

Mechanical and Barrier Properties of Cardboard and 3D Packaging Coated with Microfibrillated Cellulose

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ABSTRACT: Microfibrillated cellulose (MFC) is increasingly used with cellulosic substrates and especially with paper materials. Its use with cardboard remains not reported and the study of mechanical and barrier properties of MFC-coated cardboard has been investigated in this article. The influence of coating process as well as the effect of MFC have been highlighted by comparing different MFC-coated cardboard samples with PE-coated cardboard samples. MFC was coated using bar coating process. Their distribution and homogeneity onto cardboard was observed using techniques such as SEM and FE-SEM. Tests such as oxygen and air permeability, bending stiffness, and compressive strength have been carried out. The coating process used impacts significantly cardboard properties by two opposite ways: on one hand it damages the structure cohesion of cardboard decreasing its compressive strength; on the other hand it increases its bending stiffness by increasing considerably the samples thickness. The addition of MFC counterbalances the negative effects of the coating process: bending stiffness and compressive strength are indeed improved by 30% in machine direction. On the contrary, MFC does not enhance much cardboard barrier properties, although it considerably increases their water absorption. Within a framework of packaging application, MFC will rather have consequent effects on cardboard's properties as blend or as part of the multilayer structure. Other applications have to be considered for its use as top layer. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40106.

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INTRODUCTION

Fiber based materials used as packaging must both be able to protect the product from outer influences as well as withstand the influence of the product. Moreover it must respond to the current society's requirements eager to have more recyclable, biodegradable and lightweight food-packaging materials.

The most often used fiber-based packaging material is cardboard, i.e., fiber-based product with basis weight mostly between 200 and 400 g/m². Its production dates from the beginning of the nineteenth century and is nowadays evolving. With the increasing price of raw materials, the wastes reduction and the evolution of society's requirements, new challenges must be considered in the production of cardboard. On the one hand, industries are looking for reducing the price and the weight of the material without modifying its mechanical properties, especially its bending stiffness. On the other hand, to achieve a better protection of the packed product against the outer threats, cardboard needs more efficient barrier properties, for example against liquids, grease, and/or gases.

Some solutions are already applied to offset these ongoing concerns, but remain insufficient. One way is to increase fillers content of the material and thus decrease the amount of fibers used.¹ The benefit is double: reduction of the amount of fibers and improvement of the opacity and printability of paperboard. However, it requires that the fillers cost is substantially lower than the fiber material one. Besides, a large amount of fillers decreases also the strength of paperboard. A compromise has thus to be found. Another way consists in using low density fibers such as thermo-mechanical cellulosic fibers. One drawback with those pulp fibers is their poor ability to form strong fiber-fiber bonds which results in insufficient strength properties. The improvement of these fiber-fiber bonds can be then performed by the addition, for example, of cationic starch. This addition rises however two main concerns: (i) cationic starch molecules tend to screen the anionic charges on cellulosic fibers. Thus, if an excess of starch is added, only one part will be retained in the sheet and the rest will circulate in the white water system causing runnability, microbiology or foaming problems; (ii) an excessive cationic starch addition can also

prevent fibers from adsorbing other cationic additives which are commonly added (e.g. retention aids, sizing agents). Instead of using cationic starch, latex has for example also been used as binder in bulk layer to improve strength properties.² However, retention problems appeared while adding latex to the wet end.

Concerning the improvement of barrier properties of cardboard, the most commonly used way consists in coating or laminating high barrier petroleum polymers on cardboard. Usually, polyethylene (PE) is used as efficient liquid, and vapor barrier. Ethylene vinyl alcohol (EVOH) is rather used as oxygen barrier. The barrier properties then reached are very efficient. However a thick layer is needed for, which induces a higher cost of production and the use of a significant amount of nonbiodegradable polymers. Another method commonly used in order to produce high barrier cardboard is the addition of an aluminium layer. Aluminium offers an oxygen and light barrier with thickness of only around 7–9 μm . Nevertheless this layer increases strongly the carbon dioxide load of the material and decreases also the recycling ability of the multilayer package.³ When considering the enhancement of the grease resistance, the current solution consists in treating or coating the cardboard with fluorinated hydrocarbons such as perfluorooctanoate (PFOA). These chemicals, however, have become the object of health and environmental concerns, mainly because of their persistence and tendency to bioaccumulate.⁴

There is thus still a need for an improved fiber-based material with high barrier properties and low density which could be both more economical and eco-friendly, intended for example to food-packaging materials and applications. The use of microfibrillated cellulose (MFC) is an emerging idea, attracting more and more researchers. Simply produced from cellulosic fibers with high shear mechanical treatment,^{5,6} its manufacturing process was patented for the first time in 1985 by Turbak et al.⁷ Since then, improvements of this process have been carried out and published to reduce the high energy consumption induced by the high shear mechanical treatment of fibers.⁸ Two main pretreatments are commonly used: enzymatic pre-treatment^{9,10} or TEMPO oxidation of cellulosic fibers.^{11–13} Depending on the cellulosic sources,^{14–16} and applied treatments, MFC will have different dimensions: diameters ranging from 10 to 60 nm^{5,6,17} and lengths longer than 1 μm .¹⁸ Its nanometer scale and high surface energy make MFC an ideal material for use in nanocomposites as mechanical reinforcement.^{5,19–21} Its ability to form a nanoporous network^{22,23} and, once dried, to make stiff and high barrier films^{24–27} have besides broadened its application areas. The enhancement of mechanical⁵ and barrier properties⁶ and their use as aqueous suspensions developed recently its application in cellulosic substrates such as papers.^{25,28–32} Nevertheless, the combination of MFC and cellulosic materials is quite recent and the first published study appeared in 2009²⁵ with the MFC coating of handsheet papers. The number of studies in paper and paper-board applications has since slightly increased: at the end of 2012, only 31 journal articles, 18 patents and 11 international conferences proceedings have been published³³ compared to the 2,300 scientific papers published in total about MFC.

Regarding the use of MFC with cardboard, up to our knowledge, the number of scientific papers counts only one journal

article³⁴ and five patents.^{1,3,35–37} Hult et al.³⁴ used MFC mixed with shellac to decrease the air permeability of a 250 g/m² paperboard. They prepared first a blend of these two compounds. Then, they carried out a multilayer strategy, i.e. coating first MFC followed by a shellac layer. Depending on the paperboard's surface coated, the air permeability decreased from 60 to 99% with coat weights ranging from 3 to 30 g/m² respectively. This was compared to a maximal decrease of 40% obtained with the coating of shellac alone. The use of MFC was thus relevant for enhancing the air barrier of paperboard. However, its combination with shellac weakened also the paperboard's structure and induced then a decrease of its tensile strength. Others also patented processes aiming to improve the barrier properties of cardboard using either coating dispersion³⁵ or multilayer process.³ The purpose is to reach high barrier properties with an on-line process without using petroleum polymers. Besides, mechanical properties must not be impaired. The first idea consists in coating a dispersion including MFC (0.5 to 20 %wt) and colloidal particles such as EVOH or latex either using roller coating, spray coating or immersion process.³⁵ Samples coated with (latex/MFC) dispersion show for example a decrease of the water vapor transmission rate of 24% compared to samples coated with an aqueous latex dispersion only. The second solution aims to produce a multilayer material with a first layer of fibers, a second with MFC and a third one with polymer such as PE or PET mainly for giving heat-sealing property.³ MFC confers density and smoothness, improving adhesion of the third layer and also decreases oxygen permeability of the multilayer material. However, the authors did not mention any analysis of mechanical properties.

Other patents are mainly focused on the price reduction by developing low density cardboard with good mechanical properties and more flexible structure. They either introduced MFC alone or with additives between plies of the base cardboard,³⁶ producing a laminate with at least one layer of MFC,³⁷ or mixed pulp with MFC, cationic and anionic polymers to make a final cardboard.¹

None of these patents looked for coating only MFC without adding polymers, additives or fillers onto cardboard surface. Our study is thus focused on this perspective. MFC alone has been coated on cardboard with bar coating process. Mechanical and barrier properties of coated materials thus obtained have been analyzed to conclude on the effect of MFC, expecting mostly an enhancement of gases and grease barrier properties. The influence of the MFC on the cardboard properties was furthermore highlighted by a comparison with the properties of the base cardboard, a polyethylene-coated cardboard and a similar cardboard samples coated with only water.

MATERIALS AND METHODS

Materials

A 300g/m² cardboard sheets have been produced and delivered by Cascades La Rochette (France). This folding cardboard, named Rochcoat®, is made of virgin pulp and mainly used in the food-packaging sector. One side is coated and ready for printing. The other side, noncoated, will be converted in this study.

The same cardboard sheets coated with Polyethylene (320 g/m² with a PE layer of about 30 ± 3 μm) have also been produced and furnished by Cascades La Rochette (France) and will be used as reference in this study.

Preparation and Characterization of MFC Suspension

The MFC suspension has been produced and furnished by FCBA (Grenoble, France). An enzymatic pretreatment has been applied on sulfite pulp (Domsjö®) using endoglucanase during 2 h. The pulp was then subjected to high-shear mechanical treatment using the homogenizer Ariete from GEA Niro Soavi® (4 passes, at 1400 bars) in order to achieve a concentration of 2 wt %.

The MFC suspension has been characterized with a Field Emission Scanning Electron Microscopy (FE-SEM) Zeiss® Ultra-55 using a working distance of 5.5 mm and an accelerating voltage of 2.00 kV. The suspension was spread onto a metal substrate using carbon tape, allowed to dry one night at room temperature and coated with a thin layer of gold. The average value of the nanofibrils diameter has been also determined by at least 50 measurements performed with the ImageJ® software.

MFC Coating onto Cardboard

The MFC suspension has been coated on this back side with a bar coating process (Endupap, France), using a 0.9 mm Mayer bar, at a speed of 5 cm s⁻¹. The coated samples were then dried with a contact drying system at 105°C, for 5 min. During this drying time, the cardboard sheets have been regularly turned over to limit the curl effect. These steps were repeated five and ten times in order to deposit five and ten MFC layers, respectively. As reference samples, water-treated cardboard sheets were obtained by coating deionized water using the same procedure described above. Here, only the coating slurry was changed: deionized water without MFC was coated onto the cardboard surface to clearly underline the influence of the successive wetting/drying cycles induced by the five and ten successive coatings of the MFC suspension (containing 98 wt % of water).

Structural Characterization of Cardboard Samples

Coated samples have been characterized by Scanning Electron Microscopy (SEM), a Quanta200® (The Netherlands), using a working distance of 10.0 mm and a high voltage of 15.0 kV. For this technique, cardboard samples were precisely cut and mounted on a metal support recovered with carbon tape for an observation of their surface and slice. Grammage and thickness (ISO 534:2011) of each sample were also measured using a Lhomargy balance (±0.01 g) and micrometer (±0.01 μm) respectively. Average values of at least 10 measurements are given.

Characterization of Transport Phenomenon of Cardboard Samples

Before each test, samples were maintained at 23°C and 50% of relative humidity (RH) for at least 24h.

Air Permeability. According to the standard ISO 5636, the air permeability was measured using Mariotte vases on samples area of 2 cm², under ambient air conditions, applying a vacuum of 2.5 kPa. The time measurement was fixed at 5 min for each sample. The average air permeability was then calculated from at least five measurements.

Oxygen Permeability. Oxygen transmission rate (OTR) was determined using a MOCON OX-TRAN® 2/21 ML (ISO 15105-2:2003). Samples were before maintained at 23°C, at 50% RH, for 48 h. Measurements have been carried out on an area of 1.1 cm². They have been repeated twice for each sample. Usually, cellulosic materials do not have a sufficient low OTR in order to be analyzed by this kind of equipment without being out-of-range. The study of our cardboard samples has been then investigated by thermo-sealing each sample with a polymer film (PE) using an office plastic sealer. The values have been compared to the OTR value of the polymer film alone to conclude on the effect of MFC coating.

Water Absorption. Following the Cobb 60 method (ISO 535), the test consists in putting a sample's area of 3.5 cm of diameter in contact with 10 mL of deionized water during 45 s. The mass of the sample before and after wetting was determined with a Lhomargy balance (±0.01 g). Cobb index represents the mass of water absorbed divided by the wet area (g/m²) and is an average value of at least five measurements.

Grease Resistance. Kit Test method (T 559-cm 02) has been investigated to evaluate the grease resistance of cardboard samples. It consists in testing the sample with one droplet of 12 solutions constituted in different parts of castor oil, n-heptane, and toluene. The solutions are numbered from 1 to 12 (Kit number), with 12 representing the highest grease resistance. From a Kit number of 8, a sample is considered grease resistant.

Characterization of the Mechanical Properties of Noncoated and Coated Cardboard Sheets

Before each test, the samples were maintained at 23°C and 50% RH for at least 24 h. The mechanical tests were also carried out under same conditions.

Bending Stiffness. According to the standard ISO 2493, the bending stiffness has been measured using a Büchel Stiffness Tester (Büchel Van der Korput, the Netherlands). Samples were previously cut into pieces of 38 × 70 mm². The bending stiffness was measured for an angle of 7.5° and the force was applied on the nontreated, water-treated, or MFC-coated side of cardboard sheets. At least 10 measurements were carried out to obtain an average value of the load needed to bend each kind of samples. The bending stiffness B (mN.m) was then calculated as followed:

$$B = \frac{FL^2}{3a\theta}$$

with F (mN), the bending force, L (m), the length of bending, a (m), the width of the test piece and θ (radian), the angle of bending.

Similar measurements were also investigated on creased cardboard samples to evaluate their resistance to folding (mN). Each piece was previously creased with a laboratory cardboard creasing press (H.E. Messmer Ltd, UK). Depending on fiber orientation and samples' thickness, the width of the groove has been adapted for a 0.7 mm width of creasing rule. For each sample in machine direction, the groove width was fixed at 1.524 mm. In cross direction, the width evolved between 1.397 and 1.651 mm depending on cardboard samples.

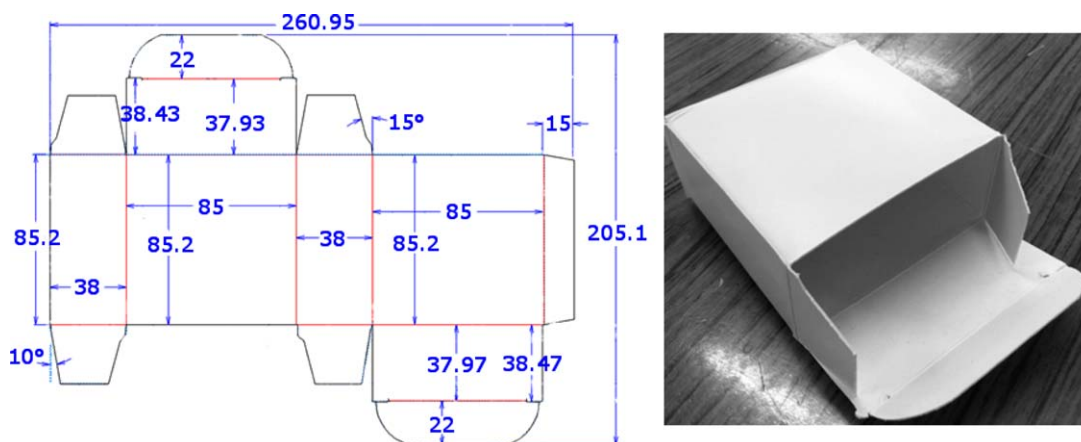


Figure 1. Box template designed with ArtiosCad® (left – dimensions in mm) and corresponding 3D-Box (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Five measurements were performed on creased cardboard samples.

Short-Span Compressive Test. This test consists in determining the compressive strength in machine and cross-directions of cardboard using a short-span compressive tester (Büchel Van der Korput, The Netherlands) according to the standard ISO 9895. A test sample, 15 mm wide, is clamped between two clamps, spaced 0.70 mm apart, which are forced towards each other at a speed of $3 \pm 1 \text{ mm min}^{-1}$ until a compressive failure occurs. The average of maximum compressive strength is given in kN/m from at least 10 measurements.

Box Compression Test. Using the software ArtiosCad®, template of final boxes ($10 \times 10 \times 5 \text{ cm}^3$) was designed on A4 cardboard sheet (Figure 1). The cardboard sheets have been cut and creased by a laboratory converting pilot (Kongsberg, France). They were then folded and glued.

Each package was designed so that the cross-direction of the material was submitted to the compressive force. As the material is less stiff in cross-direction, even a slight increase of the

compressive force of the box will be perceived. The compression test was carried out using a crush tester (Noviprofibre, France) with a maximal compressive load reaching 5 kN (TAPPI method 804). The box was maintained between two parallel plates. The upper plate went down at a speed of $12 \pm 2 \text{ mm min}^{-1}$. An average value of the compressive force was calculated from at least 10 measurements.

RESULTS AND DISCUSSION

Characterization of the MFC Suspension

The MFC suspension produced from sulfite pulp at a concentration of 2 wt % looks like a white gel [Figure 2(a)]. This gel is made of microfibrils with diameters of about $33 \pm 8 \text{ nm}$ [Figure 2(b)]. This value is consistent with the diameter values found in literature.^{5,6} The microfibrils form an entangled and tight network, which makes the measurement of their length impossible at lower magnification. In literature, the length of MFC is estimated longer than $1 \mu\text{m}$. Very recently, Ishii et al.¹⁸ determined for the first time a more accurate value of the length of TEMPO oxidized MFC. Based on dynamic

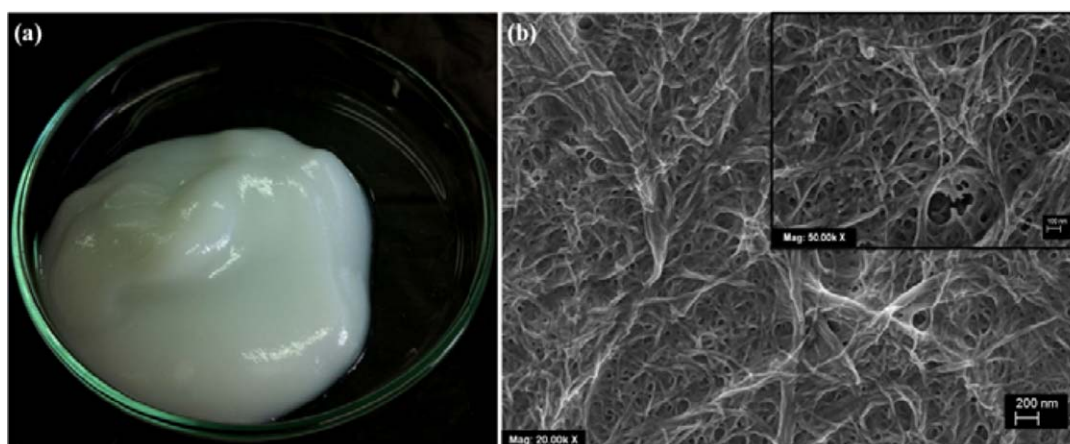


Figure 2. (a) MFC suspension (2 wt %) produced from sulfite pulp (Domsjö®), enzymatically pretreated and mechanically treated with a GEA Ariete® homogenizer. (b) FE-SEM images of the MFC suspension (2 wt %) at a magnitude of 20.00 k and 50.00 k. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Structure and Barrier Properties of the MFC-Coated and Water-Treated Cardboard Samples as a Function of the Number of Layers and Water Treatments

Samples	Structure properties			Barrier properties				
	Grammage (g/m ²)	Thickness (μm)	Bulk	Oxygen permeability (cm ³ /m ² .day)	Air permeability (cm ³ /m ² .Pa.s)	Water absorption (g/m ²)	Grease resistance (Kit Number)	
Base cardboard	303±2	501±8	1.65±0.01	12±0	0.17±0.01	43±7	0	
PE coated cardboard	320±1	535±1	1.67±0.01	-	0.12±0.005	5±3	12	
Water treatment	×1	301±2	579±17	1.92±0.05	-	0.16±0.01	51±4	0
	×5	304±4	602±11	1.98±0.02	-	0.16±0.01	89±8	0
	×10	304±2	619±9	2.04±0.01	-	0.15±0.01	84±11	0
MFC coating	×1	304±3	574±5	1.89±0.02	-	0.18±0.01	67±10	0
	×5	309±1	595±7	1.92±0.01	14±2	0.18±0.01	94±4	1.5±0.5
	×10	317±1	624±5	1.97±0.01	13±1	0.18±0.01	114±7	2.5±0.5

The sample named "PE coated cardboard" is the base cardboard coated with poly(ethylene) by the supplier. It is a reference as matter of barrier properties.

viscoelasticity measurements, they obtained a mean length of 2.2 μm, which matches perfectly with previous estimations. Nevertheless, any other accurate value has been given regarding enzymatically pretreated MFC.

Thanks to these dimensions, the interest in using MFC is focused on the microfibers entanglement, which forms a specific network. Indeed, in previous works, this network has strongly contributed in the enhancement of mechanical and barrier properties of different materials.^{19–21,25,38} From this perspective, the effect of this network formed while coating will be analyzed in this study on cardboard properties.

MFC-Coated Cardboards Samples

A4 cardboard sheets were coated with the 2 wt % MFC suspension using bar coating process. Due to the consequent viscosity of the MFC gel, the coating of only one layer of MFC was not enough to recover the whole surface of the cellulosic substrate. That is why the coating process has been repeated five and ten times in order to improve the homogeneity of coating but also to increase the MFC coat weight deposited (from 1 g/m² with one layer to 14 g/m² with 10 MFC layers). Indeed, the base cardboard already owns a basis weight of 300 g/m². The improvement of its properties will depend on the quantity, i.e. coat weight, deposited, but usually no more than 15–20 g/m² are coated onto the surface. It is worth keeping in mind that even our highest level of coating (14 g/m²) corresponds to only 5% of the total material basis weight. Table I summarizes the structure properties of the different samples. Figure 3 shows SEM images of the surface of cardboard samples coated with one, five, and ten MFC layers. After one coat, compared to reference, the surface is clearly not entirely recovered. From 5 MFC coats, the fibers of the base cardboard are not perceived and MFC recovers the whole surface. Regarding the cross-section of these same samples (Figure 4), MFC is barely distinguished on the cardboard coated only once. Looking at the 5× and 10× MFC-coated cardboard, the MFC coat stands out clearly from thickness of the base cardboard (Figure 4). A MFC

coat weight of about 6 and 14 g/m² is indeed deposited compared to 1 g/m² in the case of one coat.

Since the MFC suspension is mainly composed of water (98 wt % for 2 wt % of microfibers), water-treated cardboard sheets have been prepared as reference. The influence of water on cellulosic materials is a well-known phenomenon. It is thus necessary to analyze the effect of successive wetting and drying cycles on cardboard in order to rightly conclude on the effect of dried MFC. Compared with MFC coating, water tends to deconstruct cardboard samples by opening the fibers network onto surface (Figure 5). Similar basis weight values are obtained, but the samples thicknesses were considerably modified by water. By opening the fibers network, cardboard samples roughness is indeed increased (by almost 36%, results not shown), which induces a thickness increase of about 20% (Table I).

This increase also induces a 20% increase of bulk values. The effect of successive wetting and drying cycles is besides highlighted by comparison with the MFC-coated cardboard samples. The bulk values of these latter are also increased but are slightly lower than those of water-treated cardboards. It is thus possible to bring matter without making denser the final material.

Barrier Properties of MFC-Coated Cardboard

A common purpose in the production of cardboard package is the research of high barrier properties. The results are given Table I.

The air permeability is affected neither by coating process nor by MFC coating. Water-treated cardboard samples present indeed similar permeability than reference, and MFC coating does not really improve this property, surely due to the insufficient MFC coat weight deposited compared with the starting material structure and basis weight (Table I). Indeed, it is noteworthy to note that the reference cardboard has already a very low air resistance (0.17 cm³ m⁻² Pa⁻¹ s⁻¹) thanks to its coated front side for printing. As the base material aims to be used as food-packaging material, it is thus coherent that very good air barrier is already achieved.

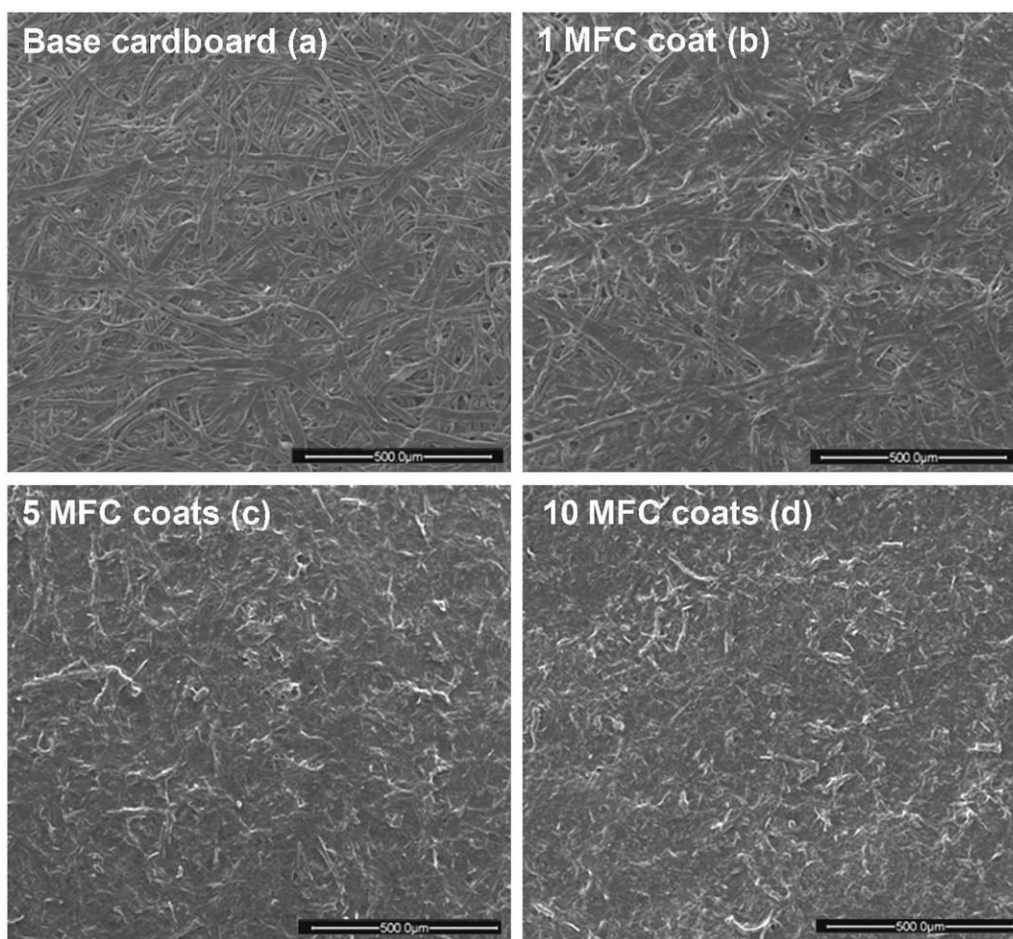


Figure 3. SEM images of the cardboard coated with MFC (b) once, (c) five and (d) ten times compared to the (a) base cardboard (Mag: $\times 100$, HV: 15 kV, WD: 10.0 mm).

As oxygen is the main cause responsible of the degradation of food products, MFC-coated cardboard samples have been submitted to oxygen permeability tests and, similarly, very good oxygen barrier is expected. Considering the values measured on samples encapsulated with a polymer film ($27 \pm 0.5 \text{ cm}^3 \text{ m}^{-2} \cdot \text{day}$), the reference cardboard owns effectively low oxygen permeability ($12 \text{ cm}^3 \text{ m}^{-2} \text{ d}^{-1}$). The value is indeed of the same order than OTR values of materials such as PVC, amylopectin, chitosan or whey protein.^{32,39} As regards the MFC-coated samples, the OTR value does not decrease as expected (Table I), and remains almost identical to reference. The MFC coat weight is probably not sufficient to improve this property, since the reference cardboard already has very good barrier properties. These results are not in accordance with literature showing a drastic improvement of OTR with only a thin MFC layers coated onto either plastic or paper.^{26,32}

Despite the very good barrier properties of this reference and according to its supplier, this cardboard is meant to receive one treatment before using it with liquid or fatty food product. To achieve a liquid and grease resistance, a poly(ethylene) (PE) layer is usually added as final treatment. In this study, the PE layer has been replaced by MFC, and the water absorption as well as the grease barrier tests have been carried out by comparison to the

commercial PE-coated cardboard (Table I). As regards water absorption, compared with the reference, the addition of the PE layer decreases significantly (by 86%) the ability of cardboard to absorb water (from 43 to 5 g m^{-2} , respectively). The effect of the coating process used in this study impacts however significantly this property. Water-treated cardboard samples absorb much more water than reference, i.e. from 43 to 84 g m^{-2} with $10\times$ water-treatments. The quantity of water absorbed increases indeed with the increasing number of water treatments (Table I). Nevertheless, from five treatments, this value begins to stabilize, which may be due to a structural balance of the fibers' network, achieved after successive wetting and drying cycles.

With the addition of MFC coats, the water absorption is increased even more strongly compared to water-treated samples. With only 1 g m^{-2} of MFC, the water absorption increases by 31%. This increase is still observed with the increasing MFC coat weight (Table I). MFC has thus a consequent impact on the cardboard capacity to absorb water, i.e. from 43 to 114 g m^{-2} . This is mostly due to the nanometer scale of MFC and its high specific area ($\times 2$ to $\times 55$ higher than cellulosic fibers).^{40,41} The hydrophilic nature of cellulose is thus amplified with the morphology of MFC, and as expected, the MFC-coated cardboard samples have a high affinity with water.

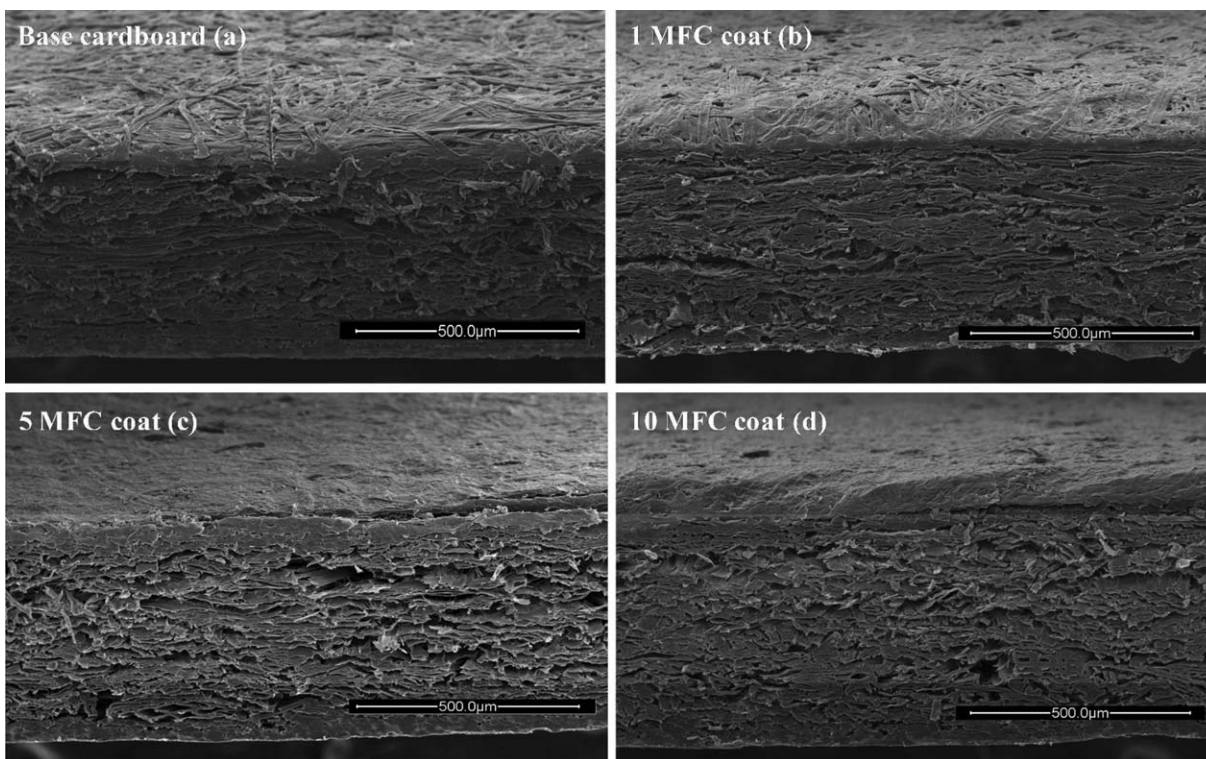


Figure 4. Cross-sections of cardboard coated (b) once, (c) five and (d) ten times compared to cross-sections of (a) reference cardboard. Pictures were taken with SEM at a magnitude of $\times 100$, a working distance of 10.0 mm and high voltage of 15 kV.

On the contrary, MFC tends to improve the grease barrier of cardboard samples (Table I), which is in accordance with previous study on paper.³² This improvement is however not enough to be considered in a food-packaging application. Compared to PE-coated cardboard samples, which have a Kit number of “12”, MFC-coated samples barely reached a Kit number of “2.5”. This value is nevertheless higher than the “0” Kit number

of reference, but insufficient in comparison with highly grease-proof PE-coated cardboard.

Mechanical Properties of MFC-Coated Cardboard Samples

Cardboard is a packaging material generally used to carry and protect from damages every kind of product. Its mechanical properties are ensured thanks to the multilayer structure, which

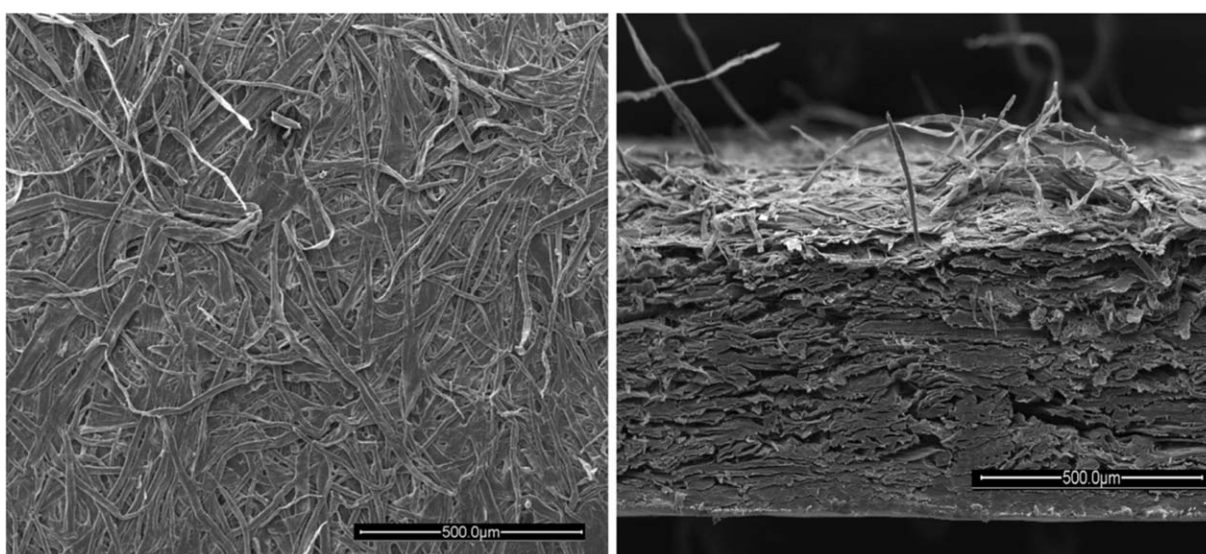


Figure 5. SEM images of surface and cross-sections of the 10 times water-treated cardboard sheets. Structure of the cardboard is damaged by this treatment. Pictures were taken at a magnitude of $\times 100$.

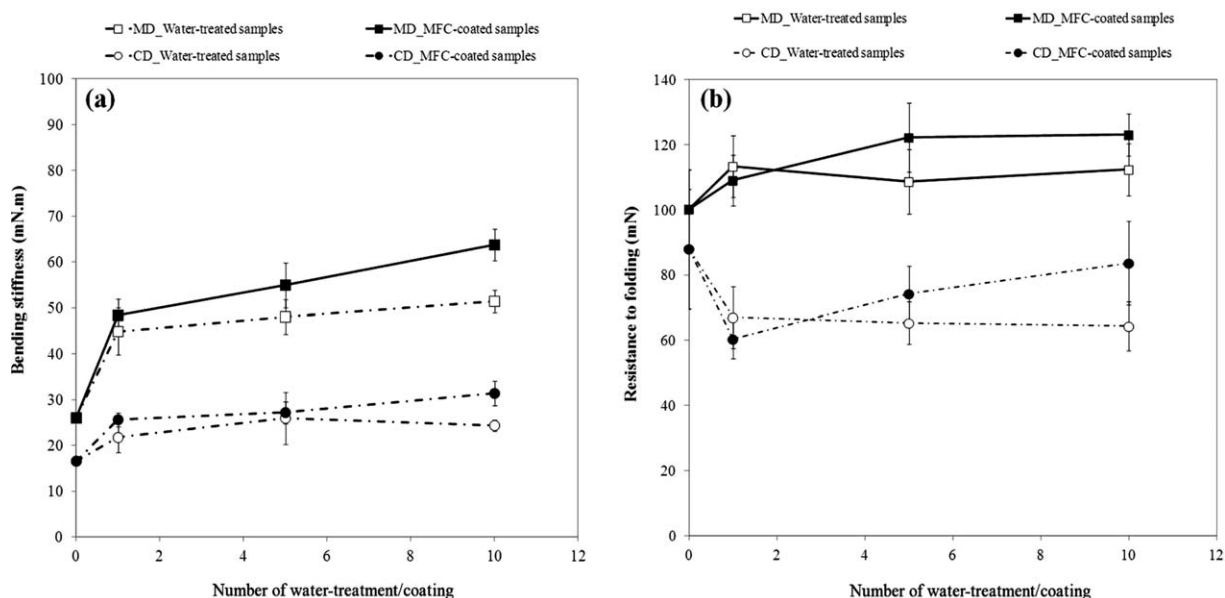


Figure 6. (a) Bending stiffness (mN.m) as a function of the number of water-treatments and MFC coats in machine (MD) and cross-directions (CD). (b) Resistance to folding (mN) of creased cardboard samples as a function of the number of treatments/coating. Both tests were carried out at 23°C and 50% RH. For each specimen, the bending stiffness and resistance to folding values are an average of at least 10 measurements.

confers a significant basis weight and thickness. The addition of one top layer could thus have a consequent effect on the mechanical properties of final cardboard, if the increase of basis weight is significant compared to those of the initial material. Otherwise, this layer can improve the bending stiffness of the material, enhance its creasability or decrease its cracking tendency. Three kinds of mechanical tests have thus been carried out: bending stiffness, short-span compressive test and box compression test.

Bending stiffness of cardboard samples was firstly evaluated in machine and cross-direction [Figure 6(a)]. Compared to reference, water-treated cardboard samples (opened squares and rounds) have an improved bending stiffness in both fibers direction (Machine direction in continuous line and Cross-direction in dotted line). This improvement is quite significant: the values are twice bigger than the bending stiffness of reference. The thickness increase (+15–25%) between reference and water-treated samples, and thus the damaged fiber network induced by coating process, explain these results. Nevertheless, the bending stiffness of water-treated cardboard samples does not evolve with the number of treatments: from one water treatment, the values remain constant in both fibers direction (about 48 mN.m in machine direction and 24 mN.m in cross-direction). Thus, the coating process with highly diluted solution influences significantly the bending stiffness of cardboard, mainly because it deconstructs the fibers network onto cardboard surface. However, the addition of MFC improves considerably this property in both fibers directions. Especially with 10 MFC layers, the increase is about 25–30% compared to water-treated samples. As the thickness values of water-treated and MFC-coated samples are similar, this enhancement is not due to the thickness increase. The mechanical reinforcement of MFC is thus clearly highlighted in spite of very small amount added. Indeed, similar

tests with PE-coated cardboard samples gave lower bending stiffness values (46 ± 4 mN.m in MD and 19 ± 2 mN.m in CD) whereas a consequent coat weight of PE (17 g/m^2) was coated.

Within a perspective of packaging application, the resistance to folding of cardboard samples has also been measured (Figure 6(b)). Each sample has first been creased with a laboratory creasing press. The effect of the creasing process on both surfaces and internal structure of cardboard is complex. There are (1) tensile strains, which are greatest in the surface and reverse-side liner plies, (2) compression in the direction perpendicular to the surface and (3) shearing strains within the cardboard, parallel with the cardboard surfaces.⁴² Thus, a wrong crease is able to damage considerably the material. Consequently, a qualitative analysis has been done to evaluate our final creased cardboard. After creasing, all cardboard samples did not have stretching in the surface. The bulge was correctly made up with a partial internal delamination of the material. Samples were able to be folded without any stretching or break.

Figure 6(b) shows the resistance to folding (mN) of cardboard samples as a function of the treatment applied. Accounting the standard deviations, no difference is noticed for one, five, and ten water-treatments in machine direction compared with reference. Resistance to folding is slightly increased by about 8–13%. However, in cross-direction, the resistance to folding is decreased by about 25% and remained at this value whatever the number of water-treatments.

As regards the MFC-coated samples, in machine direction, a slight enhancement of this property is noticed for 5 and 10 MFC coats by comparison with water-treated samples (up to 10%). Nevertheless, whatever the treatments applied, each sample has a better resistance to folding than reference and values are increasing with the quantity of MFC. In cross-direction, the

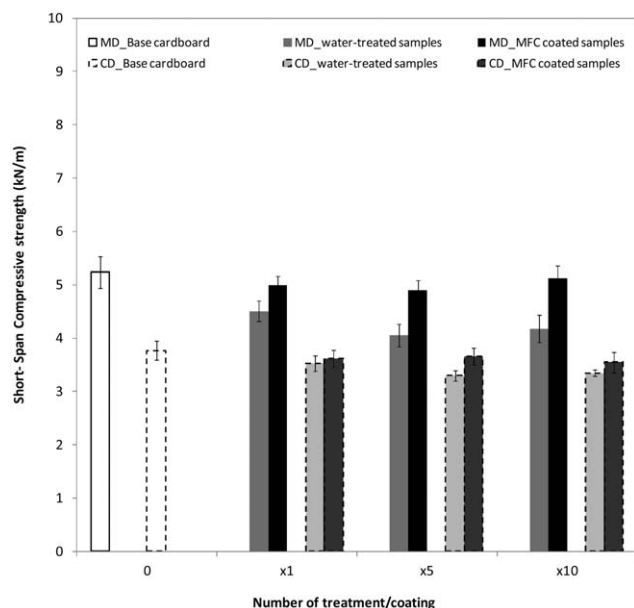


Figure 7. Short-Span Compressive strength (kN/m) as a function of the increasing number of water-treatments and MFC coats. The test has been carried out in machine (MD) and cross-direction (CD), at 23°C and 50% RH. At least ten measurements were done for each different sample.

improvement of the resistance is a few better with MFC (up to 30%) compared to water-treated samples. Although an enhancement is noticed with the addition of MFC, the resistance to folding of MFC-coated cardboard remains either lower or equal to the resistance of reference in cross-direction.

MFC induces thus an improvement of the resistance to folding of cardboard samples. The effect is highlighted in machine direction, whereas in cross-direction, MFC counterbalances the loss of resistance induced by the coating process when a coat weight of 14 g m^{-2} is achieved.

The second mechanical test carried out consists in evaluating the compressive strength of cardboard samples. This mechanical property depends mostly on the cohesion of cardboard structure and also, on its stiffness.

Figure 7 presents the results obtained for each cardboard sample. The coating process has here again a significant negative effect on this mechanical property. Indeed, as regards the short-span compressive strength of water-treated samples, the values are decreased by 10–20% compared to reference cardboard in both fibers directions. The coating process used with water has thus a negative effect on cardboard samples and damages their cohesion. Due to the successive wetting and drying cycles, layers of cardboard have indeed lost their cohesion throughout the thickness: by opening the fibers structure, some hydrogen bonds were broken.

With the addition of MFC, the effect of coating process is counterbalanced. Indeed, the compressive strength is increased by 10–25% from one to ten MFC coats respectively in machine direction and by 2%, 11%, and 6% for one, five, and ten MFC coats respectively in cross-direction. The improvement is more consequent in machine direction than in cross-direction. Intui-

tively, this difference was not expected as usually improvements of mechanical properties are more significant in cross-direction. Nevertheless, MFC offsets the effect of water and allows a better cohesion of the material. One explanation is that MFC replace the hydrogen binding damaged by water by other and stronger MFC/MFC and MFC/cellulosic fibers bindings. Even if MFC does not penetrate into the cardboard structure, it prevents water to damage the cardboard surface and thus, to penetrate and deteriorate more its inner structure.

Finally, within a perspective of packaging application, the last mechanical property tested was carried out on a 3D packaging made from the different cardboard samples (Figure 8). The purpose here is to conclude on the resistance of a box submitted to a compressive force. Figure 8 shows the compressive strength (N) needed to crush the different boxes (made with reference, the PE- and MFC-coated cardboard). The MFC-coated cardboard boxes have been compared with PE boxes. Compared with reference, PE boxes present a better compressive resistance. The PE layer improves indeed of 14% this mechanical property. The MFC-coated boxes have also an improved compressive resistance compared to reference (+5 and 10%), similarly than PE boxes. These results are logical and interrelate the previous one dealing with the bending stiffness and short-span compressive tests. Box compression strength (BCT) is indeed linked to both mechanical properties. As MFC improves the bending stiffness in cross-direction and does not damage the short-span compressive strength (SCT) in CD, these enhancements also impact on box compression strength in CD. Nevertheless, the differences are slight in comparison with base cardboard. Regarding the bending stiffness and SCT values of MFC-coated cardboard samples in MD, a more significant improvement of BCT values could be indeed expected.

These results are however very positive as MFC could replace PE without modifying mechanical properties and thus could be

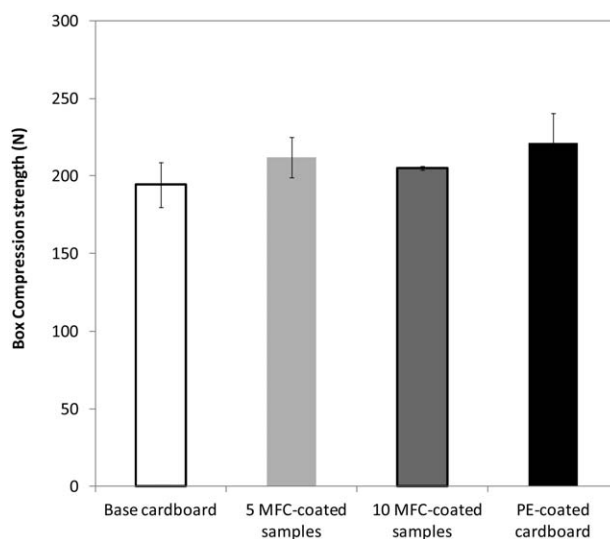


Figure 8. Strength (N) needed to crush cardboard boxes made with reference, ×5 and ×10 MFC-coated and PE-coated cardboard samples. Resistance of boxes was tested in cross-direction. These tests were carried out at 23°C and 50% RH.

a good environmentally friendly proposal. Furthermore, lower coat weights were applied with MFC inducing a more lightweight and biodegradable material for equal properties.

CONCLUSIONS

The study of mechanical and barrier properties of MFC-coated cardboard samples has been investigated. Due to the high water content of the MFC suspension, its coating without adding any additives or fillers could presume to a consequent effect of water on the cardboard properties. Thus, water-treated cardboard samples have been considered as references to rightly distinguish the effects of coating process from those of MFC on cardboard properties.

The coating process has a major impact on the final properties of treated cardboard samples. Contrary to barrier properties, which are not significantly modified, mechanical properties are the most influenced by the successive wetting and drying cycles. They improved indeed significantly the bending stiffness of cardboard samples, whereas it damages its structure cohesion and weakens its compressive strength.

The addition of MFC does not enhance much the cardboard barrier properties surely due to the low MFC coat weight deposited. Only the water absorption is drastically modified, and a clear effect of the MFC is highlighted with the compressive strength and bending stiffness results.

Contrary to previous studies dealing with MFC coating onto paper substrates,^{32,43} the same use considering cardboard substrate does not lead to similar improvements and conclusions. This is mainly due to the high basis weight of cardboard compared to a paper substrate. The amount of MFC coated onto cardboard should be, in proportion, be at least the same as the amount coated onto paper substrates. From this perspective, the quantity of MFC should be increased by either increasing the number of MFC coating, or making the MFC suspension more concentrated. Nevertheless, both solutions are for now not conceivable.

Within the framework of packaging application, MFC will rather have consequent effects on cardboard properties as blend in the inner layers or as part of the multilayer structure than as top layer. Its use as top layer has indeed to be considered in other applications such as highly absorbent materials for box or food-basket. This MFC-coated cardboard could be also used for high-added value applications, such as bactericide or drug delivery systems (e.g., antibacterial packaging) and this, without damaging its mechanical properties.

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REFERENCES

1. Axrup, L.; Heiskanen, I.; Backfolk, K.; Riikonen, M. (Stora Enso). Patent WO 2012/039668 A1, March 03, 2012.

2. Fredlund, M.; Karlsson, A.; Norlander L. (Stora Kopparberg Bergslags Ab). Patent WO 2000/014333 A1, March 16, 2000.
3. Axrup, L.; Heiskanen, I.; Backfolk, K. (Stora Enso Oy). Patent WO 2011/078770 A1, June 30, 2011.
4. Murphy, B. C.; Fabri, O. J. (Nelson Mullins Riley & Scarborough, LLP). Patent US 2009/0098303 A1, April 16, 2009.
5. Siró, I.; Plackett, D. *Cellulose* **2010**, *17*, 459.
6. Lavoine, N.; Desloges, I.; Dufresne, A.; Bras, J. *Carbohydr. Polym.* **2012**, submitted.
7. Turbak, A. F.; Snyder, F. W.; Sandberg, K. R. (International Telephone and Telegraph Corporation, N.Y.). U.S. Patent 4,483,743, November 20, 1984.
8. Spence, K. L.; Venditti, R. A.; Rojas, O. J.; Habibi, Y.; Pawlak J. *J. Cellulose* **2011**, *18*, 1097.
9. Pääkkö, M.; Ankerfors, M.; Kosonen, H.; Nykänen, A.; Ahola, S.; Österberg, M.; Ruokolainen, J.; Laine, J.; Larsson, P. T.; Ikkala, O.; Lindström, T. *Biomacromolecules* **2007**, *8*, 1934.
10. Chen, W. S.; Yu, H. P.; Liu, Y. X.; Li, Q. *Adv. Mater. Res.* **2009**, *87–88*, 393.
11. Saito, T.; Kimura, S.; Nishiyama, Y.; Isogai A. *Biomacromolecules* **2007**, *8*, 2485.
12. Saito, T.; Isogai, A. *Biomacromolecules* **2004**, *5*, 1983.
13. Isogai, A.; Saito, T.; Fukuzumi, H. *Nanoscale* **2011**, *3*, 71.
14. Zhang, J.; Song, H.; Lin, L.; Zhuang, J.; Pang, C.; Liu, S. *Biomass Bioenergy* **2010**, *39*, 78.
15. Alila, S.; Besbes, I.; Vilar, M. R.; Mutjé, P.; Boufi, S. *Ind. Crops Prod.* **2012**, *41*, 250.
16. Dinand, E.; Maureaux, A.; Chanzy, H.; Vincent, I.; Vignon, M. R. (Saint-Louis Sucre S. A.). Patent WO/1984/003286A, March 03, 2002.
17. Klemm, D.; Kramer, F.; Moritz, S.; Lindström, T.; Ankerfors, M.; Gray, D.; Dorris A. *Angew. Chem., Int. Ed.* **2011**, *50*, 5438.
18. Ishii, D.; Saito, T.; Isogai A. *Biomacromolecules* **2011**, *12*, 548.
19. Zimmermann, T.; Bordeanu, N.; Strub, E. *Carbohydr. Polym.* **2010**, *79*, 1086.
20. Shields, R. J.; Bhattacharyya, D.; Fakirov, S. *Composites Part A* **2008**, *39*, 940.
21. Fujisawa, S.; Ikeuchi, T.; Takeuchi, M.; Saito, T.; Isogai A. *Biomacromolecules* **2012**, *13*, 2188.
22. Nemoto, J.; Soyama, T.; Saito, T.; Isogai, A. *Biomacromolecules* **2012**, *13*, 943.
23. Arola, S.; Malho, J.-M.; Laaksonen, P.; Lille, M.; Linder, M. B. *Soft Matter* **2012**, *9*, 1319.
24. Yang, Q.; Fukuzumi, H.; Saito, T.; Isogai, A.; Zhang, L. *Biomacromolecules* **2011**, *12*, 2766.
25. Syverud, K.; Stenius, P. *Cellulose* **2009**, *16*, 75.
26. Fukuzumi, H.; Saito, T.; Iwata, T.; Kumamoto, Y.; Isogai, A. *Biomacromolecules* **2009**, *10*, 162.
27. Chinga-Carrasco, G.; Syverud, K. *J. Nanopart. Res.* **2010**, *12*, 841.

28. Taipale, T.; Österberg, M.; Nykänen, A.; Ruokolainen, J.; Laine, J. *Cellulose* **2010**, *17*, 1005.
29. Ramos, Ó. L.; Fernandes, J. C.; Silva, S. I.; Pintado, M. E.; Malcata, F. X. *Crit. Rev. Food Sci. Nutr.* **2011**, *52*, 533.
30. Hamada, H.; Beckvermit, J.; Bousfield, W. D. Proceedings of the TAPPI PaperCon 2010 Conference, Atlanta, USA, May 2–5, **2010**.
31. Eriksen, Ø.; Syverud, K.; Gregersen, Ø. W. *Nord. Pulp Pap. Res. J.* **2008**, *23*, 299.
32. Aulin, C.; Gällstedt, M.; Lindström, T. *Cellulose* **2010**, *17*, 559.
33. Bardet, R.; Bras, J. In: *Handbook series on Green Materials*, **2013**, in press.
34. Hult, E. L.; Iotti, M.; Lenes, M. *Cellulose* **2010**, *17*, 575.
35. Heiskanen, I.; Backfolk, K.; Axrup, L. (Stora Enso Oyj). Patent WO 2011/056130 A1, May 12, **2011**.
36. Heiskanen, I.; Axrup, L.; Laitinen R. (Stora Enso Oyj). Patent WO2011/056135 A1, May 12, **2011**.
37. Wildlock, Y.; Heijnesson-Hultén, A. (Akzo Nobel N. V.). Patent WO 2008/076056 A1, Sept 19, **2008**.
38. Plackett, D.; Anturi, H.; Hedenqvist, M.; Ankerfors, M.; Gällstedt, M.; Lindström, T.; Siró, I. *J. Appl. Polym. Sci.* **2010**, *117*, 3601.
39. Aulin, C. Novel oil resistant cellulosic materials. Ph.D. Thesis, KTH Chemical Science and Engineering, Stockholm, Sweden, **2009**.
40. Spence, K. L.; Venditti, R. A.; Habibi, Y.; Rojas, O. J.; Pawlak, J. J. *Bioresour. Technol.* **2010**, *101*, 5961.
41. Siqueira, G.; Tapin-Lingua, S.; Bras, J.; Da Silva Perez, D.; Dufresne, A. *Cellulose* **2010**, *17*, 1147.
42. Kirwan, J. M. In *Paper and Paperboard - Packaging Technology*, Eds.; Blackwell Publishing: London, **2005**, p 262.
43. Lavoine, N.; Desloges, I.; Khelifi, B.; Bras J. *J. Mater. Sci.* **2013**, submitted.