material is also produced and commercialised by Smart fibre AG.

Highly-Filled Cellulose Microcomposites

For cellulose micro composites with high concentrations of particles (80–95%, w/w) the textile-physical parameters are poor, but the shape of larger structures (diameter up to 5 mm) are stable. This type of composites can be used as a ‘‘green’’ pre-shaped material. As example given, special oxides can pre-shaped, and after the pyrolysis of cellulose and thermal treatment of the shape, piezo ceramic parts are accessible.[13] Other ceramic material can formed to hollow fibres, solid fibres with an effective length up to 100 m, fleece structures, films or beads. After a thermal treatment pure ceramic products with structures down to 10 μm in two dimensions, like pipes, membranes, fibres or nonwoven structures.[14,15]

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