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Amination and thiolation of chloroacetyl cellulose through reactive dissolution in *N*,*N*-dimethylformamide

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ABSTRACT

The synthesis and characterization of aminoacetyl cellulose and thioacetyl cellulose is presented in this paper. Cellulose was first chemically modified with chloroacetyl chloride using *N*,*N*-dimethylformamide (DMF) as reaction medium. The maximum substitution of hydroxyl groups of cellulose was achieved reacting in the presence of 6 equiv. of chloroacetyl chloride over 24 h at 60 °C. DMF were then recovered by fractional distillation of the media. In the next step, chloroacetyl cellulose was reacted with either secondary amines or thiols. The reactions were initially heterogeneous in hot DMF. As the reactions proceeded, homogenous mixtures were obtained. Highly substituted cellulose derivatives were achieved via this method. The success of the reactions was confirmed by ATR-IR and NMR spectroscopy. Various pulps were used as cellulose source. The resulting products were found to be thermally stable and have glass transition temperatures around 120 °C. Gel permeation chromatography (GPC) indicated that degradation of the cellulose backbone had occurred. The cellulose derivatives were then processed into films. Their potential, as packaging films, was then studied from the view-point of their moisture and oxygen barrier properties, as well as their tensile properties.

1. Introduction

Cellulose has found a wide range of applications in food, printing, cosmetics, pharmacy, therapeutics, paper making and in the textile industry, due to its versatility, low cost, renewability and biodegradability (Klemm, Schmauder, & Heinze, 2002). Chemical modification of this highly crystalline and insoluble homo-polymer allows for wider application, through altering its physiochemical properties and rendering cellulose into a more processable state.

Cellulose can be modified through the reactive dissolution approach (Labafzadeh, Kavakka, Sievänen, Asikkala, & Kilpeläinen, 2012). This means that the reaction is initially heterogeneous, in the absence of costly and toxic direct-dissolution solvents (e.g. ionic liquids). As the reaction proceeds a homogenous mixture is obtained. The reactive dissolution approach affords a number of additional advantages, including ease of work up and production of highly substituted derivatives. However, it suffers from a lack of selectivity or poor homogeneity in the substitution pattern, which are typically observed with other heterogeneous cellulose modification reactions.

Among the many modifications of cellulose, there have been some attempts to introduce amine and thiol functionalities into the molecular structure. They are useful in applications such as films, filaments, sizing agents, protective colloids, water resistant coatings for medicines and removable coatings on photographic films (Fulkerson & Mench, 1958, 1963; Hiatt, Mench, & Fulkerson, 1964; Nadeau & Thompson, 1957). A few patents and articles have described the preparation of chloroacetyl cellulose, followed by amination with a variety of secondary or tertiary amines (Dreyfus, 1929; Fulkerson & Mench, 1958, 1963; Hiatt & Emerson, 1960; Hiatt et al., 1964; Maim, Mench, Williams, & Hiatt, 1950). Hiatt et al. (1964) were prepared cellulose acetate diethylaminoacetate by the reaction of diethylamine with cellulose acetate chloroacetate using dioxane as medium. Fulkerson and coauthors (1958) claimed that nitrogen containing cellulose derivatives can be prepared from cellulose acetate chloroacetate and ethyl cellulose chloroacetate using a reaction medium such as dioxane, methyl ethyl ketone and acetone. Another recent study by Zhong, Chai,

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and Fu (2012) has also shown that chloroacetyl cellulose can be efficiently made in dimethylacetamide (DMA)/LiCl solvent system. However, to the best of our knowledge, no publications are available using dimethylformamide (DMF) as the reaction medium. This should allow for a more recyclable process in comparison to, e.g. DMA/LiCl. Furthermore, no data has been presented on the thermal and mechanical properties of the products. We also have found only a few investigations dealing with the introduction of thiol moieties into polysaccharide chains (Silva Filho et al., 2013; Siqueira Petri et al., 1999; Tingaut, Hauert, & Zimmermann, 2011). However, it seems that no studies have highlighted the possibility of functionalizing cellulose substrates, bearing aliphatic halide linkers, with thiols through nucleophilic substitution. Furthermore, there is no data available on the properties of these materials.

This study aimed to synthesize and characterize new cellulose derivatives by incorporating either amine or thiol groups into the polysaccharide chain through nucleophilic substitution at cellulose chloroacetyl derivatives. The reactions were carried out through reactive dissolution in DMF. The optimum conditions for preparation of cellulose derivatives were determined. The potential of the derivatives, as packaging films, was studied from the view-point of their moisture and oxygen barrier properties, as well as their tensile properties. Additionally, different types of pulp including softwood dissolving pulp (SWDP), hardwood kraft pulp (HKP) and hemicellulose-poor hardwood kraft pulp (HPHKP) were used as raw material, with microcrystalline cellulose (MCC) as a reference.

2. Experimental

2.1. Materials

All chemicals were purchased from commercial sources and used as such. SWDP was provided by Domsjö (Sweden). It contained 3.5% hemicelluloses and less than 0.5% lignin, with a viscosity of 520 ml/g. HKP was provided by Kaskinen (Finland). It included 24.7% hemicelluloses, with a viscosity of 870 ml/g. HPHKP was prepared from HKP by VTT (Finland) and contained 13.7% hemicelluloses. SWDP and HKP were fibrillated in hot ethanol and dried in vacuum to promote the penetration of reagents into the fibrous materials. HPHKP samples were used as received.

2.2. Chloroacetylation of cellulose

Cellulosic pulp (0.25 g, 1.54 mmol), DMF (10 ml) and chloroacetyl chloride (6 equiv./AGU) were introduced into a 20 ml vial. The mixture was refluxed at 60 °C, under inert atmosphere. After 24 h, a clear homogenous solution was obtained and modified cellulose was isolated by precipitation with methanol. The samples were then triturated with methanol and dried under vacuum. The final white chloroacetyl cellulose products were obtained with weight percent gains (WPGs) of 84–108%, depending on the substrate used.

2.3. Amination of chloroacetyl cellulose

Chloroacetyl cellulose (0.25 g, 0.72 mmol, DS∼2.4) and DMF (10 ml) were placed in a 20 ml vial. Morpholine or piperidine was then added (6 equiv./AGU or 12.8 equiv./chloroacetyl cellulose). The mixture was refluxed for 24 h at 90 °C. The modified polymers were then precipitated, with diethyl ether in case of morpholine and with distilled water in case of piperidine. Morpholine treated samples were further triturated with methanol and dried under vacuum. WPGs of 4–20% were achieved for the dried polymers.

2.4. Thiolation of chloroacetyl cellulose

Chloroacetyl cellulose (0.25 g, 0.72 mmol) was placed in a 20 ml vial. DMF (10 ml) and thiophenol (6 equiv./AGU or 12.8 equiv./chloroacetyl cellulose) were then added while stirring. The reaction was performed at 90 °C for 24 h. The crude product was isolated by precipitation with distilled water. The sample was further triturated with distilled water and then dried under vacuum. WPG of 12% was achieved.

2.5. Solvent recovery after chloroacetylation

Recovery of reagents and byproducts from reaction mixture was also investigated. Chloroacetyl cellulose was isolated by precipitation with distilled water. Water was first removed using a standard rotary evaporation, with water bath-heating. DMF could then be recovered by vacuum distillation, using a water aspirator, in a 91% yield. This was shown to be high purity by ^{1}H and ^{13}C NMR (see supporting information). The remaining residue was a mixture of chloroacetic acid and traces of DMF, by ^{1}H and ^{13}C NMR (see supporting information).

2.6. Characterization of cellulose derivatives

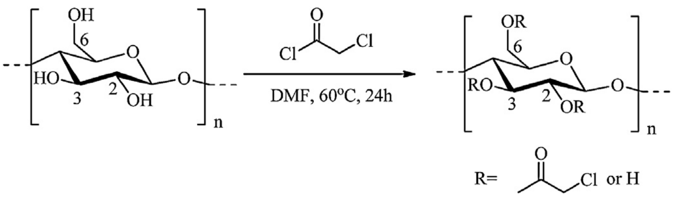
Attenuated total reflection infrared (ATR-IR) spectra were obtained on a Brüker Alpha ATR-FT-IR spectrometer.

Quantitative ^{1}H and ^{13}C NMR were performed using a Varian Unity INOVA 600 spectrometer (600 MHz proton frequency) equipped with a 5 mm direct detection broadband probe-head in DMSO-d_6 at 27 °C. Heteronuclear single quantum coherence spectroscopy (HSQC) and diffusion ordered spectroscopy (DOSY) were measured on a Varian Unity INOVA 500 NMR spectrometer (500 MHz proton frequency) equipped with 5-mm triple-resonance (^{1}H, ^{13}C and ^{15}N) gradient probe-head. Quantitative ^{13}C NMR was used for DS determination of chloreacetyl cellulose. 10,000 scans were collected with a prerelaxation time of 30 s and a pulse width of 45°. The DS of other derivatives were estimated roughly using ATR-IR. Carbonyl peak intensities of the aminoacetyl cellulose and thioacetyl cellulose were compared with the chloroacetyl cellulose. Also, disappearance of the peaks corresponding to CH_2—Cl stretching confirmed the complete replacement of the chlorine with amine or thiol groups.

Thermal properties of cellulose derivatives were analyzed by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was performed using a Mettler TGA/SDTA 851e over a temperature range of 50–600 °C and with a heating rate of 10 °C/min in 50 ml/min N_2. The thermal decomposition temperature (T_d) was taken as the onset of significant ($\geq$0.5%) weight loss. DSC was performed using a TA instruments DSC Q200. All experiments were conducted over a temperature range of 50–200 °C, with a heating rate of 10 °C/min and cooling rate of 5 °C/min, under an atmosphere of nitrogen. The heating/cooling/heating sequence was used. After cooling, the data from second run was analyzed.

Gel permeation chromatography (GPC) was used to determine the molar mass distribution of derivatives, calibrated against pullulan standards. The gel permeation column was an Agilent PLgel organic 10 μm MIXED-B (7.5 mm × 300 mm). DMA/0.5% (w/v) LiCl was used as the mobile phase at a flow rate of 0.5 ml/min at room temperature. The untreated pulp solutions in DMA/LiCl were prepared by a modified method described by Westermark and Gustafsson (1994).

Each product was cast as a film for further analyses. Cellulose derivatives were dissolved in THF (polymer concentration: 2%), were cast onto a flat-bottomed petri dish, and the solvent was allowed to evaporate in air at room temperature. Water vapor



Scheme 1. Reaction scheme for the preparation of chloroacetyl cellulose.

transmission rates (WVTR) were determined gravimetrically using a film area of 5 cm^2. The samples were placed between aluminum masks sealing the sample cups (ø 63.5 mm) containing 43 g of $CaCl_2$ as a desiccant (air gap of 6 mm). The cups were placed in a desiccator cabinet with a constant air velocity of 0.15 m/s. The temperature of the cabinet was 22 °C, and the relative humidity (RH) was maintained at 52% with saturated $Mg(NO_3)_2$ solution. The cups were weighed at intervals of 12–48 h. The WVTR values were calculated from a linear regression of the slope of the weight gain versus time by division of the slope by the film area. Water vapor permeability (WVP) was obtained by multiplication of the WVTR by the thickness of the film and division by the water vapor partial pressure difference between the two sides of the film (Mikkonen et al., 2009). An Ox-Tran Twin instrument (Modern Controls, Inc.) with a coulometric sensor was used to study the transmission rate of oxygen through the films (⌀ 5 cm^2). In order to condition the samples to correspond to the inner RH of the instrument, they were stabilized inside the instrument (20 h) prior the measurements. During the measurement, samples were exposed to 100% oxygen on one side and to a mixture of 98% nitrogen and 2% hydrogen on the other side. The measurements were carried out at 22 °C and at normal atmospheric pressure.

3. Results and discussion

The polar aprotic nature of DMF, as reaction medium, allowed for the preparation of cellulose derivatives, through reactive dissolution. It has been found that DMF is a suitable solvent for derivatization of polysaccharides, including cellulose, without the addition of any catalyst (Clermont & Bender, 1972; Krouit, Granet, & Krausz, 2008). This also allows for a more recyclable process in comparison to other solvents, e.g. DMA/LiCl or ionic liquids. Chloroacetyl chloride is a bifunctional compound capable of forming linkages, e.g. with alcohols, amines and thiols (Izard & Morgan, 1949). Thus, cellulose chloroacetates, from various cellulose sources, were first obtained and used as the starting materials for further reactions with amines and thiols.

3.1. *Synthesis of cellulose derivatives*

3.1.1. *Chloroacetyl cellulose*

Chloroacetyl cellulose with high DS values are accessible by the reaction of the biopolymer with chloroacetyl chloride (**1**) in dimethylformamide (DMF) (Scheme 1). The reactions were initially heterogeneous (i.e. cellulose was insoluble) and gradually became homogeneous, as the cellulose reacted.

The optimum reaction conditions were determined according to the molar ratio of **1** per anhydroglucose unit (AGU), the reaction temperature and the pulp concentration in DMF, to obtain the maximum DS and high yields. It was found that a reaction temperature of 60 °C, 6 mole of **1** per AGU and 2.5% concentration of cellulose in DMF resulted in a clear mixture after 24 h (see supporting information).

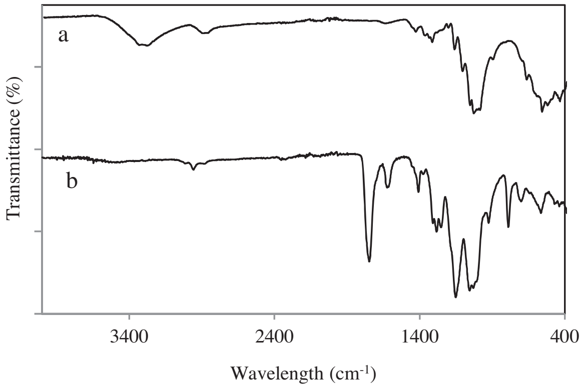


Fig. 1. ATR-IR spectra of (a) unmodified SWDP and (b) chloroacetyl SWDP.

Acylation of different sources of cellulose, containing different amount of hemicelluloses, was then performed under optimized conditions. SWDP, HKP and HPHKP were reacted with **1** and ATR-IR spectroscopy was used to analyze the products. The appearance of the carbonyl peak (C=O), around 1750 cm^{-1}, along with partial disappearance of hydroxyl groups (OH), around 3330 cm^{-1}, confirm the efficiency of acylation and preparation of highly substituted cellulose esters. Moreover, new peaks at 790 cm^{-1} and a triplet at 1290 cm^{-1} appear to be CH_2—Cl stretching of the chloroacetyl group (Fig. 1 and supporting information). The molecular structure of the chloroacetyl cellulose was also evaluated by means of NMR spectroscopy.

A ^{1}H NMR spectrum of chloroacetyl cellulose, recorded in DMSO-d_6, displays resonances at 3–5.5 ppm and a singlet at 4.3 ppm, which is assigned to the aliphatic glucose protons and the methylene protons of the chloroacetyl groups, respectively (Fig. 2). A ^{13}C NMR spectrum illustrates the carbonyl carbon at 167 ppm and the methylene carbon of the chloroacetyl group at 40.7 ppm, which overlaps with the solvent signal (Fig. 2). The full NMR spectra of all the synthesized products are shown in supporting information.

The overlapping signals in the ^{1}H NMR spectra limit the use of this technique for the DS determination. ^{31}P NMR could not be applied as the samples were not soluble in the phosphitylating mixture (King et al., 2010). Consequently, the DS values were determined using quantitative ^{13}C NMR. The DS values were estimated by the integrated ratio of carbonyl verses the anomeric carbon (C_1 in AGU) resonances. By comparing the ATR-IR results with the Q-^{13}C NMR results, it become obvious that highly functionalized cellulose chloroacetates were obtained (Table 1). Consistent DS values were achieved for different sources of cellulose. Thus, it clearly reveals that the amount of hemicelluloses present in the different pulps does not significantly interfere with the efficiency of the reaction. The yields of chloroacetyl cellulose, from HKP and HPHKP, seem to decrease with increasing hemicellulose content; however, the DS values remain the same. This may indicate a loss of hemicelluloses during the workup procedure yielding mainly higher MW cellulose-rich material.

Table 1
Chloroacetyl cellulose yield, DS and onset decomposition temperature, prepared at 60 °C, 6 mole of chloroacetyl chloride per AGU and 2.5% concentration of cellulose in DMF for 24 h.

Substrate	DS	Yield (%)	$T_{d(onset)}$ (°C)
Avicel	2.4	98	302
SWDP[a]	2.4	94	301
HPHKP[b]	2.4[d]	92	297
HKP[c]	2.4[d]	86	298

[a] Softwood dissolving pulp.
[b] Hemicellulose-poor hardwood kraft pulp.
[c] Hardwood kraft pulp.
[d] The DS value is stated as the DS, based on the assumption that there is no hemicellulose in the sample.

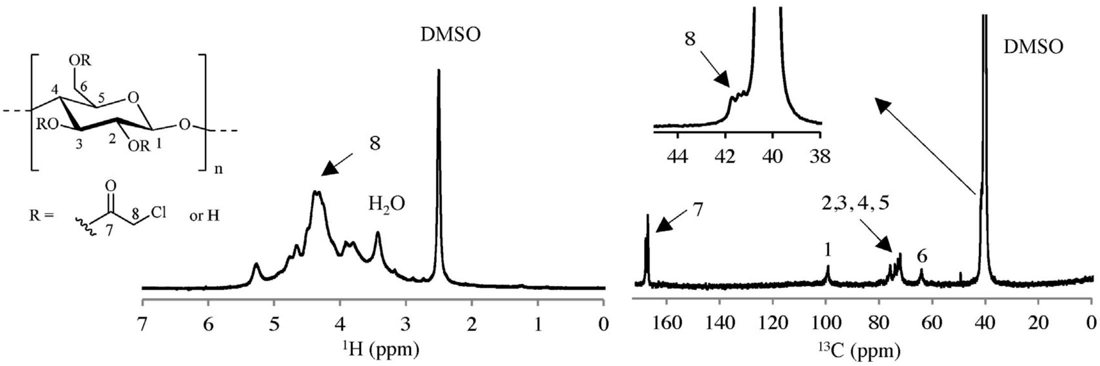


Fig. 2. ^{1}H (left) and ^{13}C NMR (right) spectra of chloroacetyl Avicel (DS 2.4), recorded in DMSO-d_6.

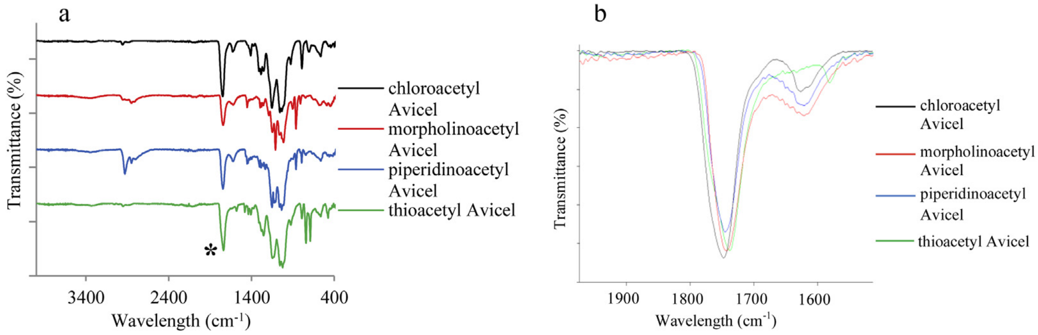


Fig. 3. (a) ATR-IR spectra and (b) carbonyl peak (at point designated by * in a) of cellulose derivatives (spectra were normalized by the intensity of the pyranose oxygen absorption at 1050 cm^{-1}).

Table 2
Amination and thiolation of chloroacetyl cellulose.

Substrate	Reactant	Yield[a] (%)	T_g (°C)	$T_{d(onset)}$ (°C)
Avicel	Piperidine	90	124	265
SWDP	Piperidine	81	119	279
HPHKP	Piperidine	78	120	285
HKP	Piperidine	75	120	273
Avicel	Morpholine	89	131	275
Avicel	Thiophenol	74	119	315

[a] Yields were calculated by taking into account that the DS is 2.4 for all derivatives.

3.1.2. Aminoacetyl cellulose

The next step was the reaction of secondary amines, such as morpholine and piperidine, with chloroacetyl cellulose esters (Table 2).

The previously prepared chloroacetyl celluloses (DS 2.4) were reacted with the amines, in the presence of DMF at 90 °C for 24 h (Scheme 2). The structure and purity of the resulting aminated celluloses were confirmed with ATR-IR and NMR spectroscopies. New peak of the attached amine group appeared at 860 cm^{-1} (C—N), in the ATR-IR spectra of piperidinoacetyl cellulose. Also, there is no absorption band around 790 cm^{-1} and 1290 cm^{-1} corresponding to the CH_2—Cl bond, which indicates that the chlorine is replaced by amine group (Fig. 3a).

Fig. 4 shows the ^{1}H and HSQC NMR spectra for piperidinoacetyl cellulose, with peak assignments (see supporting information for NMR spectra of morpholinoacetyl cellulose). ATR-IR and NMR results further verify the successful integration of amino moieties with the biopolymer. In addition, DOSY NMR was used to confirm the purity of the products (King et al., 2010). DOSY measures molecular mobilities, i.e. diffusion rates in an NMR sample. Diffusion coefficient (D) of a molecule is proportional to its hydrodynamic volume. Therefore, DOSY offers a way to resolve different compounds in a mixture based on differences in the size and

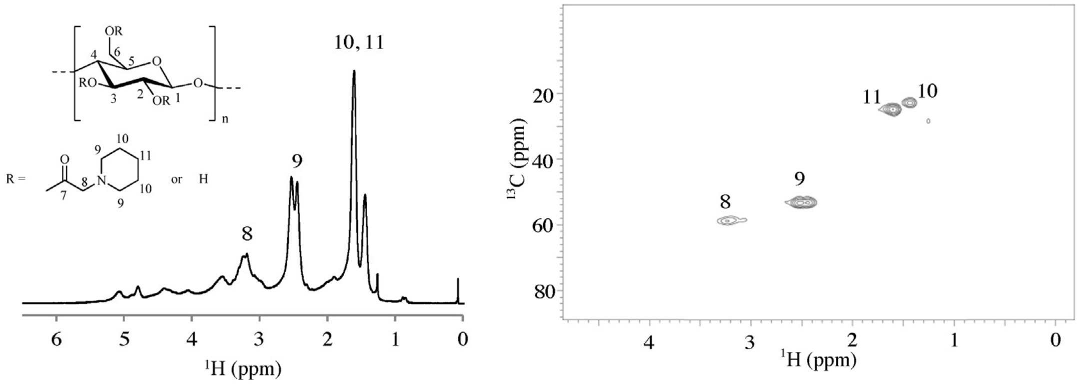
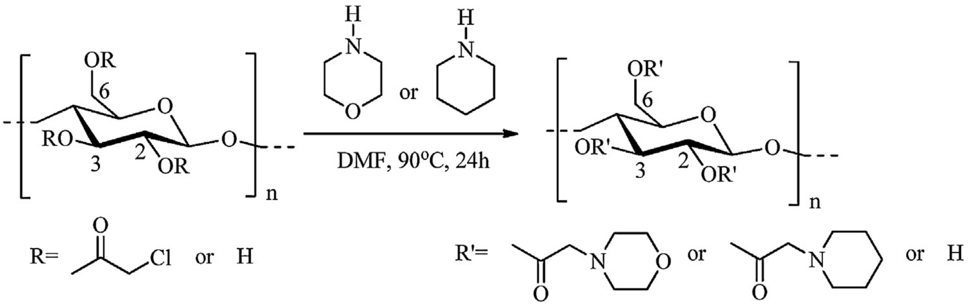


Fig. 4. ^{1}H (left) and HSQC NMR (right) spectra of piperidinoacetyl SWDP in $CDCl_3$.



Scheme 2. The reaction scheme of the preparation of aminoacetyl cellulose.

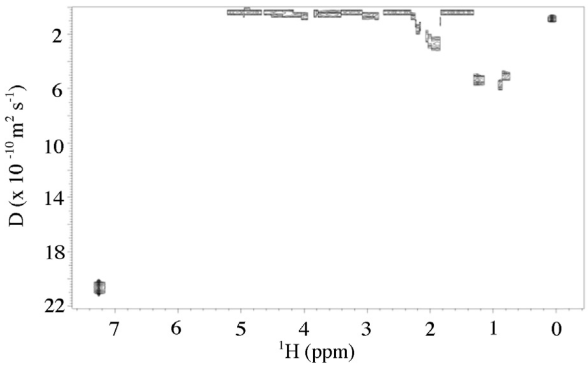


Fig. 5. DOSY NMR spectrum of piperidinoacetyl SWDP in $CDCl_3$. Synthesis of thioacetyl cellulose.

shape of the molecule. Fig. 5 illustrates the DOSY NMR of SWDP piperidinoacetate. In this figure, large molecules with lower *D* appear at the upper part of the spectrum, while small molecules with higher *D* appear at the bottom of the spectrum. Characterization of the final products with DOSY NMR confirmed that high purity derivatives were obtained (data shown in Fig. 5 and supporting information).

DS measurement of aminated cellulose derivatives using quantitative ^{13}C NMR was virtually impossible due to the poor quality spectra. Thus, DS was roughly estimated using ATR-IR by comparing carbonyl peaks of all derivatives (Fig. 3). Besides, absorptions related to CH_2—Cl stretching of chloroacetyl group have disappeared. Apparently, identical DS values of around 2.4 were obtained for all derivatives. This can be also verified by the HSQC spectrum of derivatives, as the peak assigned to the chloroacetyl methylene group (4.3 ppm) has disappeared entirely. This observation confirms the complete substitution of chlorine by amine groups (Fig. 4). Additionally, various pulp samples showed identical results and it

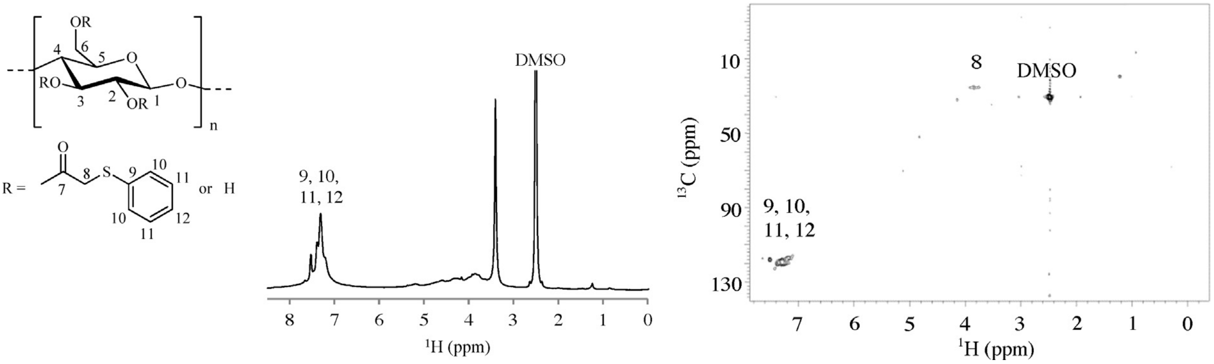


Fig. 6. ¹H (left) and HSQC NMR (right) spectra of thioacetyl Avicel in DMSO-d_6.

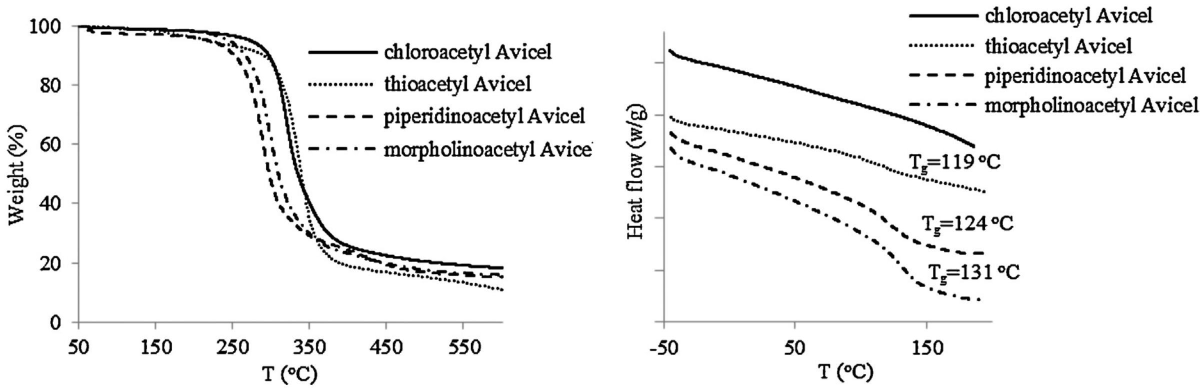
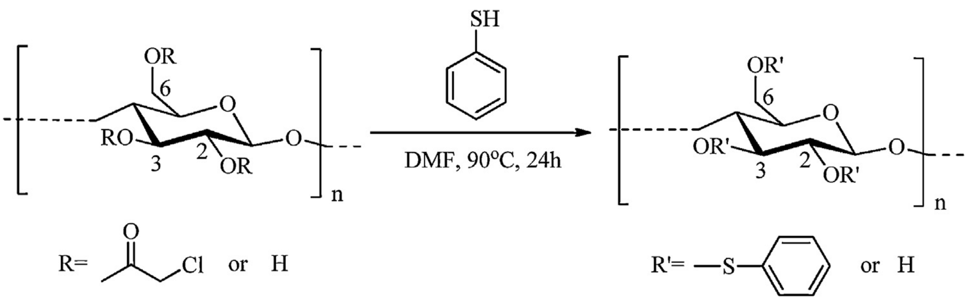


Fig. 7. TGA (left) and DSC (right) thermograms of the acyl cellulose derivatives.



Scheme 3. Thiolation of chloroacetyl cellulose.

can be concluded that they are suitable starting materials for the production of aminoacetyl celluloses.

3.1.3. *Thioacetyl cellulose*

A thioether functionality was also introduced onto the cellulose backbone through reaction of thiophenol with chloroacetyl cellulose, in DMF as reaction medium (Scheme 3). The structure of thioacetyl cellulose was determined through different spectroscopy techniques. The characteristic vibrations of the grafted group were easily identified using ATR-IR, namely the carbonyl stretching vibration at 1750 cm^{-1} (C=O), the C—S bond at 690 cm^{-1} and 741 cm^{-1}, and the aromatic ring at around 1440 cm^{-1} and 1480 cm^{-1} (Fig. 3a). The ^{1}H NMR spectrum of this material in DMSO-d_6 showed a multiplet at 7.4 ppm for the aryl ring. Its HSQC NMR spectrum showed a resonance at 3.8 and 35 ppm (^{1}H and ^{13}C) attributed to the thioacetyl methylene group (Fig. 6). The complete absence of the chloroacetyl methylene resonances at 4.3 and 40.7 ppm confirms the complete reaction of thiophenol, with the chlorine in chloroacetyl cellulose. This is in agreement with the ATR-IR results (Fig. 3). A DOSY spectrum of the thioacetyl Avicel product illustrates the purity of the product and absence of any small by-products (supporting information).

3.2. *Thermal properties of the acyl cellulose derivatives*

Thermal analysis of the prepared derivatives was carried out using TGA and DSC. Decomposition pattern and thermal stability of the modified celluloses vary with the type of substituent. TGA studies reveal that the decomposition temperatures (T_d) of the cellulose derivatives are lower than for intact Avicel and pulp (around 320 °C and 328 °C, respectively) (Tables 1 and 2). Chloroacetylation, amination and thiolation of cellulose do not improve the thermal stability of cellulose (Fig. 7).

This observed decrease in T_d can be explained by reduction in the crystallinity of cellulose (Yin et al., 2007).

The DSC thermograms for chloroacetyl cellulose are similar to those of intact cellulose. No notable phase-transitions are observed for chloroacetyl cellulose (Fig. 7). However, the amination and thiolation process induces a reverse phase transition which can be attributed to glass transition temperature (T_g) (Fig. 7 and Table 2). Therefore, it can be concluded that the treatment of chloroacetyl cellulose, with amines and thiols, has a considerable effect on the thermal properties of the materials.

3.3. *Molecular weight distribution of the acyl cellulose derivatives*

Molecular weight distributions for the derivatives were determined using GPC. Fig. 8 shows the molecular weight distribution (MWD) of HKP derivatives. The two fairly separated peaks in the MWD of untreated HKP represent the cellulose fraction (high molecular range) and the hemicellulose fraction (low molecular range). The broad shape of the cellulose fraction shows that cellulose in HKP is polydisperse and contains polymer chains of unequal length. Also, it was remarkable that the derivatization introduced major changes in the MWD of the pulp and resulted in a reduction of the molecular weight compared with the untreated pulp (Fig. 8). MWD of other samples have been shown in supporting information and it can be concluded that degradation of polymer chain has occurred during derivatization. Due to the electrophilic reactivity of the chloroacetyl functionality, crosslinking with cellulose OH functionalities may also possible, for these kinds of cellulose derivatives. However, no high MW tails are observed in the GPCs for the derivatives, indicating that no crosslinking has occurred.

3.4. *Mechanical and barrier properties of acyl cellulose derivative films*

The cellulose derivatives can be converted into films, which have interesting mechanical and barrier property, suitable for packaging applications. Biomaterials with the potential for use in the packaging sector should provide high mechanical properties, in addition to good barrier properties for oxygen and water vapor (Paunonen, 2013; Rhim, Park, & Ha, 2013; Sebti, Ham-Pichavant, & Coma, 2002). The prepared cellulose derivatives were converted into films, by dissolution in THF, casting onto a flat-bottomed petri dish, and evaporation of the solvent. Polymer films were only prepared from piperidinoacetyl cellulose due to its high solubility in THF. Other derivatives were only slightly soluble in organic solvents, resulting in heterogeneous and weak films. Mechanical and barrier properties of the film were determined according to the procedure described above. Piperidonoacetyl cellulose film was extremely brittle, hence, its mechanical properties could not be determined. It was also found that the film possessed poor oxygen-barrier properties. The water vapor transmission rate (WVTR) and water vapor permeability (WVP), through a 40 μm

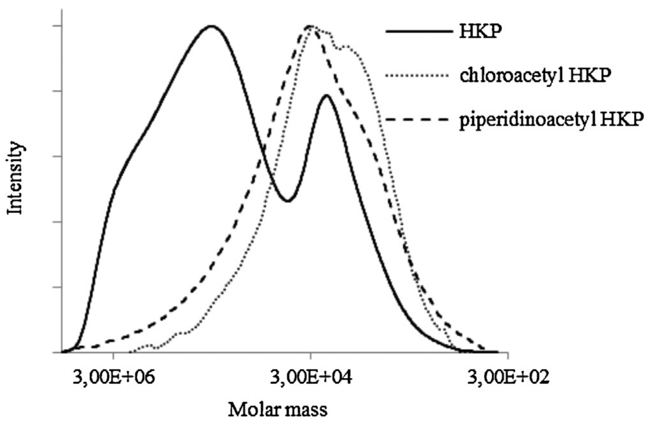


Fig. 8. Molecular weight distributions for acyl HKP derivatives.

thick film of piperidinoacetyl cellulose, were about 139 g m^{-2} day^{-1} and 3.9 g mm kpa^{-1} m^{-2} day^{-1}, respectively. The WVTR value was lower than for microfibrillated cellulose acetate (167 g m^{-2} day^{-1}) (Rodionova, Lenes, Eriksen, & Gregersen, 2011). However, the WVTR value was higher than the value obtained for low density polyethylene (20 g m^{-2} day^{-1} for a 1 mm thick film) (Lavoine, Desloges, Dufresne, & Bras, 2012).

3.5. Chloroacetylation reaction sustainability

As the chloroactyl cellulose is clearly an interesting electrophilic cellulose synthon, it is in our interest to demonstrate the recyclability of all reaction components. Some of the benefits gained from using DMF as the reaction medium is that it is a conventional, cheap, easily handled and recyclable reaction media. Avoiding the use of the cellulose direct-dissolution media DMA/LiCl, mitigates the extra cost of recycling DMA and LiCl from reagent byproducts. In the pure DMF reaction, water can be used to quench the reaction, without altering the product DS. DMF and water can be fractionally distilled from the mixture, after the precipitation step. The residual chloroacetyl chloride reagent is converted to chloroacetic acid and HCl. This can then be converted back to the chloroacetyl chloride using standard purification and conversion chemistries. DMF was recovered by vacuum distillation, using water aspirator, with an unoptimized yield of 91%. ^{1}H and ^{13}C NMR spectra of the distilled DMF are shown in supporting information and confirm the purity of DMF.

4. Conclusion

In conclusion, we have introduced amine and a thiol functionalities into cellulose, through reactive dissolution in DMF. The reaction of cellulose with chloroacetyl chloride and then with amines/thiol was initially heterogeneous. After heating in DMF the reactions turned homogeneous. Highly substituted cellulose derivatives were obtained (DS 2.4). Also, DMF can easily be recovered by simple distillation in good yield. This allows for a more recyclable process to this important synthon, compared to other reported media. The thermal stabilities of cellulose derivatives did not show improvement, compared to intact cellulose. However, the glass transition temperature was observed to be around 120 °C for all derivatives. It can be concluded that amination and thiolation of cellulose has a considerable effect on the thermal properties of the material. It was also shown that various types of pulps could be good candidates, as raw material for the preparation of aminoacetyl cellulose. The quality of product is similar for all cases highlighting robust reactions. It was also found that the prepared cellulose derivatives are not suitable for packaging applications due to their poor mechanical and oxygen barrier properties. Due to the fact that nucleophilic thiols and amines can be modified further, mainly by reaction with electrophiles or with oxidants, this synthesis strategy may allow for the production of a wider range of materials, with variable properties.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.03.077.

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