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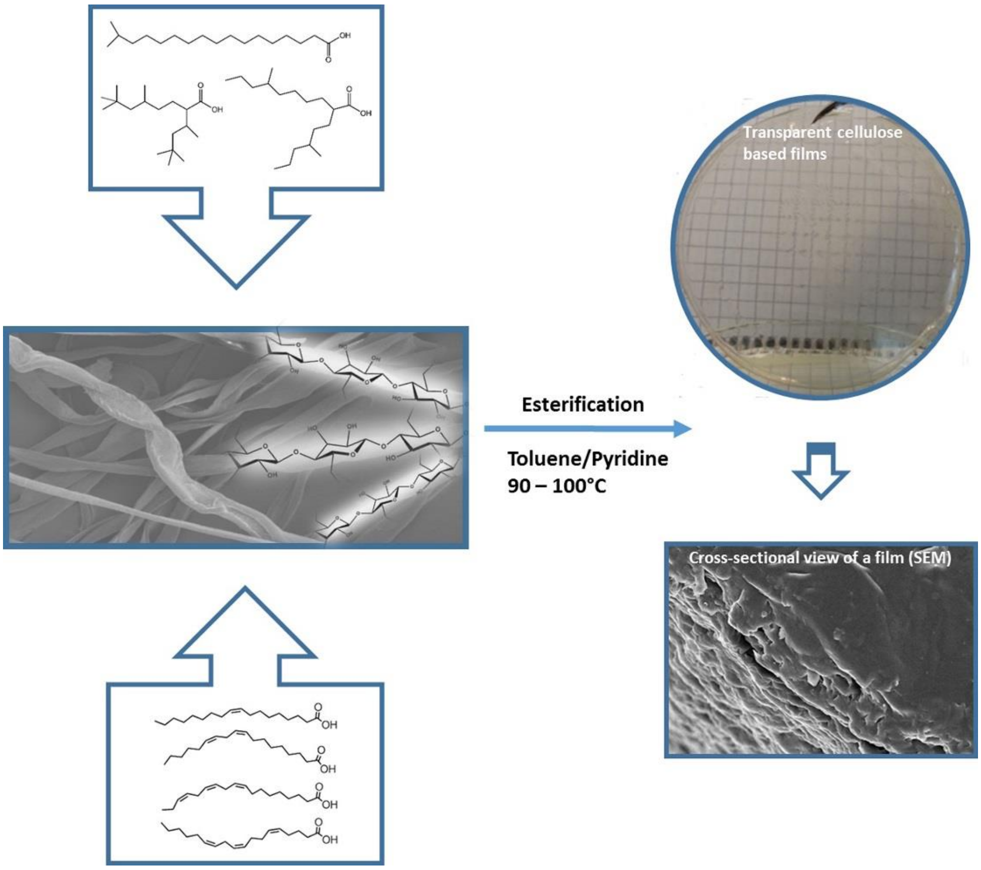

Bio-based films were prepared by acylation of cellulose with saturated, unsaturated and branched fatty acids. The products showed increased thermal stability, low water vapour transmission rates and enhanced tensile and elastic properties.

Journal Name

ARTICLE

Cellulose fatty acid esters as sustainable film materials - effect of side chain structure on barrier and mechanical properties

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Cellulose is mainly utilized by industry for paper and packaging materials. Due to ecological awareness this biopolymer has recently received an increasing amount of attention as a renewable alternative for replacing traditional oil based products. In this work, hydrophobic cellulose based materials were prepared by acylation of cellulose with tall oil fatty acid based saturated, unsaturated and branched fatty acids. Films were prepared by casting, and their oxygen and water vapour permeabilities as well as mechanical and thermal properties were characterized. Unsaturation and branching had a significant effect on the properties of the films. Comparing these materials with already existing commercial products showed that fatty acid modification of cellulose yields films with increased thermal stability, low water vapour transmission rates and enhanced tensile and elastic properties.

Introduction

Even though cellulose is the most widely available biopolymer, its use as chemical raw material started only 150 years ago.[1] A major part of cellulose is still utilized in paper, paperboard and tissue production but significant research efforts are made worldwide to find ways to produce other valuable products. The packaging industry, for example, is currently experiencing a steadily growing demand for new biodegradable materials as a replacement for plastics made from fossil feedstock. Aside from the obvious ecological benefits, cellulose offers a good starting point for material applications, and desired properties can be introduced through chemical modification – esters, ethers, and carbamates being among the most common derivatives. [2-4]

Hydrophobic derivatives of cellulose, like decanoic or palmitic acid esters of cellulose, have been reported to form films with potential to be used as biodegradable coating materials.[2] To introduce plasticity and water repellency, an obvious approach is to modify cellulose with hydrophobic structures such as fatty acids or alkene ketene dimers (AKD).[5-7] Tall oil fatty acids (TOFA), a side-stream of pulping industry from coniferous trees, are an ecological option to be utilized as hydrophobicity inducing components (Fig. 1 a). TOFA originates from distillation of crude tall oil and is a mixture of mostly unsaturated and non-conjugated fatty acids, such as oleic, linoleic and pinolenic acid. [8, 9] Like cellulose, TOFA is a low-cost, sustainable, non-edible and renewable starting material that has various applications as surfactants, cleaners and other chemical derivatives, to name a few. However, it should be noted that TOFA is a mixture of several types of fatty acids and in Kraft pulping conditions especially trienoic acids, like pinolenic acid, are isomerized resulting in the formation of conjugated structures, which easily undergo Diels Alder type cyclization reactions. As a result, cyclized by-products (Fig. 1 b) may be formed.[10] Conjugated structures may thus cause eg. cross-linking, resulting in problems with solubility. Unmodified TOFA is also prone to autoxidation causing instability of TOFA-based materials.[11, 12] These reactions may also take part in "ageing" of the synthesized products. Luckily, these side reactions may be accounted for by eg. hydrogenation. This way the unsaturated structures may be reduced into less reactive saturated forms.

In order to synthesize materials applicable as films, high DS is required as intact or low DS fibers decrease the solubility and inhibit plasticity of the cellulosic materials. High DS for cellulose can be achieved with either homogeneous or heterogeneous reactions. Typical solvents for these are *e.g.* DMA/LiCl or ionic liquids.[5, 13-17] High DS derivatives can also be obtained with "reactive dissolution"-types of reactions.[18] In these, the reaction starts heterogeneously, but as the reaction proceeds the product dissolves into the reaction media, eventually forming a homogeneous solution of the dissolved high DS product.

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Fig. 1. Examples of components of, a) tall oil fatty acid, b) cyclised by-products from TOFA, and c) isostearic acid. [8, 9]

In this work a mixture of toluene and pyridine was used as the reaction media. This offered an efficient media to carry out the acylating reactions. TOFA, modified TOFA and its components (Fig. 1 a and c) were used to acylate dissolving pulp. All of the acylating reagents had 18 carbon atoms, but differed in the degree of saturation (stearic- and oleic acid, hydrogenated TOFA) and chain branching (isostearic acid).The acylating reagents were chosen so that the effect of the degree of saturation and branching on the film properties could be compared. In order to study the differences arising due to the modification the products were dissolved in chloroform and casted as films. The obtained films were characterized for their oxygen- and water vapour permeabilities, as well as their thermal and mechanical properties.

Experimental

Materials

Dissolving pulp was obtained from Domsjö Mill (Sweden). Oleoyl chloride (85 %), oxalyl chloride (98 %) and the hydrogenation catalyst 10 % Pd/C were purchased from Sigma-Aldrich. Isostearic acid (Prisorine 3501 was obtained from, Uniqema and TOFA (Sylfat 2LT) from Arizona Chemicals. Toluene was purchased from VWR Chemicals and was dried by azeotropic distillation. Pyridine was purchased from Fisher Chemicals and dimethylformamide from VWR Chemicals.

Synthesis of fatty acid derivatives of cellulose

TOFA was hydrogenated in ethanol under atmospheric pressure using 10 % Pd/C as a catalyst. TOFA was first dissolved in 400 ml of ethanol in a 1 l round bottom flask with a magnetic stirrer. Then Pd/C (1.6 g) was dispersed into 10 ml of ethanol and added into the flask. Hydrogen gas was passed into the flask until gas consumption ceased. The catalyst was filtered off with suction. Ethyl acetate (100 ml) and hexane (100 ml) were added as co-solvents in order to prevent crystallization of the hydrogenated product during the filtration. Full hydrogenation of TOFA was verified with ^{1}H-NMR spectroscopy, which confirmed the absence of double bonds. The end of partial hydrogenation was approximated to the midpoint of the amount of hydrogen consumed in the full hydrogenation.

Preparation of fatty acid chlorides

All acid chlorides were synthesized in dry conditions under Ar-atmosphere with oxalyl chloride in dry toluene.[19] Isostearic acid (4 g, 14 mmol) was dissolved in 40 ml of dry toluene in a two-neck round bottom flask equipped with a magnetic stirrer and a condenser. Oxalyl chloride (1.5 ml, 17.2 mmol) was added dropwise into the flask. After that the catalyst, two drops of DMF, was added and the reaction mixture was heated at 40 °C for 30 min. Toluene was evaporated in a rotavapor and the acid chloride was used immediately without further purification.

General esterification procedure

Pulp sheets (2.7 g) were cut into small pieces and impregnated in 15 ml of pyridine for 1 h at 100 °C. Acid chloride (70–75 mmol) was dissolved in 250 ml of dry toluene, and cellulose in pyridine was added. The reaction mixture was stirred and heated at 90–100 °C for 2–3 days.[20] Upon completion, at which point the reaction mixture is highly swollen and in one phase, 200 ml of chloroform was added. The dissolved cellulose derivative was precipitated with methanol and filtered. Second precipitation with methanol from chloroform was done in order to ensure purity of the product. The mass of the products increased 4–5 times from the original indicating a high DS.

(^{1}H-NMR ($CDCl_3$): δ (ppm) 0.80-1.60 (aliphatic CH_3 and CH_2), 2.00-2.20 ($CH_2C{=}O$), 3.30-5.20 (protons of cellulose backbone), 5.30 (-CH=CH-; only for oleic acid and partially hydrogenated TOFA); IR: 1735 cm^{-1} (C=O), 3200–3500 cm^{-1} (OH), 2980–3030 cm^{-1} (alkene C-H, only for oleic acid and partially hydrogenated TOFA), 1600–1650 cm^{-1} (C=C, only for oleic acid and partially hydrogenated TOFA); DS: 2.23 (modification with fully hydrogenated TOFA), 2.53 (modification with oleic acid), 2.69 (modification with isostearic acid), 2.86 (modification with partially hydrogenated TOFA)).

Film casting

Films were prepared by drying 2 % solutions (20 ml in $CHCl_3$) of the dissolved cellulose derivatives on a petri dish (ø 13.5 cm) at room temperature and atmospheric pressure. Thickness and width of the films were measured with a commercial digital caliper (0.01 mm accuracy) from several points and average values were calculated. Average thicknesses of the films were 224 µm (isostearic acid modification), 205 µm (oleic acid modification) and 221 µm (partly hydrogenated TOFA modification).

Structural characterization of the products

FTIR spectra were measured with Bruker ALPHA FT-IR (ATR, diamond plate) instrument operated by OPUS 6.5 software.

^{1}H-NMR spectra were recorded with a Varian Inova 300 MHz NMR spectrometer at 27 °C. The degree of substitution (DS) of the cellulose derivatives was determined with ^{31}P NMR using a method described by King *et al.*[15] Quantitative ^{31}P-NMR spectra (27 °C) were recorded with a Varian Unity Inova 600 MHz NMR spectrometer.

Hitachi S-4800 field emission scanning electron microscope (FESEM) was used for imaging of the samples. Prior to the imaging a Cressingtong 208HR high resolution sputter coater was used for applying a 2.5 or 5.0 nm layer of Pt/Pd on the samples.

Material properties of the cellulose derivatives

Thermogravimetric analysis (TGA) was carried out with a Mettler Toledo SDTA851 instrument. The conditions for decomposing the materials were following: heating from 50 to 600 °C with a rate of 10 °C/min under constant nitrogen gas flow of 50 ml N_2/min. TA Instrument DSC Q200 with a RSC 90 cooling system was used for differential scanning calorimetric (DSC) analyses. Measurements were done with two heating ramps from -50 °C to 250 °C (10 °C/min and 50 ml N_2/min).

An Instron 33R4465 universal testing machine (Instron Corp.) with a load cell of 100 N was used for the analysis of tensile properties. Tensile strain and elastic modulus were determined at constant conditions of 22 °C and 50 % relative humidity (RH). The initial grip distance was 30 mm, and the rate of grip separation was 5 mm/min. The sample area was 5 mm x 70 mm, and 10 consecutive measurements were made for each sample.

Fig. 2 Pictures of the films made from dissolving pulp with, a) isostearic acid, and b) partially hydrogenated TOFA.

Transmission rate of water vapour was 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 RH was maintained at 52 % with saturated $Mg(NO_3)_2$ solution. The cups were weighed at intervals of 12–48 h. The water vapour transmission rates (WVTR) were calculated from a linear regression of the slope of the weight gain versus time by division of the slope by the film area.[21]

An Ox-Tran Twin instrument (Modern Controls, Inc.) with a coulometric sensor was used to study the transmission rate of oxygen (OTR) through the films (ø 5 cm^2). In order to condition the samples to correspond the inner RH of the instrument they were stabilized inside the instrument (20 h) prior the measurements. During the measurement, the samples were exposed to 100 % oxygen on one side and a mixture of 98 % nitrogen and 2 % hydrogen on the other side. The measurements were carried out at 22 °C and normal atmospheric pressure.

RESULTS AND DISCUSSION

The cellulose esters of oleic and isostearic acids were soluble in chloroform in high concentrations and resulted clear and transparent films (Fig. 2 a). Also the hydrogenated TOFA-cellulose esters were soluble in chloroform and films could be prepared. However, films from the fully hydrogenated TOFA-cellulose could not be further analyzed due to shrinking and brittleness. Films from the partially hydrogenated TOFA-cellulose were white and elastic but not completely transparent (Fig. 2 b). The brittleness of the fully hydrogenated TOFA-cellulose is thought to be caused by the higher order in structure due to linear and saturated fatty acid tails (Supplementary information). The only insoluble product was the unmodified TOFA-cellulose. Despite the high DS this resembled a dense plastic-like material. This is probably due to reactions of the unsaturated structures (Fig. 1). Without the hydrogenation procedure the product may undergo cross-linking within the material resulting in insolubility.

Structural analysis of the cellulose esters

IR-spectroscopy allowed us to verify and compare the acylation reactions. As the DS increases, the intensity of the carbonyl (C=O, 1735 cm^{-1}) signal increases and correspondingly, the intensity of the hydroxyl (-OH, 3200–3500 cm^{-1}) signal decreases (Fig. 3). In addition, two regions in the IR spectra of oleic acid and partially hydrogenated TOFA cellulose derivatives could be used for detection of unsaturation. Expansions I and II (Fig. 3) show signals arising from the stretching of the alkene C-H bond at 2980–3030 cm^{-1} and stretching of the carbon-carbon double bond at 1600–1650 cm^{-1}.

^{1}H- and ^{31}P NMR were used to verify the structures and DS of the materials. The ^{1}H NMR spectra showed typical chemical shifts of cellulose esters (Table 1). These were mainly the signals from the protons of the anhydro glucose units of cellulose and aliphatic methylene and methyl protons. Cellulose modified with oleic acid had a high intensity signal and partially hydrogenated TOFA had a weak signal at the double bond region, as expected. This corresponds to the results also from IR, showing these two materials still having unsaturation. ^{31}P-NMR was used for the measurement of the DS of the materials.[15] This showed that the materials had relatively high DS, ranging from 2.23 to 2.86 (Table 1).

Table 1. The chemical shifts (^{1}H NMR) and corresponding DS (^{31}P NMR) of the synthesized cellulose esters.

Thermal properties of the cellulose esters

Thermogravimetric analysis was used to study the decomposition of the materials. Mass loss of 5 % upon heating was set as the decomposition temperature. Decomposition occurred in a single step at a range between 327–342 °C. The isostearic acid, oleic acid and fully hydrogenated TOFA-cellulose derivatives decomposed at 341–342 °C. Partially hydrogenated TOFA-cellulose had a somewhat lower temperature of decomposition at 327 °C. Comparing these values to the unmodified pulp (320 °C), an increase of 7–22 °C in thermal stability was achieved. The lowest value of partially hydrogenated TOFA-cellulose is attributed to side reactions and byproducts caused by the composition of TOFA that has not been hydrogenated. These byproducts are expected to be more reactive causing a lower decomposition temperature.

Differential scanning calorimetry was used to study the melting properties of the derivatives. Specifically, the second heating was important for the analysis as temperature history of the samples would only then be comparable. The isostearic acid and partially hydrogenated TOFA derivatives showed glass transitions (T_g) at 104 °C and 119 °C respectively (Fig. 4). The difference between the onsets and offsets were quite long, ranging from 32 °C for isostearic acid-cellulose to 62 °C for partially hydrogenated TOFA-cellulose. No melting points were apparent for these samples. As with unmodified dissolving pulp, the oleic acid ester of cellulose does not have phase transformations within the temperature range of -50–250 °C. The tilted structure of the oleic acid moieties is expected to cause amorphicity, which the absence of melting points confirms. This was verified also with XRD measurements (Supplementary information).

Fig. 3 FTIR spectra of the fatty acid and TOFA-modified celluloses. Magnifications represent absorptions from alkene C-H stretching (I) and C=C stretching (II).

Fig. 4 DSC diagram showing the second heating step for a measurement. Glass transitions are shown for partly hydrogenated TOFA- and isostearic acid modified celluloses with their onset and offset temperatures, as well as the corresponding T_g. Also the melting point, for fully hydrogenated TOFA-cellulose, is seen at 36.46 °C. For illustration the curves were overlapped within the Y-axis, meaning that the original heatflow values do not apply in this diagram.

Fully hydrogenated TOFA-cellulose was the only sample with a distinct melting point (Tm), at 36 °C, and an accompanying crystallization point (Tc), at 27 °C (Fig. 4). This clear melting point verifies the sample having crystallinity. This is also seen on x-ray diffractograms, where the fully hydrogenated TOFA-cellulose has the smallest peak width implying highest degree in order (Supplementary information). This is due to the hydrogenation of TOFA, which will result in a greater amount of saturated fatty acids capable of forming crystallinity within the sample. The difference for the onset and offset of the Tm (at 36 °C) was from -12 °C to 81 °C, altogether 93 °C.

Reason for the wide temperature range in the Tg and Tm transitions lies in the structure of the materials. Since the fatty acids used in the esterifications are mixtures, the following products exhibit non-uniform substitution and are constructed of various types of structures. This can be seen as peak broadening whereas a uniform material would have a more narrow range of thermal response.

Tensile properties of the cellulose ester films

The stress-strain curves were analyzed to gain information on the film properties of the cellulose derivatives. For barrier applications, the tensile properties are of importance, as the film should be flexible enough to withstand physical forces without losing its barrier properties. The maximum strain and elongation show how much the sample can increase in length before breaking, and the elastic modulus is a measure of stiffness of an elastic material, i.e. stiffer material has higher elastic modulus.

The cellulose ester of isostearic acid showed a maximum strain of 101 % meaning a length twice from the original (Fig. 5 a). Oleic acid and partially hydrogenated TOFA-modified films had maximum strains of 57 % and 45 %, respectively (Fig. 5 a). In a study by Crépy[22] it was shown that the length of the fatty acid chains in cellulosic derivatives increases the ductility. Isostearic acid is composed of C18 fatty acids with various types of branching in the chains, so the high maximum strain cannot be accounted just by the chain length. Instead, the disorder caused by the branching seems to have a major effect enabling the material to be deformed easily. Crépy[22] also reported that unsaturation prevents chain elongation resulting in a decrease of the maximum strain. This is in agreement with our results (Fig. 5 a), as the cellulose esters of oleic acid and partially hydrogenated TOFA had significantly shorter maximum elongations.

Comparison of the elastic moduli showed the oleic acid modified material being the stiffest with a modulus of 50.13 MPa. This can be attributed to the uniform structure of the material, as the constitution of oleic acid is the most pure to start with. Regardless of the double bond tilting the otherwise 'linear' fatty acid structure, a more ordered packing of the fatty acid chains is possible, thus resulting in a stiffer material. Conversely, isostearic acid, with elastic modulus of 30.15 MPa, is known to have a very heterogeneous composition due to the various branched structures making dense packing of the side chains difficult. Similarly, the partially hydrogenated TOFA, with elastic modulus of 35.05 MPa, has a high heterogeneity due to the mono- and polyunsaturated fatty acids along with other structures. This complexity in the starting materials, and disorder in the products, therefore leads to a lower elastic modulus.

Comparing the results from this study to other reports shows clear similarities. For example, films made from lauric acid esters (C12) of microcrystalline cellulose have been shown to have elastic moduli from 19 to 9 MPa and maximum strains of 90 to 360 % with varying DS.[23] Comparisons were also made to commercial polyethylene with modulus and maximum strain at 300 MPa and 1100 % respectively. This proves fatty acid modified cellulose esters in this work having more formable structure, but lower tensile strength.

Oxygen and water vapour permeability of the cellulose ester films

The transmission rate of oxygen gas through the fatty acid modified films was measured. The results showed that none of these materials as such are applicable as oxygen barriers. Precise values for OTR could not be measured by this method since the concentration of oxygen passing through the film was too high for the sensor.

As barriers for water vapour, the films from the fatty acid celluloses functioned well and gave reasonably low water vapour transmission rates from 21.65 and 22.35 g/m^2·d for the isostearic acid and oleic acid modified films, respectively, and 43.36 g/m^2·d for the partially hydrogenated TOFA films. However, there was significant variation in the film thickness (170, 202 and 131 μm respectively), which has a crucial effect on the WVTR. Therefore, water vapour permeability is preferred as it takes thickness into account. Values for the WVPs (Fig. 5 b) showed a trend where the permeability grows from 2.55 and 3.09 g·mm/kPa·m2·d for isostearic acid and oleic acid modified films, to 3.90 g·mm/kPa·m2·d for the partially hydrogenated TOFA films.

Fig. 5 Diagram showing, a) the maximum strain (values on the left side of the column) and elastic modulus (values on the right side of the columns); and b) the water vapour permeabilities for of the fatty acid modified cellulose films.

As expected, hydrophobicity has a crucial effect on the WVP and it can be seen that the isostearic acid functionalities showed the highest retardation for water vapour. WVP properties have been shown to be affected by the amount of methylene groups in a study by Bras[24], namely the barrier properties increase as the content of methylene increases. Also, the inverse relation of WVP to OTR was reported showing the oxygen permeability increasing as the water vapour permeability decreases. Bras[24] concluded that oxygen permeability is mainly dictated by spatial effects, whereas the WVP is dominated by hydrophobicity and polarity. These conclusions are in agreement with our results, where the films showed good barrier properties for water vapour, but lack in barrier properties for oxygen.

Acetylation of cellulose has been shown to have an impact on the WVTR. For example, Rodionova[25] reported the decrease of WVP of microfibrillated cellulose from 234 to 167 g/m^2·d due to acetylation. Comparing these values to the transmission rates measured in this study shows the fatty acid modified cellulose films having very low values even though the material is consisting of a dissolving pulp with a higher degree of polymerization. The WVTR of low density polyethylene is around 20 g/m^2·d.[26] Thus, the fatty acid and TOFA esters of cellulose show very promising properties for film and packaging applications. For example, food packaging could benefit from an ecological barrier material retarding moisture, but enabling gas permeation.

Surface morphology of the films

Scanning electron microscopy was used for the surface analysis of the films. The starting materials before film casting were used as a reference to see how their original morphology changes due to dissolution and casting. The differences were clear and two main types of materials stood out. The isostearic acid modified material had lost its fibrillar morphology and was densely packed into a uniform layered structure (Fig. 6 a), which is also in good agreement with the tensile properties. The rest of the films shared a more fibrillar and random construction (Fig. 6 b). As expected from the structure of the uncasted material, the isostearic acid modified films were smoother than the films casted from the more fibrillar materials (Fig. 6 c and d). The difference was, however, surprisingly big, as the films from isostearic acid derivatives were very smooth, while the other films were constructed of multiple thin layers with a more uneven structure. Cross-sectional views from the films revealed these differences even better, showing the isostearic acid modified films having a uniform structure (Fig. 6 e and f). Thus, it is easy to understand the differences in the appearance and properties of the films, as isostearic acid derivatives yielded fully transparent and flexible films, but partially hydrogened TOFA- and oleic acid derivatives more blurry films.

Fig. 6 Images from scanning electron microscopy. Isostearic acid modified cellulose, a) before film casting, c) as a film and e) cross-sectional view. Oleic acid modified cellulose similarily, b) before film casting, d) as a film and f) cross-sectional view.

Conclusions

Films based on cellulose esterified with tall oil based fatty acids were shown to have potential as hydrophobic films or barriers. Materials modified with isostearic acid, oleic acid and partially hydrogenated TOFA were able to form elastic, flexible and transparent films. Unsaturation and branching of reactants had significant effects on the properties of the films. After modifications thermal stability increased (7–22 °C) and relatively low glass transition temperatures (104–119 °C) were measured. Maximum strain (up to 101%) and elastic moduli (30–50 MPa) were comparable to the values of commercial products. Permeability to water vapour showed also excellent values (2.55–3.90 g·mm/kPa·m2·d) comparable to low density polyethylene, for instance. The results are encouraging and show good values in comparison to other similar commercial materials. However, to further improve the properties of these materials and the suitability for larger scale applications, variation of the substituents, optimization of the reactions and control of the DS should be studied more closely.

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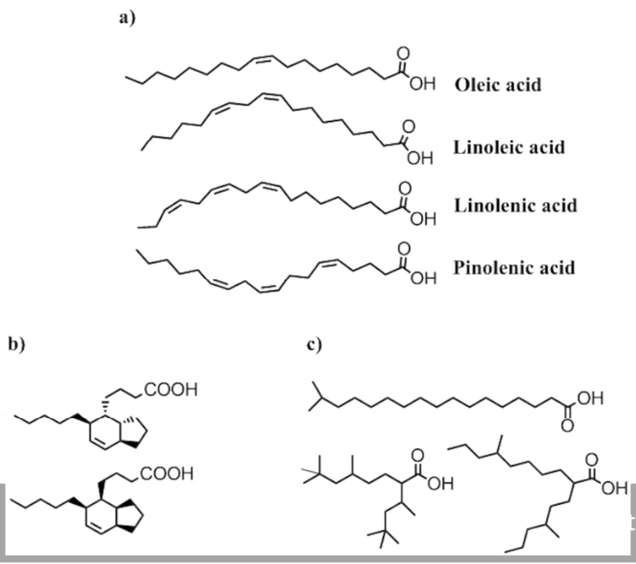

Fig. 1. Examples of components of, a) tall oil fatty acid, b) cyclised by-products from TOFA, and c) isostearic acid.

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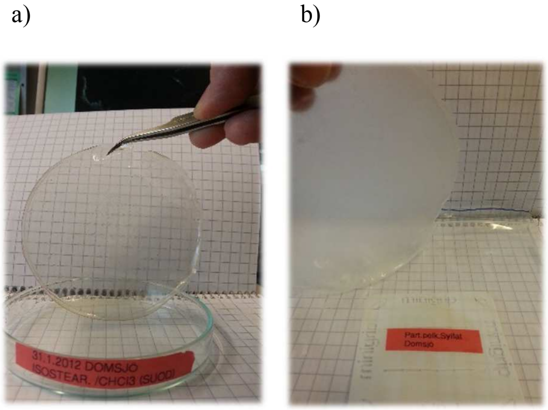


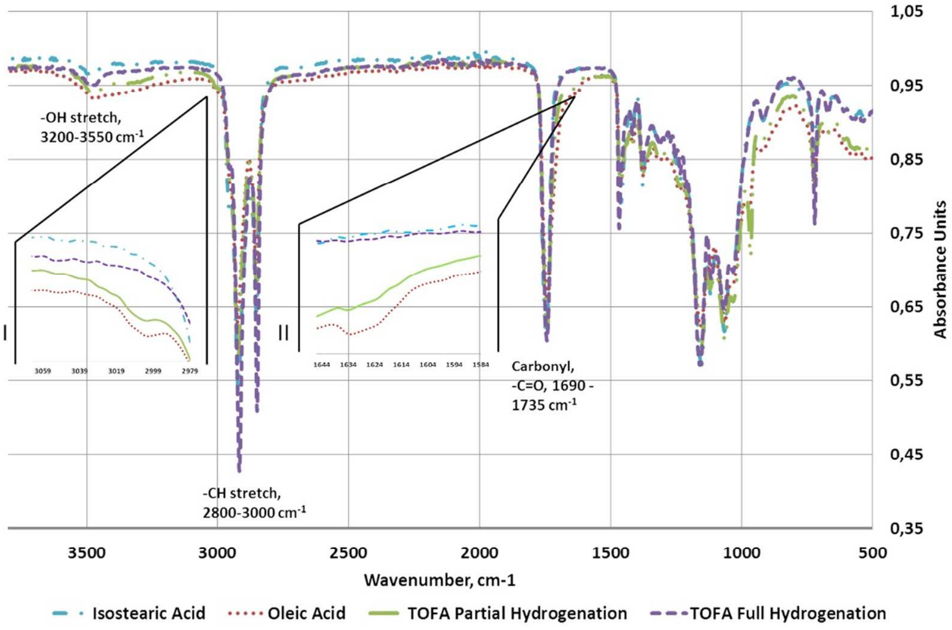


Fig. 3 FTIR spectra of the fatty acid and TOFA-modified celluloses. Magnifications represent absorptions from alkene C-H stretching (I) and C=C stretching (II).

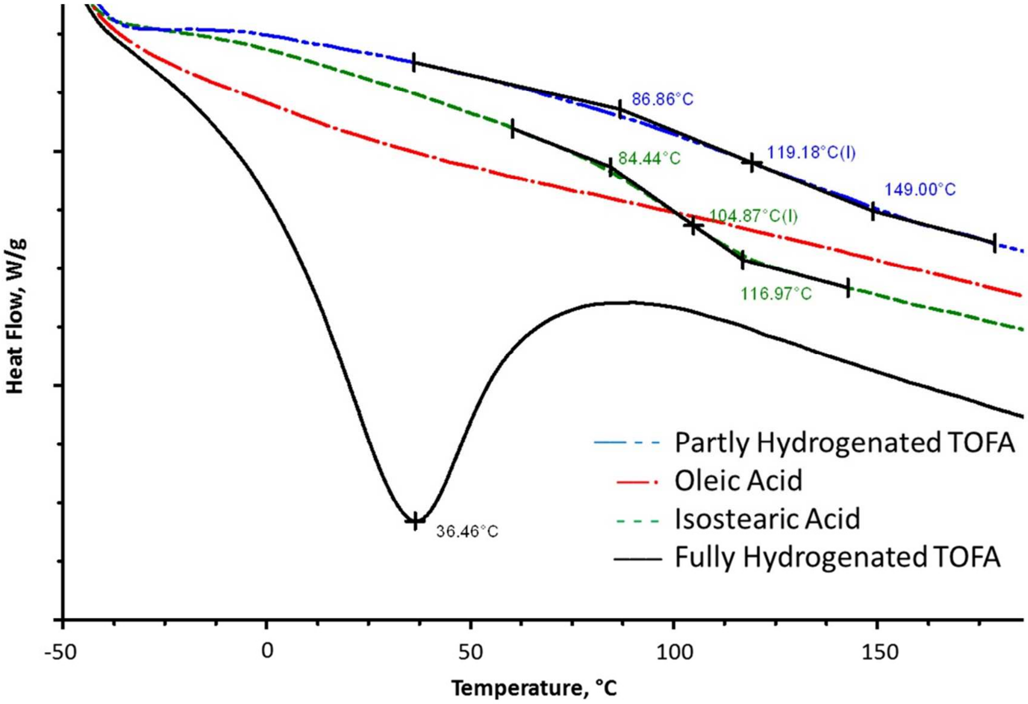
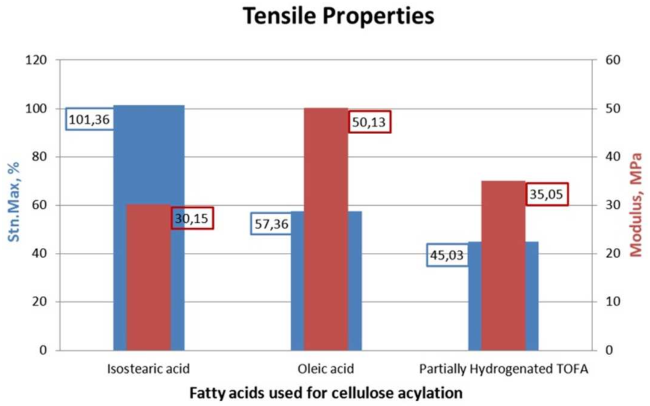


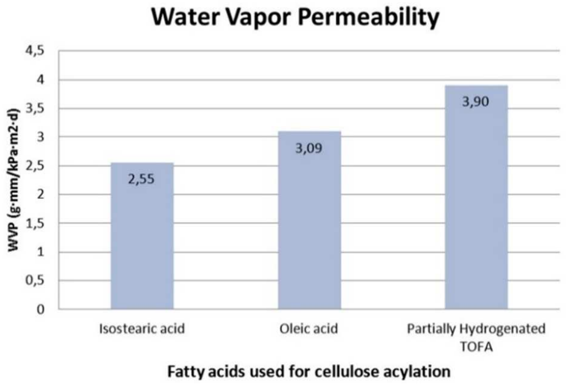
Fig. 4 DSC diagram showing the second heating step for a measurement. Glass transitions are shown for partly hydrogenated TOFA- and isostearic acid modified celluloses with their onset and offset temperatures, as well as the corresponding T_g. Also the melting point, for fully hydrogenated TOFA-cellulose, is seen at 36.46 °C. For illustration the curves were overlapped within the Y-axis, meaning that the original heatflow values do not apply in this diagram.



a)

b)

Fig. 5 Diagram showing, a) the maximum strain (values on the left side of the column) and elastic modulus (values on the right side of the columns); and b) the water vapour permeabilities for of the fatty acid modified cellulose films.



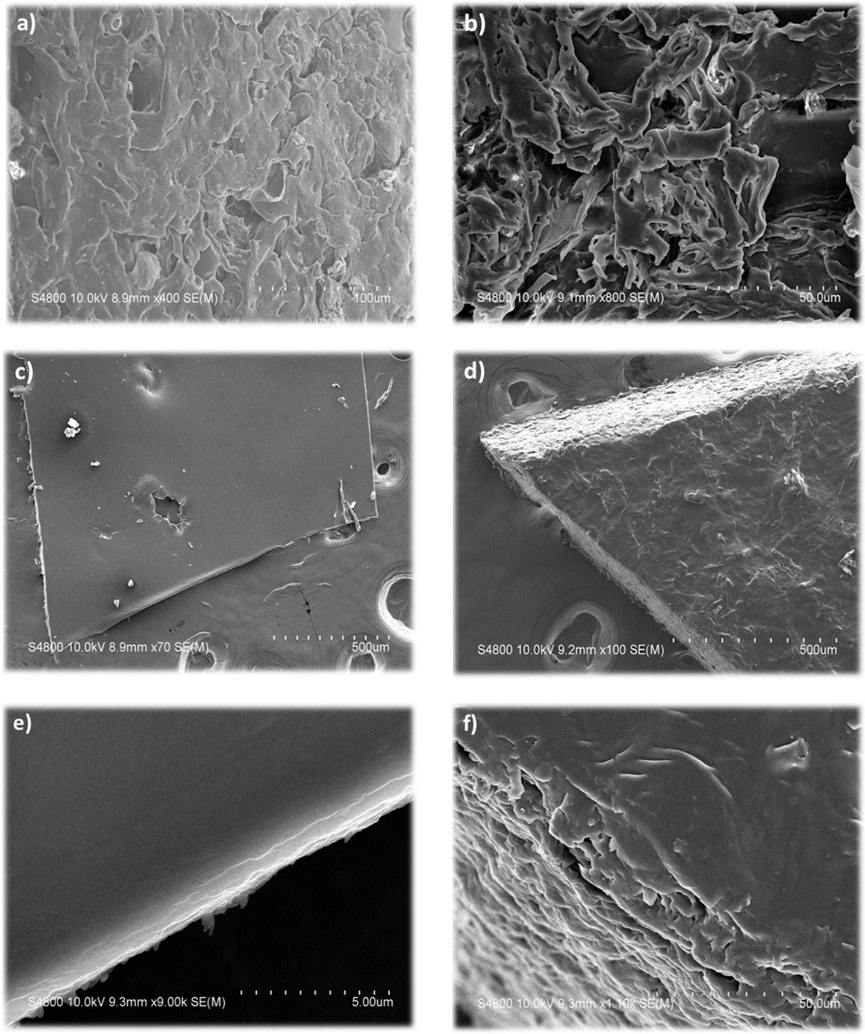


Fig. 6 Images from scanning electron microscopy. Isostearic acid modified cellulose, a) before film casting, c) as a film and e) cross-sectional view. Oleic acid modified cellulose similarily, b) before film casting, d) as a film and f) cross-sectional view.

	Hydrogenated TOFA ester, ppm	Partially hydrogenated TOFA ester, ppm	Oleic acid ester, ppm	Isostearic acid ester, ppm
CH_3 and CH_2	0.80 – 1.60	0.80 – 1.60	0.80 – 1.60	0.80 – 1.60
H_{AGU}	3.30-5.20	3.30-5.20	3.30-5.20	3.30-5.20
$CH_2C=O$	2.00-2.20	2.00-2.20	2.00-2.20	2.00-2.20
-CH=CH-	-	5.30	5.30	-
$DS_{31P\text{-}NMR}$	*2.23*	*2.86*	*2.53*	*2.69*

Table 1. The chemical shifts (^{1}H NMR) and corresponding DS (^{31}P NMR) of the synthesized cellulose esters.