

CHEMICAL MODIFICATION OF PULP FIBRES FOR THE PRODUCTION OF THERMOFORMABLE PAPER

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ABSTRACT

Enhancing the usability of paper based materials in forming processes is one major objective to pave the way for a sustainable and bio-based economy. Therefore, modifications of either the forming process or the paper material will provide future opportunities. The present study focuses on the concept of chemical pulp fibre modification as a factor influencing the formability of paper materials made thereof. Specifically, covalent attachment of ester moieties with different chain lengths onto cellulose pulp fibres, a surface polymer grafting and a two-step glycol cleavage-reduction approach were chosen as modification strategies. The resulting materials were characterised regarding their chemical composition and thermomechanical properties. To evaluate their formability, a temperature controlled tensile test was used.

INTRODUCTION

For the purpose of producing primary packaging products with complex shapes like trays, yoghurt cups, inserts or blisters, petroleum-based polymers like polypropylene, polyethylene terephthalate or polystyrene are processed using so-called thermoforming methods. In these methods, flat sheets are heated and then moulded to receive three-dimensional objects.¹ Paper, containing mainly cellulose as the most abundant biopolymer on earth, would be a sustainable as well as an

environment-friendly alternative. However, formability of paper is limited because the material behaviour differs strongly from that of common polymers, mainly since plastic material deformation is possible to only a small extent due to the lack of cellulose thermoplasticity.² Therefore an extensive usage of paper-based materials in high-quality industrial forming processes has not been possible yet or is limited to simple geometries.

In order to enhance the usability of paper like materials in these processes, a modification of either the forming process or the paper material itself is necessary, which is the basis for extensive research efforts. The present work is dedicated to the adaptation of different forming techniques, such as deep-drawing, thermoforming, hydroforming, press-forming or hot-stamping, to the requirements of paper materials on the one hand, and to the fabrication of suitable materials on the other hand.³ However, since the necessary material properties depend strongly on the forming technique used both aspects have to be considered together. A general classification into sliding and fixed blank processes turned out to be useful. The corresponding material limitations and requirements are stated in Table 1.^{4,5}

Whereas sliding blank processes are more or less suitable for paper, *fixed blank* forming (mainly thermoforming) is the predominant method used in industry. Therefore research has been carried out to improve the elongation potential of paper, which has been identified as one of the main factors determining its formability.^{4,6} Physical concepts containing axial compression of the fibre network, or the pulp fibres themselves, led to potential strain values of around 20%, which is far beyond the limits typical for paper.⁷⁻¹² However, to compete with petroleum-based thermoplastics in fixed blank sheet forming processes, even higher elongation is required.¹³

Several examples show that chemical cellulose modification pathways lead to significant changes in the thermomechanical properties of the initial material.¹⁴⁻¹⁸

Table 1. Material requirements on different principles of sheet forming^{4,5}

<i>Category</i>	<i>Sliding blank processes</i>	<i>Fixed blank processes</i>
Primary limitation	Formation of wrinkles	Insufficient elongation
Requirements	High compressive strain and strength	High tensile strain and strength
	Low density	Low static paper to metal friction
	High dynamic paper to metal friction	Low elastic recoverable strain
	Low elastic recoverable strain	
	High fibre mobility	

This leads to the assumption that thermoformable paper-based materials can be fabricated in this way. It has to be shown that the resulting thermoplastic properties are adequate to meet the requirements of thermoforming processes.

The present study focuses on the concept of chemical pulp fibre modification as a factor influencing the thermoformability of paper materials made thereof. Specifically, covalent attachment of ester moieties with different chain lengths onto cellulose pulp fibres, surface polymer grafting and a two-step glycol cleavage-reduction approach were chosen as modification strategies. The resulting materials were characterised regarding their chemical composition and thermo-mechanical properties. To evaluate their formability, a temperature controlled tensile test was used.

EXPERIMENTAL

Modification procedures

All chemical reactions were carried out with unbeaten Northern Bleached Softwood Kraft Pulp (NBSK) as cellulose source. Pulp sheets were disintegrated in tap water and dried at room temperature. All commercially available chemical reagents were used as delivered unless otherwise stated. Syntheses under microwave irradiation were performed in a *Siemens Top-Line electronic* microwave.

Acetylation

Acetylation of pulp was performed according to a modified solvent-free method.¹⁹ An example protocol is comprised of the following steps: Acetic anhydride (600 mL, 6.35 mol) and sulphuric acid (98%, 0.6 mL, 11.0 mmol) were mixed in a large diameter beaker, and NBSK pulp (120.0 g dry, 740 mmol) was added. The resulting mixture was vigorously stirred by hand for 1 min and left to react for 5 h at room temperature almost without stirring, i.e. the reaction mixture was agitated only once per hour. Afterwards, the acetylated pulp was filtered over a Büchner funnel equipped with a filter and suspended in water. Filtration, two additional washings in water and air drying led to a pale white acetylated pulp material (120.8 g, DS = 0.27).

Hexanoylation

Cellulose pulp was hexanoylated in a heterogeneous manner.¹⁶ Before the modification reaction, a solvent exchange was done: NBSK (40.0 g dry, 247 mmol) was disintegrated in water (1 L) and filtered off subsequently. This procedure was

repeated twice with acetone (500 mL each) and then twice with dichloromethane (500 mL each). The resulting pulp material was dried at 50 °C in an oven overnight. Afterwards, toluene (1 L), hexanoyl chloride (33.3 g, 247 mmol) and pyridine (23.4 mL, 296 mmol) were added and the mixture was refluxed for 6 h. The reaction mixture was filtered over a Büchner funnel equipped with a filter, and the modified pulp material was washed two times with dichloromethane (500 mL each) and acetone (500 mL each). Soxhlet purification of the material with dichloromethane for 8 h and subsequent air drying led to a pale white hexanoylated pulp product (47.7 g, DS = 0.82).

Polycaprolactone grafting

Grafting-from polymerisation with caprolactone was carried out using different methods based on modified literature procedures:^{18–22}

Method A: Before the modification reaction a solvent exchange was done as described above for ‘Hexanoylation’. The prepared NBSK pulp (40.0 g dry, 247 mmol) was dispersed in toluene (1 L), and ϵ -caprolactone (782 g, 6.86 mol) as well as tin (II) 2-ethylhexanoate (13.8 mL, 42.5 mmol) were added. The resulting mixture was stirred under reflux for 5 h after which the flask was removed from the heating source and quenched by the addition of tetrahydrofurane. Washing with dichloromethane and subsequent Soxhlet extraction for 24 h with dichloromethane led to pale white PCL grafted pulp fibres (41.2 g, DS = 0.26).

Method B: Before the modification reaction a solvent exchange was done as described above for ‘Hexanoylation’. The prepared NBSK pulp (40.0 g dry, 247 mmol) was poured into a beaker, and ϵ -caprolactone (1512 g, 13.3 mol) was added. The resulting mixture was stirred vigorously, and tin (II) 2-ethylhexanoate (5.6 mL, 17.3 mmol) was added afterwards. After additional stirring the reaction mixture was placed in a microwave for 5 min at 360 W. The mixture was cooled down subsequently, and Soxhlet extracted with dichloromethane for 24 h. Drying at room temperature led to a yellowish PCL-g-cellulosic pulp (43.1g, DS = 0.28).

Method C: ϵ -caprolactone (84.4 g, 741 mmol) and phosphoric acid (85%, 2.2 mL, 37 μ mol) were diluted in water (500 mL) under vigorous stirring, and the solution was added to NBSK pulp (40.0 g dry, 247 mmol) in a beaker. This mixture was stirred by hand for 2 min and placed in a preheated drying oven (95 °C) for 24 h. Afterwards, the mixture was cooled down to room temperature. The resulting crude bulk material was Soxhlet extracted with dichloromethane for 6 h in order to remove PCL homopolymer, and afterwards intensely washed with water to

remove any acidic traces. Air drying at room temperature led to pale white PCL-g-cellulosic pulp fibres (48.7 g dry, DS = 0.42).

Glycol cleavage and reduction

An example protocol for the two-step synthesis of dialcohol cellulose following a modified literature procedure^{23,24} is given below: NBSK pulp (250 g dry, 1.54 mol) was suspended in water (11.4 L) in a baffled round bottom flask, and isopropanol (716 mL) as well as NaIO₄ (330 g, 1.54 mol) were added. The flask was fit onto a rotary evaporator with reflux setup and rotated for 8 h at 50 °C in the dark. Afterwards, the reaction mixture was filtered over a Büchner funnel equipped with a filter, and the modified pulp was washed intensely with water three times. Air drying yielded dialdehyde cellulose (DO = 0.44) which in turn was suspended in 37.5 mM NaH₂PO₄ solution (16.7 L). Afterwards, sodium borohydride (123 g, 3.25 mol) was added in small portions to slow down the accompanying hydrogen evolution. The reaction mixture was stirred for 4 h at room temperature and subsequently filtered over a Büchner funnel equipped with a filter. Intense washing with water and air-drying led to a colourless dialcohol cellulose pulp (86.8 g, 533 mmol).

Analysis of modified pulp materials

Quantitative determination of ester moieties was carried out via saponification and subsequent acid-base titration of the resulting free carboxylic groups.^{25,26} Carbonyl functions were determined after conversion into the corresponding oximes.^{23,27} For esterified and polycaprolactone grafted samples the degree of substitution (DS) is given as the amount of monomeric substituents per anhydroglucose unit. For dialcohol cellulose fibres, the degree of oxidation (DO) is given as the percentage of C2-C3 cleaved anhydroglucose units.

Fibre dimensional analyses were performed with an optical *Metso FiberLab* measurement system according to TAPPI T271om-02. Infrared spectra (IR) were recorded using a *Bruker Tensor 27* Fourier transform infrared spectrometer in the attenuated total reflectance (ATR) mode from 600 to 4000 cm⁻¹ and at a resolution of 2 cm⁻¹ within 32 scans. Spectra were baseline corrected. Water retention values (WRV) were measured according to ISO 23714:2007.

Sheet forming

The Rapid-Köthen method was used to produce laboratory sheets in accordance with ISO 5269-2. Pulping was carried out in accordance with ISO 5263. The laboratory sheets were prepared with a constant grammage of 250 g/m² and a

deviation of $\pm 15 \text{ g/m}^2$. Drying was performed in a restrained manner by placing the wet fibre web between two sheets of siliconised paper and exposing it to $94 \text{ }^\circ\text{C}$ under a reduced pressure of 960 mbars for 30 min. The esterified and polycaprolactone grafted samples were additionally hot pressed at 523 N/cm^2 and $180 \text{ }^\circ\text{C}$ for 5 min using a *Vogt P300S* laboratory press. The resulting sheets were stored at $23 \text{ }^\circ\text{C}$ and 50% rH.

Temperature-controlled tensile test

The tensile properties of paper samples were measured according to DIN EN ISO 1924-2. However, the method was modified for higher test temperatures: A vertical tensile tester *TIRA test 2805* was equipped with a ceramic heating element containing two heating surfaces (45 mm length). The sample was placed in the tensile tester with a free clamping length of 50 mm and leaving a 2 mm gap between both heating surfaces. After heating the sample for 30 s, the test was started. For each sample, tensile tests were performed at 23, 75, 125 and $170 \text{ }^\circ\text{C}$ and an ambient humidity of 50% rH. An experiment with combined optical strain measurement was carried out using an additional *Pike F-100B* camera system with *VEDDAC 6 (Chemnitzer Werkstoffmechanik GmbH)* software. In these tests, heat was applied by a *Bosch GHG 660* digital heat gun instead of the above-mentioned ceramic heating element, where error bars represent standard deviation.

Moulding experiments

Moulding trials were carried out with only some of the paper samples obtained. A fixed blank deep drawing setup comprising mainly a cavity and a stamp according to Figure 1 was used. The sheets were clamped between two stainless steel plates and radiation-heated from below. The temperature was measured at the upper sheet surface with a *DIAS Pyrospot DT 4L* contactless infrared thermometer (recording wavelength 8–14 μm , emissivity 0.9) located in the centre of the stamp. After reaching the desired temperature the stamp was moved into the sheet at a feed rate of 0.5 mm/s. The maximum drawing height was determined by evaluating the failure limits at preselected stamp levels in 2 mm steps. Formability strain was calculated by means of the formula

$$\varepsilon_F = \frac{2h + d}{d}$$

where ε_F is the formability strain (%), h is the maximum drawing height (mm) and d is the initial free diameter (mm) of the sheet sample.

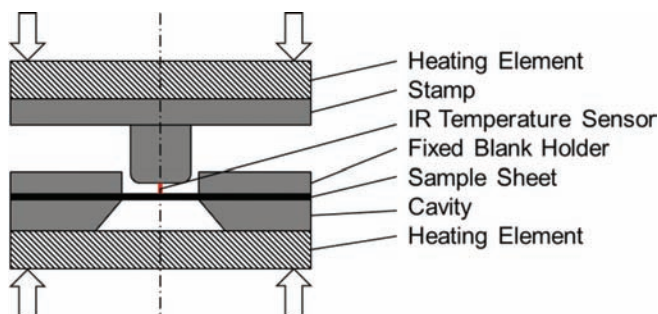


Figure 1. Schematic of the fixed blank laboratory thermoforming device used.

RESULTS AND DISCUSSION

Chemical modification of pulp fibres

In the first part of the study covalent esterification, namely acetylation, hexanoylation and different types of polycaprolactone grafting were carried out in order to provide the individual pulp fibres with thermoplastic intra-fibre bonds. While it is well known that thermoplastic cellulose derivatives may be achieved by esterification in a homogeneous manner,²⁸ preserving the formerly rigid pulp fibre architecture is a major requirement for the subsequent production of paper materials. To achieve this, heterogeneous synthetic procedures in non-swelling media were used. Table 2 shows the esterified cellulose pulps and a basic characterization thereof.

Acetylation experiments were carried out using the acetic anhydride-sulphuric acid system according to a previously reported solvent-free procedure¹⁹ (Figure 2). Following this strategy, highly acetylated fibres with bulk DS values up to 2.50 (Ac-3) were generated. It has to be noted that the initial fibre structure was retained even at this high value. A heterogeneous modification strategy using hexanoyl chloride and pyridine in toluene¹⁶ proved to be successful for the surface hexanoylation of pulp fibres. In order to diminish the formation of free hexanoic acid resulting from water in the reaction mixture and to sufficiently separate the individual fibres, the pulp materials were solvent-exchanged prior to the reaction. Following this strategy cellulose hexanoates were obtained with DS values of up to 0.82.

To substitute the cellulosic hydroxy groups with longer alkyl chains we chose graft polymerisation with polycaprolactone in three different ways (Figure 3):

Table 2. Modified pulp materials with basic properties. WRV = water retention value, $L_c(l)$ = length weighted mean fibre contour length, $Fines_c(l)$ = length weighted fines content based on contour length.

Entry	Sample	Bulk DS/DO	WRV [g/g]	$L_c(l)$ [mm]	$Fines_c(l)$ [%]	Wall thickness [μm]
1	Ref	0	0.84	2.1	3.1	8.0
2	Ac-1	0.27	0.53	1.8	5.4	7.9
3	Ac-2	0.45	–	1.6	7.6	7.7
4	Ac-3	2.50	0.25	1.5	3.0	9.8
5	Hex-1	0.08	0.40	2.0	3.0	7.8
6	Hex-2	0.51	–	0.6	17.3	9.9
7	Hex-3	0.82	0.13	0.8	11.5	9.3
8	PCL-A	0.26	0.51	2.3	1.2	9.0
9	PCL-B	0.28	0.44	1.89	2.1	8.9
10	PCL-C	0.42	0.23	1.4	3.7	8.9
11	DAI-1	0.22	1.33	2.1	1.4	6.8
12	DAI-2	0.39	–	1.4	2.3	4.6
13	DAI-3	0.44	2.57	1.1	1.4	3.0

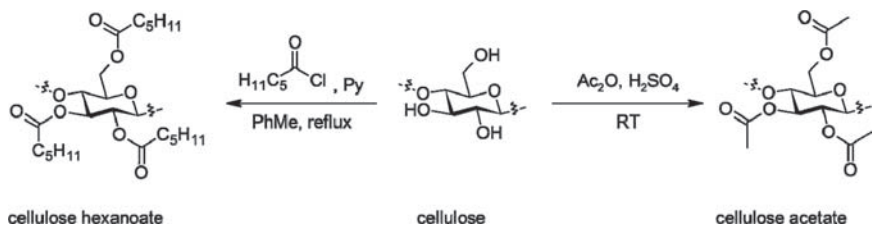


Figure 2. Esterification of cellulose to cellulose hexanoate and cellulose acetate.

Additionally to the standard procedure of tin (II) catalysed grafting-from polymerisation in refluxing toluene^{18,20} (Method A) or in a solvent-free manner²¹ (Method B) an environment-friendly Brønstedt acid catalysed transformation developed in our laboratories²² (Method C) was carried out. The resulting samples were obtained by optimised procedures and represent the maximum modification values achieved during our research. From this point onwards, method C led to the highest degree of substitution of 0.42.

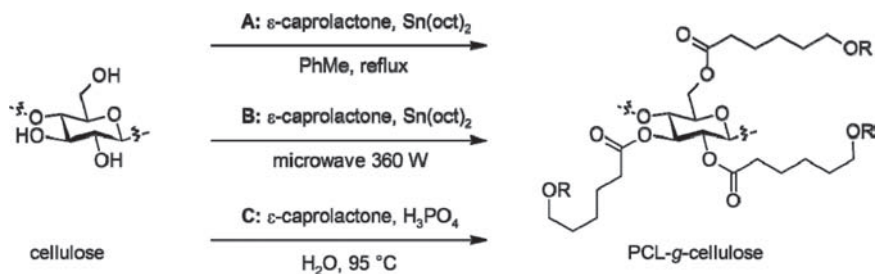


Figure 3. Different methods for grafting polycaprolactone from cellulose fibres. oct = 2-ethylhexanoate, R = further 6-hydroxyhexanoyl moieties.

In addition to the titrative DS determination, the chemically modified pulp materials were subjected to FTIR spectroscopy. Compared to the FTIR spectrum of unmodified pulp, the esterified as well as PCL-grafted samples (Figure 4) showed significant C=O stretching vibration at $\approx 1730\text{ cm}^{-1}$ confirming the successful formation of covalent bonds between cellulose and the respective substituent. The hexanoate and PCL-g-cellulose spectra showed stretching vibrations at $\approx 2870\text{ cm}^{-1}$ resulting from the substituent's alkyl moieties which are less frequent in acetylated celluloses. Additionally, a decrease in O–H stretching vibration at $\approx 3300\text{ cm}^{-1}$ was observed resulting from decreased free hydroxy functions. In the case of the acetylated sample, hydroxyl groups could hardly be detected, indicating a very high degree of substitution. This was also in agreement with the value determined by titration.

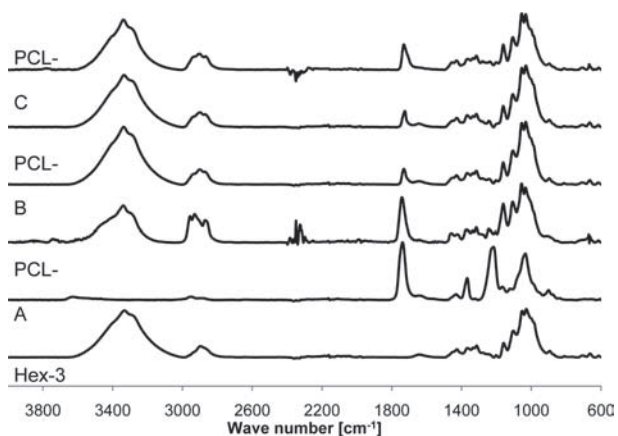


Figure 4. FTIR spectra of esterified and polymer grafted pulps.

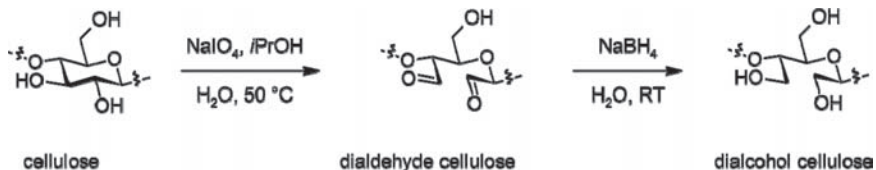


Figure 5. Glycol cleavage-reduction sequence leading to dialcohol cellulose. iPr = 2-propyl.

In the second part of the study, we prepared fibres consisting partly of dialcohol cellulose. For this purpose, a modified two-step protocol was used where the anhydroglucose rings were cleaved chemoselectively during an oxidative Malaprade reaction, and the resulting aldehydes were reduced to the corresponding primary alcohols under standard conditions (Figure 5).^{23,24} This synthesis process led to pulp fibres with up to 44% cleaved anhydroglucose units.

Fibre properties

As result of a successful surface modification, we expected changes in the hydrophilic properties of modified pulp samples and the water retention value as an empirical factor indicating the amount of bound water. For all esterified as well as polymer grafted pulps, a decrease in water retention values was observed caused by the attachment of hydrophobic substituents onto cellulose backbones.

By contrast, a significant increase in water retention was observed in the oxidised-reduced pulp samples with increasing degrees of substitution. This indicates an increased accessibility of the hydrophilic cellulose chains and thus extended molecular mobility of individual cellulose nanofibrils.²³

We furthermore investigated changes in the fibre morphology of modified pulp materials. All samples had kept their fibre character. Esterification and polymer grafting reactions led to fibre shortening and increased fines content especially in the case of higher modification degrees resulting from a combination of shear force application and chemical degradation. Especially hexanoylation led to considerable fibre shortening. However, considering the harsh reaction conditions the values were according to our expectations. Interestingly we also noticed an increase in fibre wall thickness of up to 2 μm with increasing modification for all esterification and caprolactone grafting methods that could be traced to an altered constitution of the fibre walls.

The oxidised/reduced samples showed moderate fibre shortening. Since the whole modification procedure took place in water and at low stock consistency,

the shear forces applied caused no dramatic mechanical stress on the fibres. However, a partial dissolution effect accompanying the chemical transformation and thus generation of water soluble fractions could be proven by a decrease in fines as well as a significant drop in fibre wall thickness from 8.0 to 3.0 μm . This result is further supported by yield losses during the modification process, especially in the case of higher oxidised samples.

Thermomechanical properties of modified pulp sheets

The above-described pulp materials were used to prepare laboratory sheets with a grammage of 250 g/m^2 . All esterified and polymer grafted pulp materials resulted in sheets with a similar appearance compared to unmodified paper despite the fact that a significantly softer feel was observed caused by weaker fibre-fibre interactions. For a thermoplastic paper compound, the sheets were hot pressed to activate the thermoplastic areas of individual pulp fibres. This fusing was to enable the entanglement of derivatised cellulose or graft chains and had been shown to be sufficient for systems containing modified pulp fibres on the one and unmodified cellulose fibres combined with latices on the other hand.^{14,16,17,29} The dialcohol cellulose sheets produced behaved differently; a consolidated material was obtained already after the sheet forming process. The samples DA1-2 and DA1-3 were nearly completely transparent. An additional hot-pressing step had been reported to change the room temperature elongation values of the materials in an unfavourable manner²⁴ and was therefore not carried out within the present study. Since the density values of all modified materials were higher than 0.9 g/cm^3 and thus different from conventional paper, the above-described sheet materials could be considered to be fibre-matrix composites.

As stated above, elongation is the major requirement for sheet materials in fixed blank forming processes. A correlation between formability strain and uniaxial strain at break values has been found earlier for commercial paper.⁴ In this work, strain at break values were recorded only at room temperature and without taking into account phase changes such as melting or glass transitions, whereas the forming process is usually executed at higher temperatures. Therefore the sheets produced in the present study were subjected to a tensile test at different temperatures.

Figure 6 shows the Young's moduli of acetylated paper sheets at temperatures between 23 and 170 $^{\circ}\text{C}$. The modulus of the unmodified reference paper ($\text{DS} = 0$) 3.0 GPa is within a paper-typical range. We noticed a drop and lower strain at break at higher temperatures (Figure 7). Both effects correspond well with earlier findings.³⁰ The acetylated samples show increased elastic moduli at lower degrees of substitution compared to the unmodified material at room temperature. We assume that the fibre-fibre bonds were fused together while the mechanical

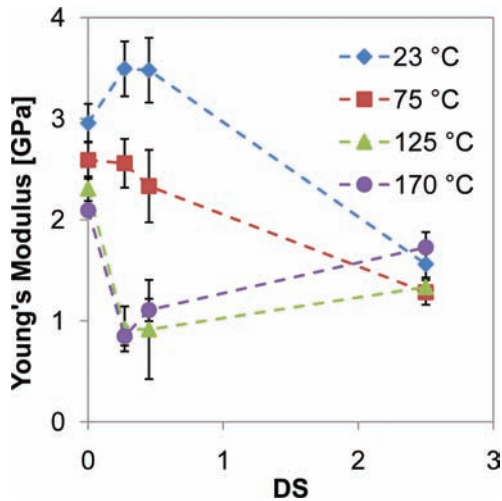


Figure 6. Young's moduli of acetylated materials at different temperatures.

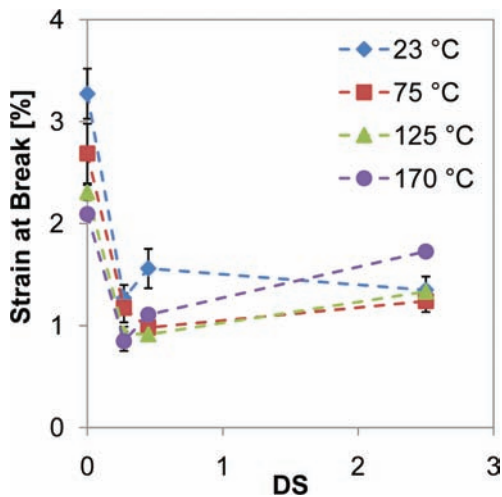


Figure 7. Strain at break values of acetylated materials at different temperatures.

strength of fibres themselves had remained. When the chemical reaction consumes more and more of the cellulose fibre wall material its stability decreases as displayed by lower moduli of the highly acetylated sample with a DS of 2.5. A strong decrease is observed at rising temperatures resulting from the softening of interfibre bondings. The elongation potential is significantly decreased by the

modification procedure. However, a reincrease was observed at the highest test temperature of 170 °C with increasing degrees of substitution which additionally confirms a thermal softening caused by changed bonding properties of the fibres.

With increasing degrees of substitution, the elastic moduli of hexanoylated pulp sheets show a development comparable to the acetylated samples (Figure 8). Thus, a first decrease due to reduced fibre-fibre interactions is followed by a dramatic increase at a DS of 0.51 resulting from successful fibre fusing. The most modified sample Hex-3 has a low Young's modulus comparable to Hex-1. This behaviour could be explained by a further deterioration of the fibres themselves during the modification reaction. Nevertheless, a significant drop in elastic moduli observed for the higher modified sheets with increasing temperatures clearly demonstrates a thermoplastic behaviour. This is in accordance with the fact that the strain at break is reduced at low substitution degrees (Figure 9). However, a continuous rise could be observed with increasing DS and temperature levels. However, even the highest strain value observed does not significantly exceed the elongation potential of the unmodified pulp sheet. We attribute this to a temperature sensitive softening/consolidation behaviour of the material corresponding well with the reported phase transition temperatures of cellulose hexanoates.³¹ Unfortunately, the fundamental mechanical properties of the compound were not changed in a beneficial way.

The polycaprolactone chains attached to single pulp fibres caused a dramatic decrease in elastic moduli (Figure 10). Despite the fact that the derivatives were

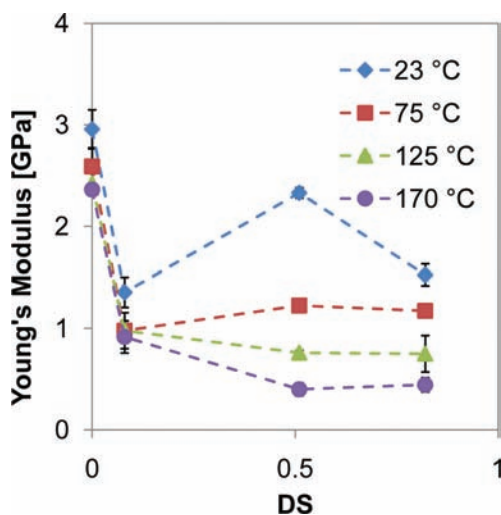


Figure 8. Young's moduli of hexanoylated materials at different temperatures.

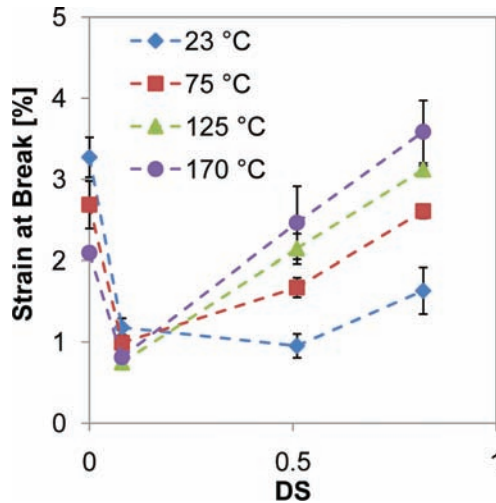


Figure 9. Strain at break values of hexanoylated materials at different temperatures.

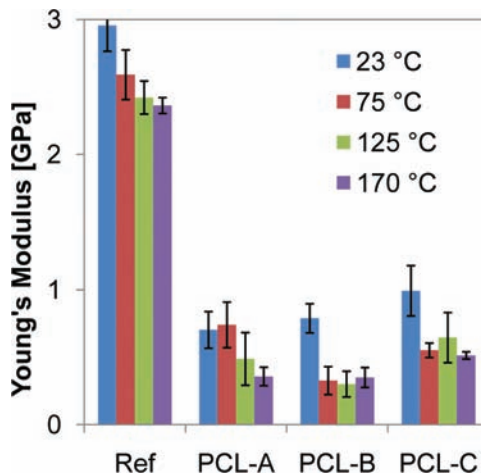


Figure 10. Young's moduli of PCL grafted materials at different temperatures.

synthesised with different methods resulting in different degrees of substitution comparable values could be found for all samples. The water-free reactions (PCL-A and PCL-B) thereby led to materials showing a sharp drop in Young's modulus even at 75 °C. Because the melting point of free polycaprolactone amounts to ≈ 60 °C the attached chains lead to a thermosensitive softening

behaviour. The same can be stated for PCL-C although the polycaprolactone grafts formed should have lower molecular masses due to the presence of water in the reaction mixture that could act as an initiator of ring opening polymerisation.³² Interestingly the thermosensitive bonds achieved that way had no positive impact on the elongation potential which even decreased to below 1% for all samples and at all temperatures (Figure 11).

As a preliminary conclusion, we state that the high strain values were not achieved by any of the fibre surface modifications performed within the scope of this study, even though thermal softening could be shown for some materials. Thus, these materials cannot be used for a fixed blank thermoforming process. However thermoplastic behaviour has also been reported for fibres obtained by the above two-step glycol cleavage-reduction strategy.

In fact, the mechanical properties of samples obtained by oxidative glycol cleavage and subsequent borohydride reduction differed widely from those of the previously synthesised ones. A strong increase in elastic moduli of up to 6.5 GPa was found at room temperature (Figure 12). However, we noticed an unexpected drop for DA1-2 that can be ascribed to a higher equilibrium moisture content of this particular sample. The dialcohol cellulose sheets exhibited elongation gains of up to 11.2% as shown for DA1-3 (Figure 13). Both values are in accordance with previously reported results.²³

A dramatic effect was noted when the temperature was raised to 75–125 °C: a sharp decrease in Young's moduli and the increase in strain at break values of up

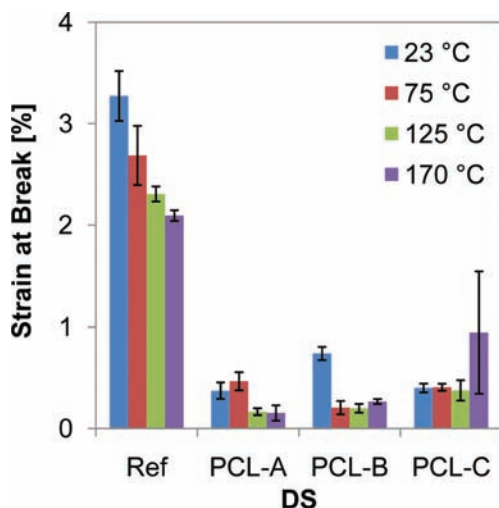


Figure 11. Strain at break values of PCL grafted materials at different temperatures.

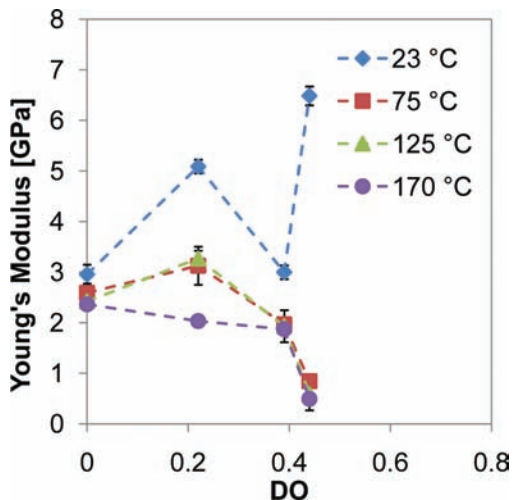


Figure 12. Young’s moduli of dialcohol cellulose modified materials at different temperatures.

to 36% was observed that correlates with the degree of oxidation. In this context, Wågberg and coworkers reported a loss in storage modulus of ≈ 70 °C for dialcohol cellulose sheets that has been explained as glass transition.²⁴ This agrees with our observations, and a thermoplasticity of the whole material could be stated that should lead to *thermoformability* too. A second change in storage modulus has been found at ≈ 160 °C and was related to a flow region of the material. Though one could expect even higher strain values near this threshold, a further temperature increase did not prove to be beneficial. Additionally, it has to be noted that there were no visible signs of melting.

Zero-span tests have previously shown that the high room temperature elongation potential of dialcohol cellulose pulp is not only caused by changes in intra-fibre bonding but also by alterations in single fibre properties.²³ In order to get some further insights into the mechanism of high formability on microscopic level, particularly at higher temperatures, we subjected a thin sheet (40 g/m^2) made of a highly modified pulp sample to an optical strain field analysis during uniaxial straining at 80 °C. Thereby we focused on one characteristic single fibre incorporated in the paper network and oriented in tensile direction. Figure 14 shows that at a global strain of 10%, the fibre undergoes a dramatic elongation of the same magnitude that exceeds by far an elongation resulting from simple decurling. Furthermore, a thinning of the fibre could be observed. This result supports the assumption that the changed constitution of single fibres is responsible for the

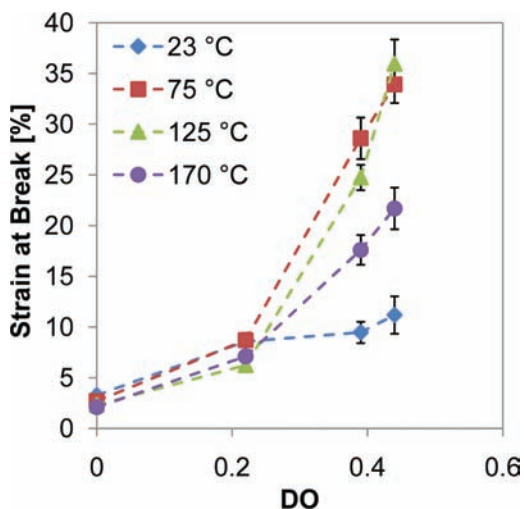


Figure 13. Strain at break values of dialcohol cellulose modified materials at different temperatures.

thermoplastic properties of the material by means of thermosensitive elongation potential. This is in accordance with earlier findings where pulp fibres were compacted in an axial direction and led to paper materials with increased room temperature elongation.^{7,8,10}

In the above-described tensile test, the material undergoes uniaxial straining. Because sheet materials undergo multiaxial strain in three-dimensional forming processes, we investigated the 3D thermoformability of samples DA1-1 and DA1-3 within a fixed blank holder process. Table 3 summarises the results compared to unmodified material.

Table 3. Drawing heights and resulting formability strains of dialcohol cellulose modified materials in comparison with unmodified pulp sheets.

Entry	Sample	Elongation at 75 °C [%]	Maximum Drawing Height [mm]	Formability Strain [%]
1	Ref	4	2	5
2	DA1-1	9	4	10
3	DA1-3	34	12	30

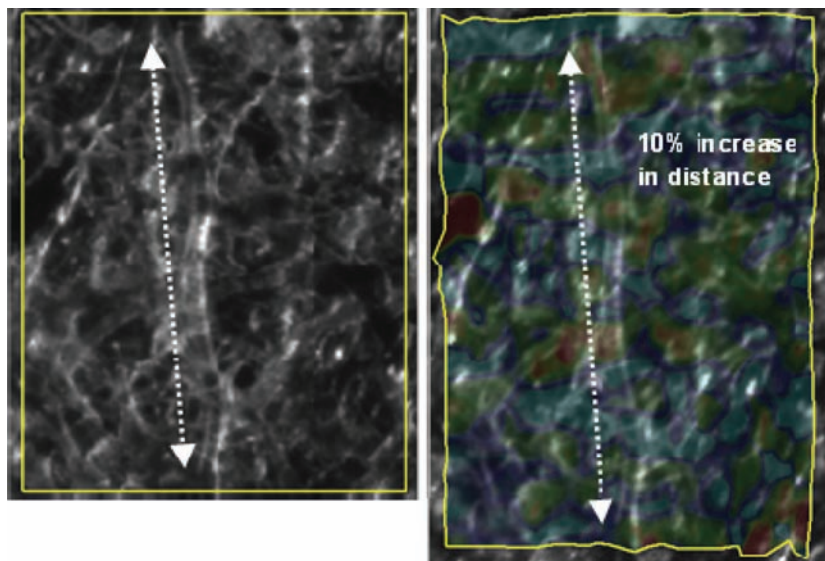


Figure 14. Paper sheet (40 g/m²) made of dialcohol cellulose pulp (DO = 41%) before (*left*) and after (*right*) straining to 10% at 100 °C. Additionally, local strain fields are marked in colour in the right picture.

The maximum drawing heights achieved for the unmodified sample (Ref) as well as the modified materials DA1-2 and DA1-3 show that the resulting formability strains are more or less in the range of the uniaxial elongation potential if straining occurs over the entire free area. Hence the uniaxial temperature controlled tensile test could be used as a suitable approximation of the elongation potential of these materials in a 3D fixed blank thermoforming process. A thermoformed cup made of DA1-3 is shown in Figure 15.

CONCLUSION

The present study has shown that a chemical surface modification of pulp fibres leads to fibre-matrix composite materials with altered thermomechanical properties. Compression moulding yielded thermofused materials at higher degrees of substitution, evidencing thermosensitive fibre bonds. However, the resulting



Figure 15. Thermoformed cup made of DA1-3 dialcohol cellulose sheet.

thermoplastic properties did not necessarily lead to high elongation values even at higher temperatures. Finally, a semi-homogeneous two step glycol cleavage-reduction protocol, where a thermoplastic dialcohol cellulose matrix is generated within cellulose fibre walls, led to thermoplastic single fibres. Sheets made thereof showed temperature sensitive strain at break values higher than 35% and could be transformed into three-dimensional objects by a laboratory forming process using fixed blank holders. In this context, it has been shown that higher elongation of fibre networks seems to be caused by higher elongation of individual fibres rather than changed inter-fiber bonding.

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32. The individual lengths of polymer grafts were not determined. However the simultaneously formed polycaprolactone homopolymers M_w showed values in the range of 20,000 g / mol (Method A) and 5000 g / mol (Method C) respectively determined by size exclusion chromatography. We sincerely thank Materia Nova, Belgium, for the measurements.

Transcription of Discussion

CHEMICAL MODIFICATION OF PULP FIBRES FOR THE PRODUCTION OF THERMOFORMABLE PAPER

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Gil Garnier Monash University

In the first part of your talk, you investigated the cellulose waxy esters as modifiers and basically you investigated the C6. Have you investigated the longer fatty acids, such as C12, or C18?

Martin Zahel Papiertechnische Stiftung

Yes, we tried to attach stearic acid as a kind of a fatty acid that is even longer to the fibre surface, but with longer chains, it gets even harder to attach them to the fibres and retain the fibre stability since the reaction regime has to be more harsh, reaction times have to be longer and so on. What we at least found out using this procedure is that it is really hard to preserve fibre lengths in such a modification, so we went to shorter alkyl chains. We used exanoylatron because it was a good compromise between degradation and chain length, and we tried to use different protocols using a polycaprolactone grafting onto fibres that in the end should lead also to even longer chains, although we know they are not as long as an industrial polycaprolactone plastic material. They seem to be really short, but we would assume that they are comparable in length to alkyl chains from fatty acids for example.

Discussion

Gil Garnier

What is the difference between getting thermoplasticity by entanglement versus interaction between the dialcohol modified fibres reaction with the hydroxyl groups of cellulose?

Martin Zahel

I would think the answer is, it does really matter where the modification occurs and what the molecular structure of the thermoplastic domains in the fibre look like. From this point, we think that the thermoplasticity of the dialcohol cellulose is due to the generation of long flexible chains out of the cellulosic or formerly cellulosic material, and I would not assume that a kind of esterification would lead to comparable thermomechanical properties of such materials since the molecular structure of those chains would look different. At this point I think also the way the chemical modification occurs does really matter and I would say one really important thing is the character of the reaction regime you use. Obviously, it is really important to have a kind of a swelling solvent that allows you to get a modification in the cellulosic fibre material in an evenly distributed manner on many sites, otherwise we know that if this modification does not occur evenly, then the thermomechanical properties are at least a result of the remaining cellulosic fractions in the fibre and if you make all those cellulosic modification reactions, there comes a point when you just get from fibrous material to a kind of a homogeneous cellulose derivative.

Wolfgang Bauer Graz University of Technology

One of the main drivers to replace plastics by paper-like materials is sustainability, so did you look at the ecological footprint of this modification or at the recyclability?

Martin Zahel

We did not take a look on the ecological footprint of this material, but what we can say now is that this tray is fully recyclable in water and you can make a paper out of it and you can form it again. We did not look at recycling cycles at this point and what would happen if, for example, a recycling process would be flooded with a lot of those modified cellulosic fibres.