

## Preparation of thermoplastic cellulose based fibre materials and their application in the manufacturing of thermoformable papers

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One of the current key research topics at Papiertechnische Stiftung (PTS) is the chemical transformation of commercially available cellulose pulp into added-value fibre materials such as thermoplastic pulp. As shown in Figure 1 the obtained cellulose derivatives were used to manufacture papers with maximum thermosensitive material elongation up to 50 % that can be thermoformed, too.

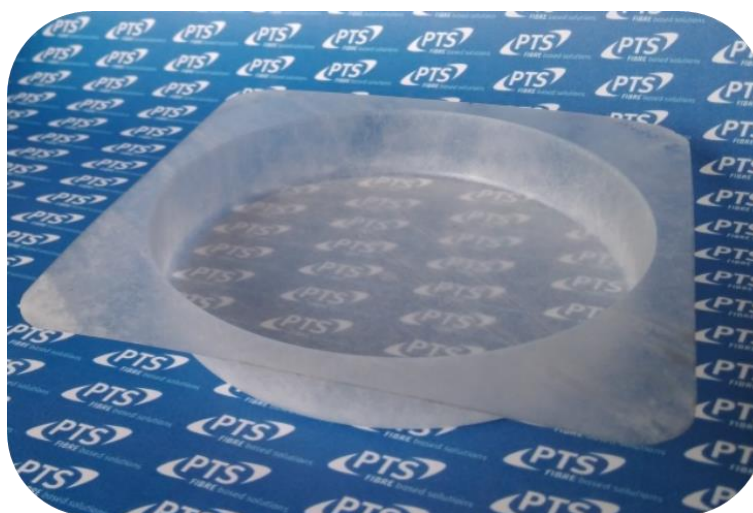


Figure 1: Thermoformed dialcohol cellulose tray

According to “Statistisches Bundesamt” in Germany 63.3 % of packaging material used in transport and packaging sector in 2017 was paper, cardboard and board, measured in terms of the volume of waste collected. [1] In the area of used sales packaging for private consumers only 21.1 % were paper-like products, while nearly half of the material was light weight packaging (plastic, composite and metal). [2] This may be attributed in particular to a high level of plastic formability, which is required for the production of large quantities of packaging products with individual and functional geometries by thermoforming and press forming techniques. Unfortunately paper materials are not suitable for those processing techniques due to their lack of thermoplasticity.

However, cellulose pulp can be modified chemically in a partial manner to provide thermoplastic papers. Therefore a simple aqueous glycol cleavage oxidation reaction with sodium periodate ( $\text{NaIO}_4$ ) to a ring-opened cellulose derivative named dialdehyde cellulose (roC-CHO) can be performed followed by a subsequent aqueous reduction by sodium borohydride ( $\text{NaBH}_4$ ) to dialcohol cellulose (roC-OH) (Figure 2). [3]-[5]

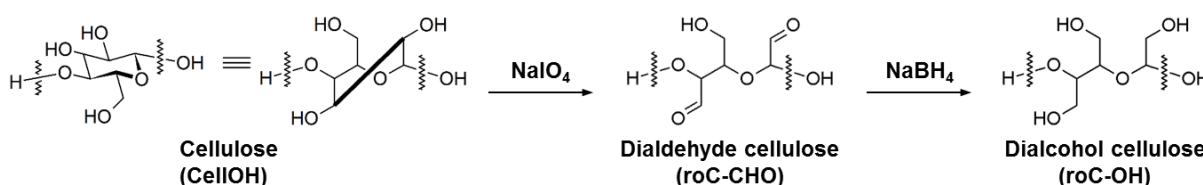


Figure 2: 2-step derivatization of cellulose to dialcohol cellulose (roC-OH)

### Optimization of reaction protocol

According to the state of the art 4.1 equivalents of  $\text{NaIO}_4$  are required for the oxidation of cellulose to roC-CHO within a reaction at room temperature at a stock consistency of 0.4 % (all values based on dry cellulose). [4] Since the theoretical necessary amount for a 100% degree of oxidation (DO)

is 1 equivalent, a large excess of chemicals is applied which makes the overall process inefficient and expensive. In addition to this  $\text{NaIO}_4$  is a hazardous chemical and its reduction would make the overall process more safely. In order to make the process more efficient, we focused on three target directions: The excess of reagents should be decreased, the stock consistency of the reaction mixture increased and the reaction times should be shortened to the maximum possible extent.

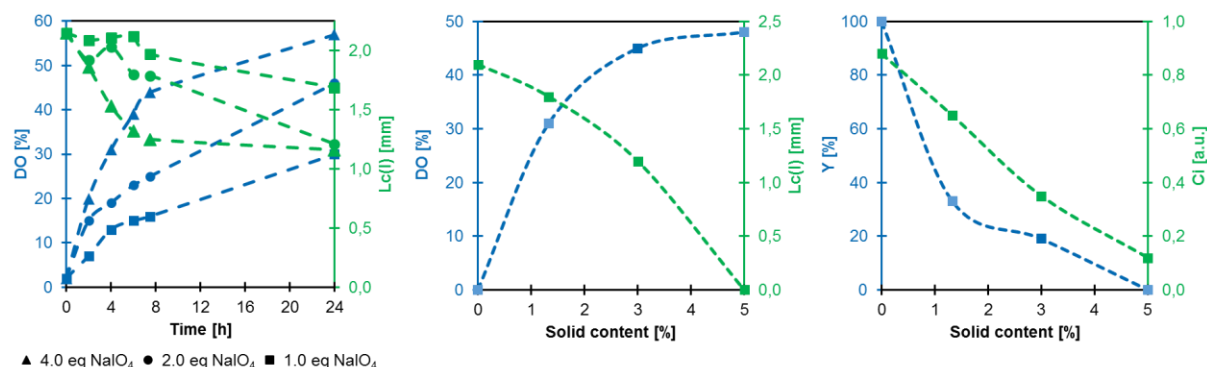


Figure 3: Optimization of oxidation reaction at 25 °C: influence of used sodium periodate amount as oxidizing agent at 1.5 % stock consistency (left) and influence of stock consistencies (based on dry fibrous material) during reaction with 1 eq  $\text{NaIO}_4$  after 24 h oxidation time (middle and right). Ci: crystallinity index; DO: degree of oxidation, proportion of modified cellulose anhydroglucose units; Lc(l): fibre contour length (length weighted); Y: reaction yield after  $\text{NaBH}_4$  reduction

On the basis of the optimization it was determined that reduction of the periodate to the theoretically necessary amount leads to about half the oxidation extent of  $\text{CellOH}$  to  $\text{roC-CHO}$  compared to the literature (Figure 3 left). However, it was possible to improve the degree of oxidation obtained in relation to the amount of periodate required and thus the efficiency of the reaction. From previous investigations it was known that the total thermosensitive material elongation is based on the elongation of the individual fibres, for which reason fibre degradation by the oxidation reaction shall be avoided. [5] From this point of view the reactions with reduced periodate amount and thus less possibilities for side reactions, but particularly with 1 equivalent  $\text{NaIO}_4$ , are advantageous.

Based on this, an optimization towards higher stock consistencies during the reaction was carried out. The optimum was found to be about 1.3 wt% (based on cellulose). For higher stock consistencies, a decreased crystallinity within the fibre structure of the respective fibres was observed, which collects with deteriorating yields after the reduction of  $\text{roC-CHO}$  to  $\text{roC-OH}$  (Figure 3 right). The explanation for this observation can be given by several reasons. Although chemical modification at cellulose start in amorphous fibre regions, crystalline parts are also modified and become amorphous. This reduces the overall crystallinity. However the aldehyde groups of  $\text{roC-CHO}$  stabilize the fibrous structure by intra- and intermolecular hemiacetal formation [6], [7] leading to a pulp with only minor visual changes in appearance and rather no yield loss. By subsequent reduction of the  $\text{roC-CHO}$  to  $\text{roC-OH}$ , the aldehyde groups are converted into hydroxyl groups, thus the possibility of hemiacetal formation is lost making strongly modified and amorphized fiber components water-soluble and reduces the yield of  $\text{roC-OH}$  pulp. [8], [9]

Next to the oxidation the reduction  $\text{roC-CHO}$  to  $\text{roC-OH}$  was investigated and optimized, too. Sodium borohydride has been proven in literature to work well in an aqueous phosphate buffer system with the chemicals and excesses listed in entry 1 of Table 1. [4]

Table 1: Optimization of reduction reaction at 25 °C applying  $\text{roC-CHO}$  with DO = 37 %

Entry	eq $\text{NaBH}_4$ (AGU)	eq $\text{NaBH}_4$ (CHO)	c $\text{NaH}_2\text{PO}_4$ [mol/l]	Residual DO [%]	Yield [%]
1	2.10	22.7	0.38	3	66
<b>2</b>	<b>1.00</b>	<b>10.8</b>	<b>0.00</b>	<b>&lt; 1</b>	<b>64</b>
3	0.37	4.0	0.00	6	66

4	0.19	2.0	0.00	9	62
5	0.19	2.0	0.38	26	86

AGU: anhydroglucose unit, CHO: aldehyde groups, DO: degree of oxidation

By adjusting the amount of borohydride, it was found that the theoretically necessary equivalents of borohydride were not sufficient for complete reduction (entry 4). In addition, it was observed that the buffer system had a negative effect on the reduction (entry 5). We were surprised by this result, but an explanation can be given as follows: A borohydride solution has its highest stability at high pH values and decomposes in acidic and neutral pH under hydrogen evolution and metaborate formation. This increases pH and therefore borohydride stability. In case of the buffered reaction the borohydride is decomposed until the buffering system is depleted, which decreases the reduction efficiency and results in higher residual DO. The reduction rate is increased by higher pH values, too. [10]

Overall, it was found that the use of 1 equivalent  $\text{NaBH}_4$  (related to AGU) leads to a complete reduction within the reaction time of 1 hour (entry 2).

### Thermomechanical Properties

For characterization of the thermomechanical properties, the pulps were transferred into sheets by Rapid-Koethen process and analyzed by DSC for their glass transition or melting behavior as well as temperature assisted tensile testing for their temperature dependent softening behavior. The results from DSC measurements are shown in Figure 4 (left). On the basis of these investigations a glass transition in the range of 85-100 °C was determined for sheets prepared from roC-OH pulps.

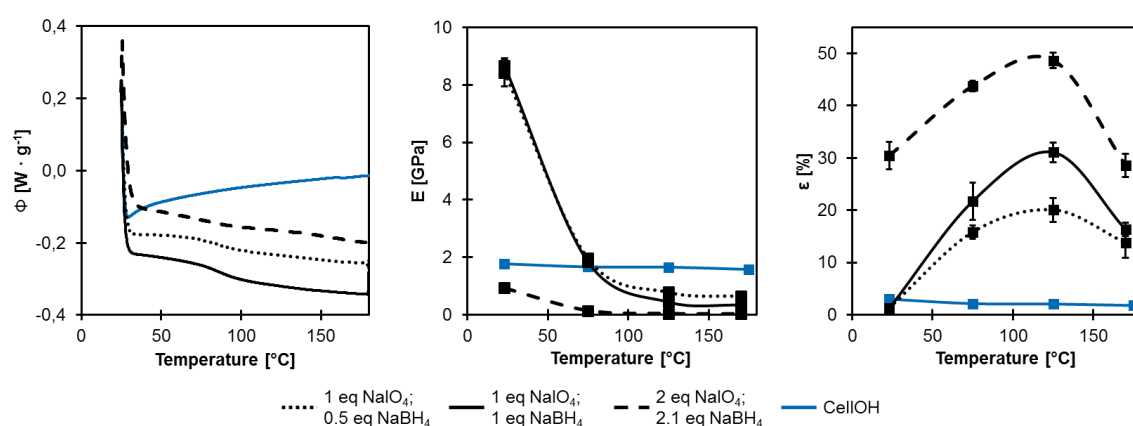


Figure 4: Influence of reaction conditions during two step roC-OH synthesis on thermomechanical properties of corresponding papers: Differentials Scanning Calorimetry (DSC) (left) and temperature assisted tensile testing: Young's modulus (E) (middle) and elongation at break ( $\epsilon$ ) (right),  $\Phi$ : heat flow

To characterize the temperature depending softening behavior and mechanical material characteristics, the temperature range 23-175 °C was investigated by temperature assisted tensile testing (Figure 3) with respect to Young's moduli (middle) and elongation at break (right).

The maximum elongation at break for all samples prepared was observed in the range of 75-125 °C, which correlates well with glass transition range. Above these temperatures the elongation at break decreases, assumably due to the evaporation of material's moisture.

In addition to the amount of periodate used for oxidation, which significantly influences the degree of oxidation, it is necessary to completely reduce the samples in order to obtain a high elongation at break. The sample which was oxidized by 1 eq  $\text{NaIO}_4$  and reduced by 0.5 eq  $\text{NaBH}_4$  shows residual aldehyde groups that form hemiacetals and hence decrease thermal elongation as well as temperature induced material's softening. Furthermore it was found out that by application of the lowest amount of 1 equivalent of periodate during oxidation, materials with the highest stiffness at ambient temperature among the investigated samples are obtainable.

## Conclusion

The possibility of 2-step reaction optimization from cellulose pulps to roC-OH pulps and the thermomechanical properties of dialcohol cellulose papers was investigated. It was found out that an increase of stock consistencies in combination with reduction of applied periodate amounts during oxidation is possible. This observation as well as the opportunity to save borohydride during reduction by non-utilization of phosphate buffering makes the overall process more effective. The obtained dialcohol cellulose papers showed temperature induced softening and maximal elongations up to 50 % in their glass transition range of 85-100 °C.

## Outlook

Deeper investigations into the subjects of impacting parameters to thermoplastic properties, fibre retention and flocculation as well as the optimization of drainage are currently being carried out at PTS. In addition, pathways for making the reactions more economically e. g. by reoxidizing the periodate/iodate liquor electrochemically [11] are under development.

## Acknowledgement

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## Literature

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