CHEMICAL MODIFICATION OF CELLULOSE

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Abstract

Thermolytic degradation of cellulose is dependant on its initial $\overline{DP}$, accessibility and on the method and temperature of the treatment. A limiting $\overline{DP}$ could be detected in the depolymerizing reaction. The deteriorating action of aggressive water could be demonstrated. Quantitative correlation was elaborated concerning the role of accessibility in the reaction between cellulose and reactive dyestuffs. The role of temperature was cleared up in the cellulose—caustic soda interaction. New bleaching process was elaborated with the use of singlet oxygen. Physical characteristics, amount of releasable formaldehyde and colouristic influence of resin finishing of cotton could be optimized.

1. Thermolytic modification of cellulose

Many details had been published on the pyrolysis ($T > 250^\circ C$) and thermal analysis of cellulose [1, 2, 3, 4, 5, 6, 7, 8]. Surprisingly few papers are, however, dealing with the changes, brought about by thermal treatments ($100^\circ C < T < 250^\circ C$) of short duration (15—600 s) frequently applied in up-to-date dyeing and finishing of cellulosic textiles.

Changes in selected chemical and physical characteristics of cellulosic fibres have been studied subsequent to their thermal treatment ($150^\circ C < T < 250^\circ C$) of short duration (30—600 s). Based upon the obtained data and on the results of further kinetic studies a hypothesis could be formulated on the mechanism of the thermal process. The reduction of thermal depolymerization of cellulose as well as the elaboration of abbreviated combined finishing processes was the aim of this work.

The result of the studies can be concluded as follows. Under the mentioned conditions cellulose was depolymerized by the thermal treatment. Hydrolysis is the dominant reaction in the thermolytic degradation.

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Depolymerized cellulose, oligomers and glucose were the detected products of degradation.

The higher was the initial degree of polymerization of cellulose ($\overline{DP}_0$) in advance to the thermal treatment, the higher were the loss in $\overline{DP}$ ($\overline{DP}_0 - \overline{DP}_t$) and the rate of the degradation. The intercept of the linear $\frac{\overline{DP}_0 - \overline{DP}_t}{t}$ versus $\overline{DP}_0$ function is the non thermolysable "limiting degree of polymerization" ($\overline{LDP}$) of the thermally treated cellulose.[10] Its value is dependent on the initial accessibility of cellulose and on they way of thermal treatment. The rate and extent of thermal depolymerization are increasing with the increase in the accessibility of cellulose.[9]

Increased depolymerization occurs subsequent to thermal treatments in the presence of compounds including structural water molecules. If, however, urea was added to such systems, the thermal degradation could significantly be breaked down. Consequently thermal release of structural water molecules, bound to cellulose or to any other compounds, makes them aggressive in hydrolytic or thermolytic reactions. A possible consequence is the hydrolysis of glucosidic linkages in cellulose. Urea may prevent this through chemical trapping of the aggressive water molecules.[10] Subsequent to short term thermal treatments, below 150°C, no significant cellulose degradation occurred at all, while in the range from 150 to 250°C thermolytic, between 250 and 290°C oxidative, and over 290°C pyrolitic depolymerizations were the dominant reactions. The extent of degradation was increased by the longer duration of the thermal treatment, while the highest rate of depolymerization occurred after a thermal treatment for 30 to 60 seconds. The latter is due to the rapid consumption and leaving of the thermally released active water molecules in and from the system. After periodical thermal treatments, including ten one minute long operations and facilities for moisture regain between two subsequent operations, bring about more definite cellulose degradation than a single thermal treatment for ten minutes.[10]

Hexamers and heptamers are the main constituents of the aqueous extract of the thermal treated cellulose. Half of their total amount can already be extracted after the first minute of thermal treatment. Random and "chain end" depolymerizations occur simultaneously. This can be concluded from the linear correlation between the Albrecht's fission number and the extractable oligomer content.[10]

The maximum in water content of cellulose, which might be activated, is not depending upon the total moisture content of the substrate, and proved to be $16.6.10^{-4}$ mol/glucose unit. [10] $1/\overline{DP}_t$ plotted against t (duration of the thermal treatment) shows a correlation, consisting of linear sections. The knickpoint in its initial range gives evidence, according to Philipp [8] on thermohydrolytic decomposition. 70—90 kJ/mol was calculated as the gross energy of activation in the hydrolytic main step of thermolysis.[10] Chemical changes in cellulose, brought about by thermal treatment could be followed by the analysis of functional groups. Evidence could be found on three simultaneous reactions: the hydrolysis of glucosidic linkages, the oxidation of the liberated aldehyde groups and the partial decarboxylation of the formed carboxylic groups.[10]

The extent and rate of water vapor sorption of cellulose can be increased by swelling, but can be decreased by thermal treatment. The two operations usually overbalance each other.

The initial part of the fixed water molecules is due to chemisorption. Over the monomolecular coverage of the substrate only weaker forces bind further adsorbed water molecules to the adsorbent. The initial active surface area of regenerated cellulose, calculated from data of its water vapor adsorption, proved to be 74,4 m^2/g. This value was reduced to 41,5 m^2/g by a thermal treatment at 210°C for 300 s.[10]

The originally 6,4% chemisorbed water content of regenerated cellulose, measured by the determination of dielectric loss factor, could be reduced to 5,0% by the similar thermal treatment.[10]

Based upon the above theoretical conclusions the earlier elaborated Thermotex process could be optimized. [11, 12]

2. Interaction between cellulose and reactive dyestuffs

The increase in the proportion of reactive dyes bound covalently to cellulose is being one of the most important problems of reactive dyeing. One has to calculate, even recently, with a significant loss in dyestuffs in this process.

The heterogeneous chemical processes could be studied, in cellulose—reactive dye systems, by means of reaction kinetics. Simultaneous chemical processes, mostly overlapping each other, have been dealt with. The dyeing process had to be optimized in order to make the formation of covalent bonds dominant with a simultaneous drop in the rate and extent of hydrolysis of reactive groups. A new linear kinetical correlation was elaborated as a model for the representation of the reactive dyeing process. [13]

Correlation could be detected between the efficiency and some characteristic constants of the reactive dyeing process. The efficiency of dyeing is mostly influenced, beside the structure and the reactivity of the dyestuff, by the accessibility of cellulose. Rapid and great initial dye pick-up could be achieved in the swollen surface layers of the fibres by meens of structure loosening chemical pretreaments.[14]

The electric charge in the surface of cellulose is characteristically influenced by the ionic strength of alkali and electrolyte, applied in the dyeing process. The diffusional transfer process in reactive dyeing is controlled by the negative charge of cellulose as well as by the affinity of the dyestuff and by the equilibrium in the adsorption of the dye on cellulose. The last two features are also depending on the ionic strength in the system.[14]

Based upon the theoretically elaborated correlations 20—30% increase in reactive dye pick-up could be achieved in a modified cotton dyeing process.

An amino acid analysis, subsequent to reactive dyeing of wool, gave evidence on the increase in the relative proportion of proline, serine and glycine as well as on the simultaneous drop in the relative proportion of alanine, leucine, iso-leucine, lysine and asparatic acid in the reactive dyed wool.[15]

3. Hot mercerizing

Rapid and more uniform penetration of caustic soda solution can be achieved in hot (60—95°C) mercerizing of cotton by means of applying the "Thermotex" principle. Mercerizing and scouring of cotton can be abbreviated to a single process if hot mercerizing is followed by steaming and rinsing.[16, 17, 18]

Parallel conformation of segments of cellulose molecules in the unit cell is changing to an antiparallel one in the course of mercerizing. Partial desintegration of microfibrils occur simultaneously to elementary fibrils. Consequently the distance is significantly diminished between two neighboring microfibrils leading to an increase in the active surface area. The rate of caustic penetration is the function of the temperature and the concentration of the alkali.[19] Definitely higher increase in the active surface area of cellulose is the consequence of hot mercerizing, rather than that of the conventional process. Less deterioration in the hand of the fabric occurs after hot treatment than after the cold one. Improved absorbance and better dimensional stability are brought about by hot mercerizing. Both treatments cause equal increase in luster of the fabric surface and in the tensile strength of the mercerized fabrics. The decrease in the total volume of pores is less after hot treatment than after the conventional one.[20, 21, 22, 23]

4. Generation and application of activated (singlet) oxygen in bleaching

Selective oxidation of impurities in the course of bleaching cellulosic fibres cannot be completely achieved by the conventional belaching operations. Degradation of cellulose is conseqeuntly unavoidable. Rapid, mild bleaching is only possible with well controlled oxidizing systems of high selectivity. Such systems could be made available by applying subsequent treatments with sodium hypochlorite and hydrogen peroxide solutions, respectively if they are applied in proper medium (C_2HCl_3, C_2Cl_4, CCl_4) and under proper conditions. Periodical variation with a number of treatments with hypochlorite and peroxide separately in aqueous system, subsequent to combined hot mercerizing and scouring, leads to mild, selective bleaching.[24, 25, 26, 27]

5. Characterisation of cellulose modified by resin finishing

Resin finishing is necessary to render cellulosic fabrics crease resistant and dimensionally stable. This modification, however, is bringing about significant loss in tensile strength and elasticity of the textiles. Most of the resin monomers are N-methylol compounds, consequently formaldehyde may be released from the finished fabrics. Change in colour and in the fastness properties of dyed or printed fabrics is very often caused by resin finishing. To reduce the loss in tensile strength and in the amount releasable formaldehyde, as well as the protection against colouristic deterioration were goals of our research work.

The loss in tensile strength could be reduced by 30—50%, due to the addition of urea to the padding solution containing N-methylol compounds and catalyst, keeping the wanted crease recovery angle unchanged. Best results could be achieved by the combination of a non reactive resin (TMM) with a reactive one (DMDHEU) and with urea (U) in the proportion of U : TMM : DMDHEU = 1 : 0.5 : 0.5. Application of a combined catalyst (proton acid and Lewis acid) in the mentioned solution, and curing at lower temperature (140°C instead of 160°C) for a shorter time ($T \leq 3$ min) leads to the wanted crease recovery with a significantly reduced loss in tensile strength.[28] Analysis and characterization of the combined resin content of the fabric gave evidence to the presence of built in urea in the crosslinks caused by DMDHEU.[29, 30] Subsequently less in number, but more elastic crosslinks are formed.

Deteriorated comfort feeling may accompany the use of resin finished clothing. This is mainly due to its reduced adsorption capacity to water vapor and to a reduced ability to water retention. Further characteristic parameters, as the initial rate and equilibrium value of the vertical water sorption were also measured.[31] The following changes could be observed on cotton fabrics after resin finishing:

	water retention %	moisture regain %
untreated	40	6—8
finished	15—20	4,5—6,5

Slower initial moisture transfer and reduced absorbance are also characteristic to resin finished cotton.[31]

The modification with urea and the use of $Zn(NO_3)_2$ as catalyst enable the keeping of the amount of releasable formaldehyde below the allowed maximal value. Inaccuracy of the standard analytical methods could be improved by measuring the kinetics of formaldehyde release and by evaluating significant data of the derived curve.[32]

Colouristic deteriorations caused by finishing with DMDHEU proved to be significatly dependent on the quality of the applied catalyst. $Zn(NO_3)_2$ is the most dangerous and $MgCl_2$ the least deterioratiang is that respect.[33, 34]

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