Sustainability

Flame-retardant cellulose that is comfortable

Durable and formaldehyde-free flame-retardant cellulose has been a challenge over many decades for researchers worldwide. It is now possible to overcome these challenges by forming a phosphorus-based physical network inside the cellulose matrix.

The development of protective textiles for emergency workers as well as technical, security, and military personnel that can reduce exposure to biological, chemical, and fire threats is becoming more important in modern society.¹⁾ Increased use of polymeric materials in every aspect of human life has led to a rise in fire incidents, which in turn has resulted in catastrophic wildfires, civilian deaths, injuries, and property damage. Therefore, novel multifunctional materials that can help minimise these threats need to be developed.

Flame-retardant cellulose is commonly used in protective clothing, drapery, upholstery, composites, and other technical applications. Commercially, cellulose textiles are made flame-retardant by special formaldehyde-based finishing treatments.²⁾ They may be durable to 50 washing cycles, but formaldehyde, being a carcinogen, requires manufacturing technologies that are heavily regulated and sometimes banned in some products. Furthermore, the OH-bonds of the cellulose are consumed (reaction with formaldehyde) after the flame-retardant treatment, which makes the fabric hydrophobic and uncomfortable. There are other, formaldehyde-free treatments for cellulose that use phosphorus moieties, which are linked to the cellulose via phosphoester or silyl

ether bonds, but these treatments are semi-durable and consume the OH-bonds as well.³⁾

A physical network inside of cellulose

The goal of our work was to develop a treatment that fulfills the following criteria: It should be formaldehyde-free, durable, and comfortable to wear. To achieve these goals, we modified the cellulose by a novel in-situ Michael addition reaction, which involves cross-linking trivinyl phosphine oxide (TVPO) with different amines.⁴⁾ This leads to a physical network inside the cellulose matrix (Figure 1).

Michael addition of TVPO and the amines can be performed at room temperature in aqueous or solvent conditions. For industrial implementation, the process needs to be faster, and therefore we performed the reaction with steam to accelerate the reaction. In laboratory trials, we dissolved the TVPO and the amines in water and applied it to the cellulose fabric, followed by drying and a steaming process in a pressure cooker (Figure 2a, p. 32).

The phosphorus content was determined using inductive coupled plasma optical emission spectroscopy (ICP-OES) before and after the material was washed for 50 cycles using standard procedure

Fig. 1. Phosphine oxide amine network inside the cellulose matrix.

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Fig. 2. a) Procedure to form a flame-retardant network in the cellulose.
b) Modification of the procedure to implement silver nanoparticles into the network to achieve flame-retardancy and antimicrobial behaviour of the fabric.

Fig. 3. a) Mechanism of a Michael Addition to form a C-C-Bond.
b) Mechanism of the Michael Addition, which is used in our work.

Fig. 4. Contact angles of water on virgin and treated cellulose are the same.

(AATCC TM-61-1996). Nearly 100 % phosphorus retention can be achieved, which shows that the treatment is durable. By adding an extra step to the process, the cellulose fabric can be multifunctionalised (Figure 2b).

This treatment process can be modified to obtain antimicrobial functionality too. After the first drying step, we further treated the fabrics with silver nitrate solution, which led to an in-situ formation of silver nanoparticles (AgNPs). These AgNPs act effectively against bacteria by releasing silver ions and accumulating in cell walls, which leads to cell death.⁵⁾

Michael addition in a nutshell

Michael addition is a named reaction that was first demonstrated by the American chemist Arthur Michael.⁴⁾ It is often used to create carbon-carbon bonds, but it can also be used to create other bonds, e.g., carbon-nitrogen bonds, carbon-phosphorus bonds, etc.

In the first step the Michael donor, which is a nucleophile, is deprotonated by a base under the elimination of water. The resulting anion reacts with the Michael acceptor – an α,β-unsaturated carbonyl compound. After protonation and tautomerism, the Michael adduct is formed (Figure 3a).

In our work, the Michael donor is an amine and reacts with the unsaturated phosphine oxide to form a carbon-nitrogen bond (Figure 3b).

Multifunctional cellulose fabrics

Virgin cellulose fibers are easy to burn and require a flame-retardant treatment to meet various safety regulations. Phosphorus-based treatments on cellulose, such as the one discussed here, form acidic species during combustion, which catalyse the formation of char (condensed phase action). This char acts as a

thermal barrier, protects the underlying polymer, and thus retards its burning.

We investigated the burning behaviour of the treated cellulose samples in various small-scale burning tests. The Limiting Oxygen Index (LOI), which defines the minimum amount of oxygen needed to burn 5 cm of fabric, is a commonly used test to evaluate the fire performance of textiles. Our treatments highly increased the LOI of the treated cellulose samples. In addition, the treated fabrics also passed the Swiss vertical burning test (BKZ-VB).

After the fire tests, a significant increase in char formation was observed, which is a clear indication for condensed phase activity of the flame retardant network.

To understand also the gas phase mode of action, we performed evolved gas analytics for blank cellulose and the treated samples.

Thermogravimetric analysis coupled with infrared spectroscopy (TGA-FTIR) showed an increase in non-flammable gases including H₂O and CO₂ and a decrease in flammable gases. This is typical for a condensed phase activity of phosphorus on cellulose. In direct insertion probe mass spectrometry (DIP-MS) measurements, the formation of PO radical and nitrogen containing species (piperazine) was observed. The PO radical can work as a flame inhibitor, and thus it is possible that the phosphorus also acts in the gas phase.

We also analysed the cellulose fabrics treated with phosphine oxide polymer and the silver nanoparticles for their antimicrobial behaviour using a contact killing test. In this procedure, the bacteria suspension is added directly to the samples. The test showed total killing of the bacterial strain when in contact with the silver-treated samples and nearly no effect for the control fabric. We repeated the antimicrobial test after washing the silver-treated fabric for 50

cycles, and no loss in antimicrobial activity was observed.

To study the comfort properties of the treated cellulose fibers, we checked the wettability and moisture transport characteristics.⁶⁾ Both the blank fabric and the treated fabric exhibited a water contact angle of 0°, which confirmed the hydrophilicity of both samples (Figure 4).

By measuring the wetted radius and wetting speed after placing a drop of water on the fabrics, we were able to evaluate the absorption properties of the fabrics. The hydrophilicity of the fabric is important for moisture uptake from the environment and control of the fabric's microclimate. A fast spreading uptake of the water allows the fabric to dry more quickly. The tests showed an increased wetted radius and a faster wetting speed for the treated

samples and therefore better moisture management.

In conclusion, we can say that we have developed a cellulose treatment that gives fabrics durable formaldehyde-free flame-retardant and antimicrobial properties and still keeps them comfortable to wear. Efforts are now under way to commercialise this technology with various industrial partners. ■

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Blick nach Asien

Kohlenstoff fixieren | Yin Li und Team haben am Institut für Mikrobiologie der Chinesischen Akademie der Wissenschaften auf Grundlage thermodynamischer und kinetischer Berechnungen einen Weg zur enzymatischen Kohlenstofffixierung entwickelt. Der Zyklus beruht auf vier Enzymen: Pyruvat-Carboxylase, Oxalacetat-Acetylhydrolase, Acetat-CoA-Ligase und Pyruvat-Synthase (POAP). Er bindet bis zu 8 nmol CO₂ pro Minute und Milligramm CO₂-fixierender Enzyme und funktioniert unter anaeroben Bedingungen bei bis zu 50 °C.

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Methan erzeugen | Ein Team der Universität von Shenzhen, des Biogas-Forschungsinstituts in Chengdu und des Max-Planck-Instituts für Marine Mikrobiologie hat ein Archaeobakterium entdeckt, das aus langkettigen Alkanen Methan bildet. Die bereits gesicherte weite Verbreitung von *Candidatus Methanoliparum* in Ölquellen könnte zu Verfahren führen, um erschöpfte Ölfelder länger zu nutzen.

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Biokunststoff | Das Unternehmen Mitsui Chemicals will Biopolypropylen erzeugen. Dazu wandelt ein rekombinanter *E.-coli*-Stamm Biomasse in den Rohstoff Isopropanol um. An der Skalierung des Fermentationsverfahrens in einen 3000-Liter-Maßstab sind das Start-up Green Earth Institute und Kyowa Hakko beteiligt; das aus Pflanzenöl-abfällen und Restöl hergestellte Naphtha kommt vom finnischen Unternehmen Neste.

Uran gewinnen | Am Institute of Physical and Chemical Technology der Chinesischen Akademie der Wissenschaften haben Liping Wen und Team ein Verfahren entwickelt, das Uran aus Meerwasser anreichert. Mit Amidoxim-funktionalisierten Polymeren entstehen nach dem Vorbild biologischer Membranen miteinander verbundene Kanäle. In Modellversuchen mit UranylNitrat über vier Wochen extrahierten diese etwa 9 mg UO₂²⁺ pro Gramm Polymer. Über vier Mrd. Tonnen Uran sollen in den Meeren enthalten sein.

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