NEW MODIFIED VISCOSE FIBERS WITH IMPROVED ABSORBENCY
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ABSTRACT
The nonwovens industry is permanently interested in new fiber materials with improved hydrophilic properties. Lenzing has developed two different modifications of viscose fibers with increased absorbency.

In cooperation with the Institute of Chemical Fibers in Lodz a modified viscose fiber was developed by incorporation of cellulose carbamate. Influences of the amount and the D.S. (degree of substitution) of carbamate, of spinning bath composition, viscose ripening index and viscose additives on absorbency, crimp and the mechanical properties of the fibers are discussed.

Another method to enhance the absorbency of viscose fibers is the incorporation of sodium alginate. In order to achieve a high yield of alginate incorporation, the spinning process has to be modified. The fibers are characterized by a high water retention.

The performance profiles of carbamate and alginate modified viscose fibers are quite different and suggest an application for specific end uses.

1. Introduction
High absorbency is an important, highly-demanded property in many nonwoven end uses such as diapers, tampons, sanitary napkins, medical sponges, baby wipes, wiping cloths and the like. Each of these applications require a high capacity for absorbing and retaining water and other aqueous fluids, particularly body fluids. The nonwoven industry is therefore permanently interested in new biodegradable fiber materials with improved hydrophilic properties and absorbency characteristics.

Different ways of improving the absorbency of viscose fibers have been proposed:

- Chemical modifications of the viscose fibre by crosslinking, polymer grafting, derivatisation, incorporation.
- Physico-mechanical modifications by variation of titer, cross section, structure (surface, crystallinity, orientation).

In this paper I would like to concentrate on chemical modifications of viscose fibers by incorporation of organic polymers. During the late seventies Lenzing developed Viscosorb, a viscose fiber with improved absorbency by incorporation of carboxymethylcellulose. Different ways were taken into consideration: the production of a modified viscose from carboxymethylated pulp, substitution reactions for the introduction of the carboxymethyl group into the cellulose and the incorporation of alkali-soluble carboxymethylcellulose. Water retention values of about 140% could be obtained.

With our know-how about the incorporation of carboxymethylcellulose as a background, we have recently developed techniques for the incorporation of two further substances: cellulose carbamate and sodium alginate.

The incorporation of cellulose carbamate is outstanding in one special aspect: after alkaline aftertreatment the fiber can be partially, perhaps even completely converted to pure cellulose again with the brilliant absorbency characteristics of the cellulose carbamate fiber still remaining. So we may classify this invention not only as one of incorporation of a cellulose derivative but also as a possible route of structural modification without permanent chemical modification.

Alginate is a biopolymer with interesting properties: apart from its excellent absorbency characteristics it is physiologically safe and used as a food additive and for wound dressings. By incorporation of alginate rayon fibers with improved absorbency could be obtained.

1.1. Theoretical Background
A correlation between absorbency (water retention) and structural characteristics of cellulosic fibers has been reported by Krässig:

\[
\text{Retention} \propto \frac{1}{(\text{crystallinity}) \cdot (\text{orientation})^7}
\]

Based on this theory a reduction of the share of crystalline regions and a lower degree of orientation of the cellulose molecules should be favourable to achieve improved absorbency.

The mechanism of increased absorbency by means of chemical modification is, however, based on the introduction of additional hydrophilic groups, which enhance the interaction of water with the hydroxyl-group of the cellulose molecule.

1.2. Test methods
When we are talking about absorbency characteristics, I would like to refer to the following standard test methods as applied in our laboratory:

- the water retention value (WRV) characterizes the fiber’s ability to retain water if defined centrifugal forces are applied.
- The water holding capacity or imbibition value (WIV) measures the amount of liquid which is absorbed between the fibers under free swell conditions according to the European Pharmacopoeia.
2. Incorporation of Cellulose Carbamate

Cellulose carbamate is produced by reaction of activated cellulose with urea or derivatives thereof. It is soluble in caustic soda. Cellulose carbamate is, however, not stable under these conditions. For this reason, temperatures must be kept low. Stability can be influenced by the D.S. of the substance and by the position of the introduced functionality.

A cellulose carbamate incorporated viscose fibre was developed at the Institute of Chemical Fibres in Lodz/Poland. The procedure is described in various publications (Polish patents PL-AL 293213 and PL 168 080). A solution of the said cellulose carbamate in caustic soda was mixed with viscose and spun into an acid spin bath.

According to the method developed at the Institute, the fibres should preferably consist of 66 to 90 % cellulose carbamate (cellulose taken as 100%). The concentration of the cellulose carbamate solution should be lower than 15%, preferably between 6 and 10%. The N-content of the cellulose carbamate solution, which is a measure of the D.S. of the cellulose carbamate, ought to be in the range of 0.5 to 4.5 %. The fibres are reported to show higher water retention and higher tenacity.

Starting from this basic technology, we investigated into the incorporation of carbamate in the lower range of 2 to 9% and found surprising effects. The incorporation leads to a maximum in crimp and water imbibition at a carbamate content of about 5%.

A reduction of the concentration of the cellulose carbamate solution improves the spinning process and prevents the clogging of the spinnerettes and the occurrence of spinning faults.

The incorporation of cellulose carbamate into the viscose fibres leads to a more or less linear increase in water retention with carbamate concentration. A value of more than 105 % can be reached by incorporation of 30% cellulose carbamate. Viscose fibres that have not been modified show values of around 80%. Crimp and water imbibition reach a maximum around 5% cellulose carbamate in the fibre, which is therefore the preferred cellulose carbamate concentration for the production of an improved absorbency viscose fibre.

Tenacity and elongation decrease with increasing concentration of cellulose carbamate. They fall, however, tolerably if concentrations in the range of 5% are considered.

The influence of cellulose carbamate concentration (D.S. 2.9% N) on absorbency

The relationship between crimp and water imbibition

The influence of cellulose carbamate concentration (D.S. 2.9% N) on mechanical fibre properties

Up to now we have only discussed the influence of cellulose carbamate concentration. The D.S. of the cellulose carbamate was kept constant at a level of 2.9%.

If we use higher substituted cellulose carbamate, the following points will be observed:

The higher the D.S. (2.9%, 3.6%; 4.7%; 5.9% N), the higher the stability of a solution in caustic soda. The viscosity of the solution goes down. As for water imbibition, a rise in the D.S. does
not improve it. Nevertheless the maximum of the curves shows
a trend towards lower concentration values. Lower crimp is ob-
served.

Influence of D.S. on the water imbibition -
concentration - curves

![Graph showing influence of D.S. on water imbibition and concentration](image)

Fig. 6

Besides the D.S. of the cellulose carbamate, the position of
the introduced functionality plays an important role. If the carba-
mate-groups are evenly distributed in position C-(2), C-(3) and
C-(6) of the glucose units, the solubility in caustic soda and the
stability of this solution improves and viscosity is lower. However,
the incorporation of this type of cellulose carbamate leads to
lower crimp, accompanied by a drop in water imbibition. If we
attribute crimp to inhomogenities in the coagulation of mixtures
of viscose and cellulose carbamate, we are not surprised
about these results. As a higher D.S. or a more even distributi-
on of functionalities both improve the solubility of the cellulose
carbamate in caustic soda, better homogenity can be achieved,
which leads to lower crimp and lower water imbibition.

A variation of the spin bath, i.e. a change of sulphuric acid,
sodium sulphate or zinc sulphate concentrations, does not lead
to higher crimp and improved water imbibition. In most cases
we can say that the higher the water imbibition, the lower the
water retention value and vice versa.

Another important parameter in the incorporation of cellulose
carbamate into viscose fibres is the viscose ripening Index. A
lower index influences crimp and water imbibition positively.

The influence of viscose additives on absorbency, crimp and
mechanical properties was tested by addition of 0,5% Berol
388, 1% Imbentin E 120/200 and 1% Symperonic 13/10. Only
Berol 388 shows significant improvements of crimp and water
imbibition as well as mechanical fibre properties.

In the following table the presented results are compiled.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Absorbency</th>
<th>Crimp</th>
<th>Mechanical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>dosage of carbamate on cellulose</td>
<td>maximum of WRV at 5%</td>
<td>linear growth of WRV with concentration</td>
<td>slight decrease of tenacity and elongation at 5%</td>
</tr>
<tr>
<td>DS of cellulose</td>
<td>higher D.S. does not improve WRV</td>
<td>no influence on WRV</td>
<td>lower crimp at higher D.S.</td>
</tr>
<tr>
<td>distribution of carbamate groups</td>
<td>even distribution</td>
<td>reduces WRV</td>
<td>even distribution reduces crimp</td>
</tr>
<tr>
<td>bath composition</td>
<td>little effect</td>
<td>little effect</td>
<td>even distribution improves spinning and mechanical properties</td>
</tr>
<tr>
<td>lower viscose ripening index</td>
<td>Improved WRV and WRV</td>
<td>higher crimp</td>
<td>lower tenacity and elongation</td>
</tr>
<tr>
<td>viscose additives (Berol388)</td>
<td>Improved WRV</td>
<td>no influence on WRV</td>
<td>higher crimp</td>
</tr>
</tbody>
</table>

Table 1

The probably most interesting feature of the described fibres is
the possibility of fully regenerating them to pure cellulose.
Cellulose carbamate can be partially or fully decomposed during
regeneration or aftertreatment. It is surprising, that even after
partial decomposition of the incorporated cellulose carbamate
the absorbency characteristics do not change significantly.
Under the aftertreatment conditions applied in our trials about
70% of the carbamate decomposed without any negative effect
on absorbency properties.

Water imbibition and decomposition of
cellulose carbamate

![Graph showing water imbibition and decomposition](image)

Fig. 8

3. Incorporation of Sodium Alginate

Alginate is a linear copolymer of (1→4)-linked β-D-mannuronate
and α-L-guluronate with excellent absorbency. It is traditionally
known as a powdery gelling and thickening agent for the food and
pharmaceutical industries. In recent years, fibres have been
produced from alginate and used for the production of high tech
wound dressings. In that process soluble sodium alginate is spun
into a calcium chloride bath under formation of calcium alginate.
Sodium/calcium alginate fibres can also be produced, with a
higher sodium content being related to better absorbency due to
the solubility of sodium alginate in water.
We have now developed a process for the incorporation of less than 10% (cellulose tanken as 100%) of this highly absorbent polymer into rayon to remarkably improve its absorbency. Depending on the different steps of secondary treatment alginic acid or a salt thereof is incorporated into the cellulosic fibre. Comparable fibres are well known from a process described in DE-OS 27 50 622, which describes the incorporation of 11 to 66% sodium alginate into rayon. Our intention, however, allows the production of alginate incorporated fibres containing, only 3 to 10% of the comparably expensive alginate. Even so, water retention values of as much as 150% can be obtained. Tenacity and elongation of the fibers decrease according to the alginate content but still remain in an acceptable range.

Careful control of temperature and residence time in all process steps performed under acidic and therefore hydrolyzing conditions is necessary, as these steps show a remarkable influence on fibre properties.

Absorbency characteristics of alginate incorporated fibres

4. Conclusion

To meet the demands of the nonwoven industry we have followed the route of incorporating cellulose derivatives or biopolymers as a means of improving the absorbency of viscose fibres.

We developed two types of fibres with improved hydrophilic properties but different absorbency characteristics. Viscose fibres modified by incorporation of cellulose carbamate show a maximum of water imbibition at 5% CC while water retention is only slightly improved. The maximum in water imbibition correlates with the maximum in crimp.

The absorbency characteristics of viscose fibres containing 8-10% alginate are quite inverse: while water retention is almost doubled, water imbibition seems to be unaffected.

Now we are going to evaluate possible applications for our absorbent fibres taking into account that different performance profiles are required for different nonwoven or textile products. As far as the carbamate fiber is concerned however, one major problem to be solved on the route to commercialization is the limited availability of the raw material cellulose carbamate. The fact, that by special aftertreatment of the fibre the cellulose carbamate may be decomposed to form pure cellulose, opens a completely new way of improving absorbency characteristics significantly without permanent chemical modification.

References:

- Y. Qin, C. Agboth, X. Wang, D. K. Gilding: Man-Made Fiber Yearbook, 29-30 (Sep 1996)
- WO 94/17227
- PL 168 090
- DE-OS 27 50 622
- PL-A1 293243