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OXYGEN AND WATER VAPOUR BARRIER FILMS WITH LOW MOISTURE SENSITIVITY FABRICATED FROM SELF-CROSS-LINKING FIBRILLATED CELLULOSE

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ABSTRACT

To replace petroleum-based barriers used in, for example, packaging applications with a bio-based alternative, the sensitivity to moisture must be lowered. The present work describes the fabrication and characterisation of cellulose-based films with remarkably improved oxygen and water-vapour-barrier properties at 80% relative humidity. This was achieved by fabricating films of self-cross-linking fibrillated cellulose after partial periodate oxidation to dialdehyde cellulose. At a relative humidity of 80%, films made of 27% and 44% oxidised cellulose, respectively, showed less than half the water vapour permeability of the untreated reference; 3.8 g·mm/(m^2·24 h·kPa) and 3.7 g·mm/(m^2·24 h·kPa) compared to 8.0 g·mm/(m^2·24 h·kPa). This was presumably due to a lower moisture uptake in the films, and consequently less swelling. In the absence of moisture, films from both unmodified and modified fibrillated cellulose were ideal oxygen barriers, but at a relative humidity of 80%, films based on 27% and 44% converted cellulose had an oxygen permeability of 2.2 ml·µm/(m^2·24 h·kPa) and 1.8 ml·µm/(m^2·24 h·kPa), respectively, compared to 9.2 ml·µm/(m^2·24 h·kPa) for the non-oxidised material.

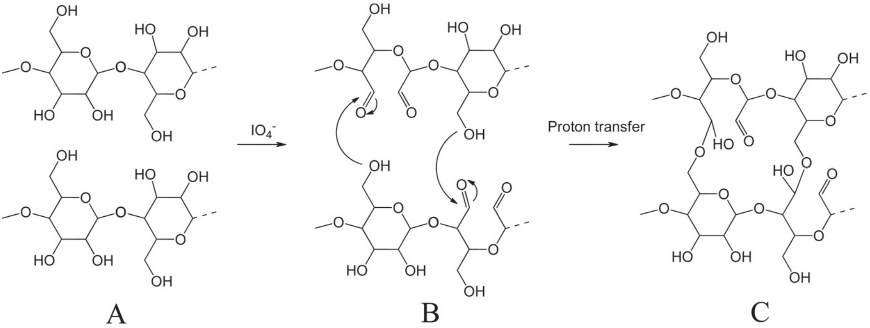
The cross-linking resulted in an embrittlement of the films, but the 27% oxidised material still had a tensile strength of 148 MPa and a tensile strain at break of 2.0%, which is sufficient in, for example, many packaging applications.

INTRODUCTION

The development of novel bio-based packaging and barrier materials that can compete with, and replace, conventional non-renewable materials is a great challenge. One of the most severe shortcomings of carbohydrate-based materials is their sensitivity to moisture. At low relative humidity various films made from starches, hemicelluloses, dissolved cellulose and fibrillated cellulose offer excellent barriers against oxygen, but as soon as the relative humidity increases, carbohydrates start to adsorb moisture and this leads to a swelling of the film and a subsequent increase in gas permeability [1–11]. To prevent water vapour transmission, carbohydrate-based films are often considered to be so poor that few researchers even make the effort to measure it, and the amount of experimental data is hence limited [2, 8, 10–13], especially over a broad relative humidity range.

There are, however, ways of reducing the affinity of cellulose to water and the water diffusivity. A commonly used approach is by covalent cross-linking, which is a well-known route to increase the dimensional stability in the face of changes in moisture content, and to reduce the diffusion of moisture [14–18]. Yang et al. [13] recently added cross-linking chemicals to cross-link fibrillar films from well-dispersed, highly charged fibrils, and the water vapour transmission was significantly lowered. Unfortunately, barrier properties were evaluated only at 50% RH, i.e. the effect of a lower moisture sorption and film swelling under high humidity was not explored. Chemical modifications such as esterification and grafting have also been explored to improve water-vapour-barrier properties [11, 19, 20], but critical mechanical and oxygen-barrier-properties were sacrificed. Another widely used approach with polysaccharides is to disperse layered silicates in the matrix polymer [7, 21, 22]. However, the dispersion of inorganic platelets in the matrix polymer and the orientation of the platelets in the final films presented serious limitations to the final properties [7, 21].

In the present investigation, the introduction of internal cross-links between aldehydes, induced by periodate oxidation of the C2–C3 bonds, and hydroxyl



Scheme 1. Schematic representation of how the C2–C3 bonds of two cellulose chains (A) are oxidised into dialdehyde cellulose (B), and finally covalently cross-linked with each other (C). The aldehyde still available in the rightmost structure may cross-link with other available hydroxyl groups, possibly the C6 hydroxyl group, as suggested by Morooka et al. [23].

groups [16, 23, 24] on a fibril level was explored. A schematic oxidation and cross-linking reaction is shown in Scheme 1. To achieve films with high density and few large pores, the modified fibres were fibrillated in a homogeniser prior to film fabrication.

MATERIALS AND METHODS

Fibres

Dried bleached kraft fibres (K44) were provided by SCA AB (Östrand pulp mill, Sweden). Before use, the fibres were soaked in water and disintegrated, and the carboxyl groups of the fibres were converted into their sodium form according to an earlier described procedure [11].

Chemicals

Sodium (meta)periodate for the oxidation of cellulose, isopropanol (≥99.8% purity) used as radical scavenger and hydroxylamine hydrochloride for the determination of the degree of oxidation were all purchased from Sigma-Aldrich. Polyethyleneimine (PEI), with a molecular weight of 60 kDa, used to promote fibril adsorption prior to AFM imaging, was purchased from Acros Organics. Other chemicals, such as hydrochloric acid and sodium hydroxide, were all of analytical grade.

Oxidation of cellulose

Under stirring, 5.4 gram of sodium periodate per gram of fibre was added to a 4 g/l fibre suspension containing 6.3% isopropanol (by volume) as radical scavenger to prevent side reactions and chain scission [25, 26]. To further prevent chain scission, the oxidation reactions were performed in the dark [27] for 12 or 36 h before the reaction was terminated by filtration and thorough washing with deionised water. The degree of conversion to dialdehyde cellulose, assuming pure cellulose as starting material, was determined to be 27% and 44%, respectively, by reaction with hydroxylamine hydrochloride and titration with sodium hydroxide according to an earlier described procedure [16, 28].

Fibril preparation

Fibrillated cellulose was prepared from treated and untreated fibres by homogenisation (Microfluidics' Microfluidizer processor M-110 EH) of 4–5 g/l suspensions at a pressure of ca. 1600 bar. The fibres were pre-homogenised once through 400 µm and 200 µm chambers connected in series, before being homogenised ten times through 200 µm and 100 µm chambers connected in series. To minimise the risk of clogging, the untreated fibres were beaten for 6000 revolutions in a PFI mill prior to homogenisation.

Fibril characterisation

To estimate the dimensions of the fibrils, a polished silicon wafer (MEMC Electronic Materials, Italy) with a pre-adsorbed PEI layer (5 min adsorption at 0.1 g/l) was dipped for 10 s in a 20 times diluted fibril suspension, followed by drying and Atomic Force Microscopy (AFM) in the tapping mode using a model MMP-12100-10 cantilever (Veeco Instruments' Multi-Mode IIIa).

Film fabrication

Prior to film fabrication, the fibrillated cellulose was diluted to approximately 2.5 g/l and sonicated for 10 min in a VWR Ultrasonic Cleaner, followed by vacuum filtration using a 325×2300 mesh Twill Dutch Double Weave (BoppUtildi, Sweden) in a Rapid Köthen sheet former (Paper Testing Instruments, Austria), using an earlier described film-preparation method [29]. After filtration, a second metal weave was placed on top of the film and the whole assembly was dried for 15 min at 93 ºC under a reduced pressure of 95 kPa. The films were stored at 23 ºC and 50% RH until further analysis.

X-ray diffraction

The crystallinity was evaluated by collecting X-ray diffraction (XRD) spectra of fibril films using an X'Pert Pro XRD (PANalytical). Diffractograms were recorded in the reflection mode in the angular range of 5–40° (2θ). CuKα radiation (1.5418 Å) was generated with an applied voltage of 45 kV and a current of 35 mA. An incremental step of 0.05° and a rate of 1 step per 10 s were used. Samples were dried in a desiccator with silica gel prior to the measurements.

Scanning electron microscopy

A high-resolution field-emission scanning microscope (FE-SEM) (Hitachi S-4800) was used to acquire micrographs of the fabricated films. In order to suppress specimen charging during imaging, the specimens were sputtered for 5–10 s using a Pt-Pd target in a 208 HR Cressington Sputter Coater.

Tensile testing

Tensile testing was performed at 23 °C and 50% RH using an Instron 5944 with a 500 N load cell. Test pieces, 5 mm wide, were clamped with a free span of 40 mm and strained at a strain rate of 10%/min. Young's modulus (E) was determined from the slope of the stress-strain curve in the low-strain region in the vicinity of 0.05% strain.

Permeability testing

The barrier properties of the films were evaluated on 5 cm^2 samples with respect to oxygen (Systech instruments' Model 8001 oxygen permeation analyser) and water vapour (MOCON PermaTran-W 3/33) according to the ASTM D-3985 and ASTM F1249-06 Standards, respectively. In terms of relative humidity, the oxygen permeability measurements were performed symmetrically, i.e. having the same relative humidity on both sides of the test specimen, whereas the water vapour permeability measurements were performed asymmetrically by feeding the detection side with dry nitrogen. Water vapour permeability was measured in quadruplicate and oxygen permeability in triplicate.

Moisture sorption

The equilibrium moisture contents at the relative humidities used for the water vapour permeability measurements, and 90% RH, were determined by placing films on a balance located in a glove box connected to a moisture generator mixing dry and wet air currents in the appropriate proportions. Dry weights were determined by drying overnight at 105 °C.

RESULTS AND DISCUSSION

Fibril characterisation

Fibrils were produced by homogenisation, either from untreated fibres or after periodate oxidation to dialdehyde cellulose at two degrees of oxidation: 27% or 44%. Figure 1 shows AFM images of these fibrils and, as can be seen, there are apparent differences between the differently treated fibrils, in terms of both size and their

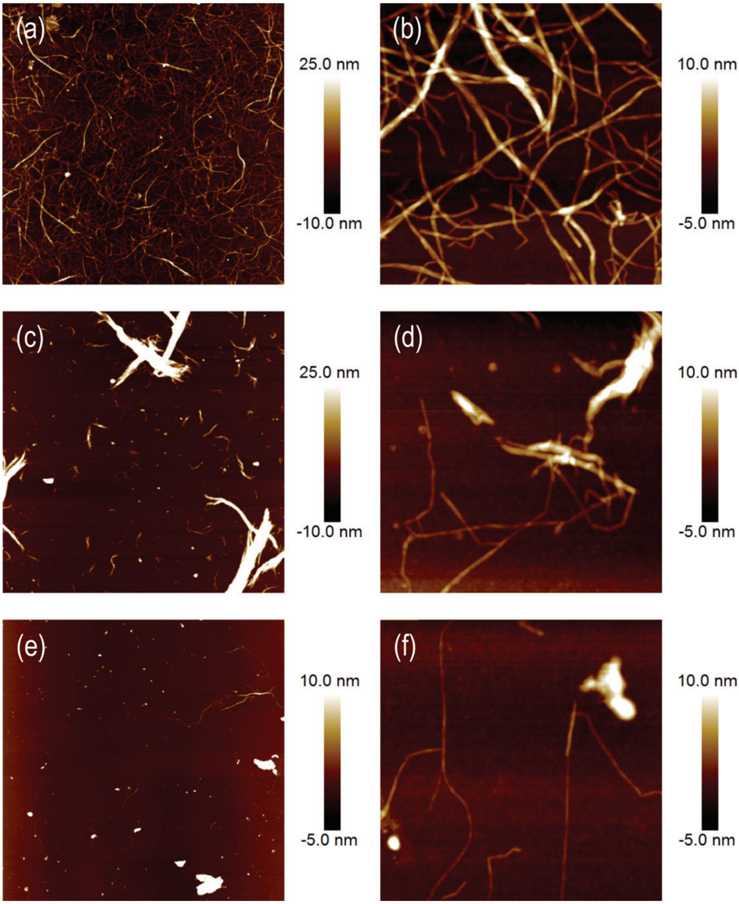


Figure 1. AFM height images, with image sizes of 10×10 μm^2 (left column) and 1×1 μm^2 (right column), of fibrils adsorbed at a concentration of ca. 0.25 g/l on PEI-pre-treated silica surfaces after ten passes through a 100 μm homogeniser chamber; (a–b) non-oxidised, (c–d) 27% oxidised, and (e–f) 44% oxidised.

affinity for the PEI-coated silica surface. The reduced affinity confirms that there is a change in chemical composition and structure of the fibrils, caused presumably not only by the conversion to dialdehyde cellulose but also by the observed material loss of ca. 15% of the material during the oxidation and subsequent washing. The removed material consists mainly of hemicelluloses and, since these contain charged groups, the charge density of the modified fibrils, and consequently their affinity for the PEI-surface, is less than that of the unmodified fibrils. Besides this difference in adsorption, there is also a distinct difference in particle shape, size, and size distribution. The untreated fibrils have fibril widths ranging from 4 to 10 nm with some larger 20 nm aggregates (Figure 1a–b), as is expected from fibrillated wood fibres [30, 31]. The surface with 27% oxidised fibrils (Figure 1c–d), which has less surface coverage than the surface with untreated fibrils, contains a larger number of fibril aggregates, indicating that the fibres were more difficult to homogenise, due presumably to cross-links introduced between individual fibrils prior to homogenisation. Nevertheless, free fibrils are present, i.e. the fibril suspension had a high size polydispersity. When the fibres, prior to homogenisation, were further oxidised to 44% oxidation (Figure 1e–f), there was even less adsorption, and there were fewer high-aspect-ratio aggregates than in the 27% oxidised material (Figure 1c), but a significant amount of large low-aspect-ratio particles. Furthermore, the single fibrils seen in Figure 1e–f are very thin; 2–5 nm.

Figure 2 shows XRD spectra of reference and modified fibrils and it is clear that the periodate oxidation significantly reduced the crystallinity of the material. The crystallinity index [32] decreased from 73% for the reference to 63% for the

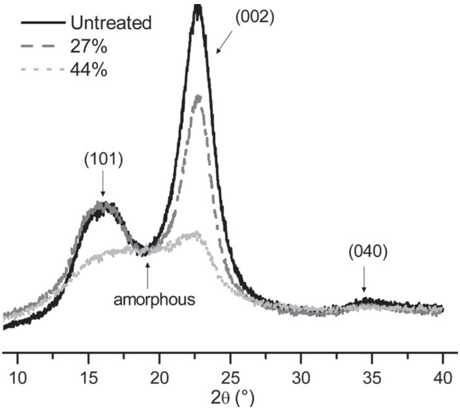


Figure 2. X-ray diffraction spectra of films made from cellulosic fibrils, untreated and periodate oxidised to 27% or 44%. Crystalline planes, as well as the region corresponding to amorphous cellulose, are marked by arrows.

27% oxidised material and 21% for the 44% oxidised material, well in accordance with earlier published results for periodate-oxidised cellulose [33, 34], and further treated dialdehyde cellulose [34, 35]. This presumably leads to thinner (Figure 1f) and more flexible fibrils [34], and is expected to affect the formation and mechanical properties of the films, as well as their barrier properties. The fact that periodate oxidation gradually reduces the crystallinity (Figure 2), with a simultaneous decrease in crystallite width [36], also makes it plausible to assume that there is a heterogeneous oxidation process that leaves behind a fibril with a highly crystalline core and a cross-linked amorphous outer layer.

Film fabrication and mechanical characterisation

As shown in Table 1, the time to fabricate the films was relatively short, i.e. it was fairly easy to dewater the fibril suspensions (without significant material loss; not shown). The two grades of oxidised fibrils were also significantly easier to dewater than the untreated grade, which may be an effect of particle size (Figure 1). The films had densities 5–10% less than 1500 kg/m^3, i.e. the density of completely non-porous cellulose [37]. This, and the fact that the films were only semi-transparent, indicates that they were somewhat porous. This was further supported by microscopy investigations, where Figure 3 shows SEM images of the three different films, all of which show the presence of small pores. The SEM images also support the difference in fibril size distribution found by AFM (Figure 1), i.e., the 27% oxidised material consisted of larger fibril aggregates than the untreated material (Figure 3b compared to 3e). In Figures 3g–i, showing the 44% oxidised material, it is interesting to note the absence of any distinct fibrillar struc-

Table 1. Film filtration times and average structural and mechanical properties. Tensile data are given with 95% confidence limits.

	Approx. filtration time (min)	*Apparent density (kg/m^3)*	*Apparent thickness (µm)*
Untreated	24	1420	34
27% oxidised	9	1400	43
44% oxidised	11	1325	46
	Young's modulus (GPa)	*Tensile stress at break (MPa)*	*Tensile strain at break (%)*
Untreated	10.1 (0.8)	225 (22)	6.08 (1.26)
27% oxidised	11.1 (0.5)	148 (10)	2.02 (0.35)
44% oxidised	6.0 (0.2)	48 (15)	0.99 (0.21)

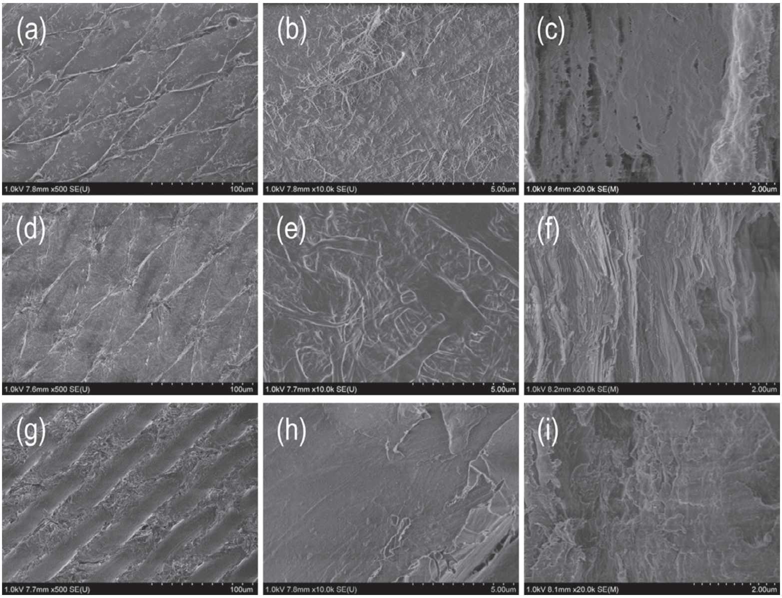


Figure 3. SEM images of films made from homogenised kraft fibres that prior to homogenisation were (a–c) untreated, (d–f) 27% periodate oxidised, and (g–i) 44% periodate oxidised. The first and second columns show top-view images at 500 and 10 000 times magnification, and the third column shows cross-section views at 20 000 times magnification. The repeating patterns in the left-hand column are imprints of the filter and drying support.

ture. The XRD spectrum (Figure 2) for the same material shows a significantly lower crystallinity than the non-oxidised and 27% oxidised material. This is in agreement with earlier findings by Kim et al. [34], who reported a lower crystallinity and a greater fibril flexibility after periodate oxidation. The film made from the most highly oxidised material was also less homogeneous in its microstructure, showing a smoother cross-section with fewer pores closer to the filter side of the film (not shown). Possibly linked to these properties, the films made of the most highly oxidised fibrils showed a different, and more distinct, imprint of the metal wire weave used for filtration and drying support (Figure 3g).

The mechanical performance of the films was significantly affected by the chemical modification. The bottom half of Table 1 shows the Young's modulus, tensile stress at break and tensile strain at break for the three different films. The films made of chemically untreated fibrils had mechanical properties similar to those reported earlier [29, 38], but, as can clearly be seen in Table 1, the chemical treatment made the films weaker and more brittle. This is well in agreement with earlier studies on the cross-linking of cellulose in general [15, 39–41], and on sodium-periodate-induced cross-linking in particular [16, 23, 42]. There is an indication of an (insignificant) increase in modulus compared to the untreated material when the cellulose is oxidised to 27% oxidation, but a distinct loss of modulus at 44% oxidation. An increase in modulus due to periodate-induced cross-links is plausible, since inter-fibrillar covalent cross-links are likely to lead to an improved stress transfer [43, 44]. However, since the periodate oxidation simultaneously reduced the material's crystallinity (Figure 2) there was a net decrease in modulus at 44% oxidation. In a discussion of mechanical properties, it is also important to keep in mind the difference in fibril size (Figure 1) and differences in network structure (Figure 3), which may affect the mechanical performance of the materials.

Film gas permeability

At 0% RH, all the films acted as ideal oxygen barriers and the oxygen permeability was below the detection limit of the instrument (0.008 ml/($m^2\cdot$24 h)), indicating a material with strong intra-molecular interaction and without interconnected pores, preventing the diffusion of non-polar gas molecules such as oxygen by any means other than as dissolved molecules. Evaluated at 50% RH, i.e. where the films are expected to contain moisture, the oxygen permeability ranged from 0.6 ml·µm/($m^2\cdot$24 h·kPa) for films made from untreated fibrils to 1.5 ml·µm/($m^2\cdot$24 h·kPa) for the most oxidised material (Figure 4a). These values are comparable with those of other cellulose-based films [1, 2, 4, 8] and other films based on carbohydrates such as starch or hemicellulose, or carbohydrate-based nanocomposite [3, 5, 7, 9, 45, 46]. However, all these materials suffer from a significant deterioration in oxygen-barrier properties with increasing relative humidity. Typically there is an increase in oxygen permeability by one or two orders of magnitude when the relative humidity is increased from 50% RH to 80% RH [1, 2, 7–9], but, for the films fabricated from self-cross-linking cellulose, Figure 4a shows that the permeabilities of the two oxidised grades remain unchanged when the relative humidity is increased to 80% RH, presumably because the fibrils are prevented from separating from each other and opening up greater diffusion paths for the oxygen molecules.

For polar molecules such as water vapour the trend was similar to that of oxygen permeability. Figure 4b shows the water vapour permeability as a function of relative humidity, and the permeability remained at the same level between 50% RH and 80% RH for the oxidised grades, whereas the films made of untreated fibrils showed a significantly higher water vapour permeability at 80% RH than at 50% RH. The permeabilities of all three films at 50% RH (3.3–4.5 g·mm/($m^2\cdot$24 h·kPa)) were similar to that of other reported cellulose-based films [8, 12, 13], except that, for example, Yang et al. [8] reported a fourfold increase in

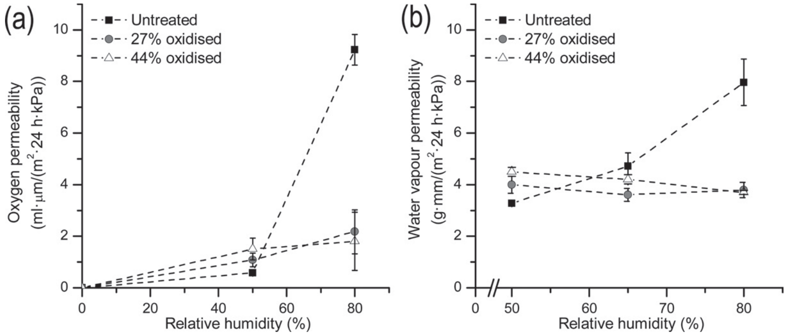


Figure 4. Permeability with respect to (a) oxygen and (b) water vapour as a function of relative humidity of films made of untreated and two degrees of oxidised cellulose; 27% and 44%. Error bars indicate standard deviations (n=3 and n=4, respectively).

permeability when the relative humidity was raised from 50% RH to 70% RH. In the case of the cross-linked cellulose in Figure 4b the permeability was the same or even slightly lower at 80% RH. These barrier properties both for oxygen and water vapour are therefore highly competitive compared to those of other carbohydrate-based barriers, but, the films are still significantly poorer barriers than most commercial synthetic polymers such as polypropylene, polyethylene or polyethylene terephthalate, which all typically have a water vapour permeability below 0.1 g·mm/(m^2·24 h·kPa) [11, 47].

To elucidate the mechanism behind the unchanged oxygen and water vapour permeabilities of the treated samples with increasing relative humidity, the equilibrium moisture content was determined at the corresponding relative humidities. Figure 5 shows how the two cross-linked films are more or less inert to moisture sorption in the relative humidity interval from 50 to 80% RH. Figure 5 also shows that the most highly oxidised material had a higher equilibrium moisture content at 50% RH, which is probably a result of the larger amount of amorphous cellulose (Figure 2) and which possibly explains why the water vapour permeability was slightly higher for this grade at 50% RH. The lack of any change in moisture content in the 50–80% RH interval shows that the cross-links formed between the fibrils prevent the adsorption and diffusion of moisture [16, 17], and limit swelling and the creation of surfaces and pores available for gas diffusion. Interestingly, the 27% oxidised films showed a rapid increase in moisture content when the relative humidity was further increased to 90%, which may indicate an increase in permeability at this, or higher, humidity if the increase in moisture content is accompanied by a structural change in the material. It has been suggested that the cross-links may partly hydrolyse with time at high relative humidity [16], but, this

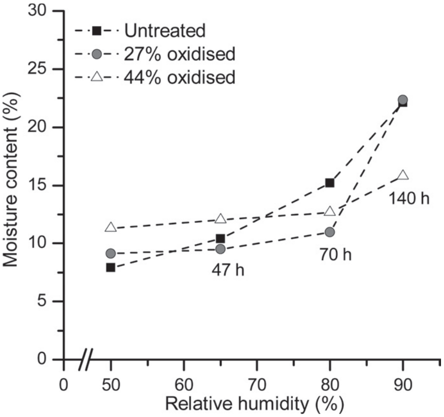


Figure 5. Equilibrium moisture content as a function of relative humidity for films made of untreated, 27% oxidised and 44% oxidised cellulose. The figures by the data points are approximate conditioning times at the respective relative humidities.

hypothesis was later rejected since soaking in water did not alter the molecular or supra-molecular structure [48].

To further understand the sorption behaviour at high relative humidity and the corresponding barrier properties, further measurements are needed. Nevertheless, the present results show that these materials have a potential for use in e.g. the packaging of dry goods that are not too sensitive to moisture, but need protection from oxidising air.

Finally, from an application point of view, it is also important to note that these self-cross-linking fibrils can be used in other ways than as films. Fibrillated cellulose can, for example, be coated onto a substrate film or board and act as a barrier coating [1].

CONCLUSIONS

Films have been fabricated from homogenised cellulose fibres partly converted (27% or 44%) to dialdehyde cellulose by periodate oxidation of the cellulose C2–C3 bond. The aldehyde groups then enable the formation of intra- and inter-fibrillar covalent bonds which reduce the moisture adsorption, and hence film swelling, when exposed to high relative humidity, and consequently hinder the increase in gas permeability often associated with increasing relative humidity. The oxygen permeabilities of the 27% and 44% oxidised cellulose were

2.2 ml·μm/(m^2·24 h·kPa) and 1.8 ml·μm/(m^2·24 h·kPa), respectively, compared to 9.2 ml·μm/(m^2·24 h·kPa) for the untreated reference at 23 ºC and 80% RH, and the corresponding water vapour permeabilities were 3.8, 3.7 and 8.0 g·mm/(m^2·24 h·kPa).

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Transcription of Discussion

OXYGEN AND WATER VAPOUR BARRIER FILMS WITH LOW MOISTURE SENSITIVITY FABRICATED FROM SELF-CROSS- LINKING FIBRILLATED CELLULOSE

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Gil Garnier Monash University

Very interesting work. Two questions: first, how long does it take for the biodegradation of your cross-linked films? Second, by how much do you depolymerise the cellulose?

Per Larsson

Firstly, we haven't really tested how long it takes to degrade them, but if you simply look at the structure of the cross-links, they are all the same kinds of bonds you have in cellulose to begin with and you can easily hydrolyse them by increasing the pH. So, I don't really think there is any major risk that there will be any major difference in biodegradability, but it needs to be tested, of course. As for depolymerisation, in this study we did not measure that, but in another study, we saw a limited change in DP.

Discussion

Gil Garnier

Why do you have such a big decrease in mechanical properties – you show a big decrease in modulus, in strength and in yield – if you don't decrease the DP?

Per Larsson

The modulus would be the most obvious one because there is less crystallinity, this is close to a complete amorphous material. It has a very low crystallinity, so that will give a lower modulus.

(Added later by the author): Since there is cross-linking, the effect of DP (prior to cross-linking) should be low since the DP of the cross-linked material would be high.

Gil Garnier

I am not convinced.

Roger Gaudreault Cascades

What is the degree of oxidisation of the fibres, in milli-mole per gram, that you got after the chemical reaction with periodate?

Per Larsson

Well, 27% oxidation that corresponds to about 3.4 milli-moles per gram of fibres.

Roger Gaudreault

After this reaction, the fibres could be oxidized using sodium hypochlorite. Could you speculate about the performance of the film in terms of oxygen and water vapour transmission rate?

Per Larsson

If you add a chlorite strep, you would end up with highly charged fibrils, so after homogenisation the fibrils would probably be very, very thin and highly dispersed; so that would be good from a film-formation point of view. Probably it would give very dense films. But just to speculate, I don't think they will work as well at high humidity. The films that I have seen using TEMPO-oxidised fibrils, and other fibrils, they all have these properties at a high humidity, i.e. having a high permeability.

Bill Sampson University of Manchester

I have got a couple of questions about your characterisation of the density and the void structure. My question, which I don't think is addressed in the article unless I've missed something, is how do you measure thickness?

Per Larsson

Ah, isn't that in there? Ten random places on the film; it is apparent thickness.

Bill Sampson

With an electronic micrometer? With a micrometer we might expect to get a density, even for a non-porous material, that is of the order of the numbers that you are getting, because of surface effects and compressibility. So, how did you obtain your z- sections that you show in these slides here?

Per Larsson

Yes, a brand new sharp razor blade.

Bill Sampson

Yes, I think in doing that, you probably created the pores that are so clear in the left hand side image. I think your films are probably not porous, I think you made the pores.

Per Larsson

Yes, it can easily happen that you create artefacts in the cross-section.

Akira Isogai University of Tokyo

Thank you for an interesting paper and I have two questions. In your case, you add aldehyde groups directly to cellulose molecules, have you ever tried to add glyoxal as an additive?

Per Larsson

No. The whole idea here is that we want really short cross-links.

Akira Isogai

Okay, and another question is that once the aldehyde-containing cellulose was heated, in your case, did some discolouration problems such as yellowing happen?

Per Larsson

Slight.

Akira Isogai

Slight? Usually when such a large amount of aldehyde groups are present in cellulose, there may be a serious discolouration problem when heated at 100 °C or so for ten minutes.

Per Larsson

But ideally, the aldehyde should have reacted.

Akira Isogai

But hemiacetals are intrinsically reversible to aldehydes and alcohols, it may be possible to have a discolouration problem for such materials once heated.

Gil Garnier Monash University

Your work is very interesting because your implicit hypothesis was that, by preventing swelling through cross-linking, you will improve the resistance to moisture and keep the permeability constant and you proved that. Now my question: what is the mechanism as you swell normal cellulose, what is the increase in porosity through which the gas comes? Is it through the cellulose itself? Is it through the pores, which are getting bigger? Can you discuss a bit?

Per Larsson

I have discussed it but I do not have any data to support my arguments. I would assume that, as it swells, you have delamination between fibrils and then you open up passages for oxygen to diffuse through. This is not the case when the cellulose is cross-linked; you maintain the existing pathways for the molecules to diffuse. You do not create any shortcuts by having swelling and delamination of fibrils.

Gil Garnier

Short question. How thick are your films and how many fibre or fibrils thick are they on average?

Per Larsson

Thickness is between approximately 30 and 40 µm; the actual figures are in the paper. It differs between the grades. All the results are normalised with respect to thickness.

Torbjörn Wahlström Stora Enso

In the beginning, you mentioned that you want to replace plastic but you didn’t even mention aluminum, but later you said it has diffusion rates down in the basement. So for cellulose-based material, you don’t see replacing it as an option?

Per Larsson

Well, not necessarily, I mean since aluminium has a very high embedded energy content, it is really desirable to replace that as well. The main thing with aluminium foil is that it is an ideal barrier; it stops all gases, so it depends on the application, what you need. Even if you were to start using these films, we need something that stops the water vapour, and that could be some conventional plastic and not necessarily aluminium foil. Also, it needs to be stated that we do not know how well these films stop UV light, an application where you usually use aluminium as a barrier.

Bill Sampson University of Manchester

What is the grammage of these films?

Per Larsson

They are 40 µm thick and you have density of 1.4 g m^{-3} (56 g m^{-2}, ed.).

Discussion

Bill Sampson

So that is quite thick for a film, isn't it? My concern is that the permeability seems to be okay for something which is very thick and heavy.

Per Larsson

The permeability is normalized with respect to its thickness. It does not really depend on the thickness in any certain way.