IMPROVING BARRIER AND STRENGTH PROPERTIES OF PAPER BY MULTI-LAYER COATING WITH BIO-BASED ADDITIVES

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This study aims to evaluate the application potential of water soluble chitosan derivatives and microfibrillated cellulose (MFC) as barrier and mechanical strength additives in coating formulas for packaging paper grades. Three water soluble chitosan derivatives with specific functionalities were obtained in laboratory (alkyl chitosan – ACh, quaternary chitosan – QCh and carboxymethyl chitosan – CCh) and applied on solid board surface as single component or in combination with MFC. Coated board samples were characterized in terms of water barrier properties (contact angle, $Cobb_{60}$ index), water vapour transmission rate (WVTR), tensile strength properties and surface structure (SEM images). The results have shown the ACh applied alone or in combination with MFC improves the water and water vapour barriers, the CCh improves tensile strength properties (15%-20%) and WVTR (~30%), while the QCh gives moderate effects on the water barrier and strength properties.

Keywords: polysaccharides, packaging paper, chitosan derivatives, microfibrillated cellulose, coating formulas

INTRODUCTION

Most packaging paper grades are subject to requirements for high mechanical strength and good barrier properties. Generally, the strength properties are controlled mainly by additives based on natural polymers, like starch and cellulose derivatives. However, the development of barrier properties is based primarily on the synthetic materials, obtained from finite resources and with negative impact on the recycling potential and biodegradability of used paper-based packaging.[1] On the other hand, recent evolution in waste management policies shifted waste treatment priorities towards recycling and reuse, alongside with the increase of consumer environmental awareness.[2] In this context, the demand for recyclable and biodegradable packaging materials obtained from renewable resources is becoming more evident and the concept of sustainability represents a driving factor for the packaging market, turning the research toward alternatives to synthetic polymers.

Packaging additives based on polysaccharides

The polysaccharides are an important group of green chemicals for paper industry due to their availability, renewability and biodegradability. The most abundant polysaccharides are cellulose and chitin.[3] Polysaccharides like cellulose, starch, alginates originate from plants or algae. Others are of animal origin, e.g. chitin and glycogen. Some microorganisms are also sources of polysaccharides, such as cellulose, alginates and other exo-polysaccharides.[4] Many polysaccharides have potential to be used in the formulation of biopackaging as substitute for synthetic polymers in developing barriers to gases, moisture, microbiota etc.

In papermaking and paper converting, starch is the most common additive. Native and modified starch is used mainly for dry strength improvement of paper, but also as retention and flocculation aid, or as a binder in coating formulas and corrugated board production. Actually, the paper industry consumes around 10% of all produced starches and most of it goes to the

surface applications like surface sizing and coating.[5] Cellulose derivatives (e.g. carboxymethylcellulose – CMC) are used as strength additives or as thickeners and binders in surface sizing and coating formulas.[6]

However, the starch and cellulose derivatives present some limitations in their application as barrier materials for food packaging paper. Main disadvantages are associated with the rheological behaviour of aqueous solutions, which allows only small coat weight and the sensitiveness to water and microbial attack of the applied films.[7] Therefore, in recent years numerous researches have aimed to develop new bio-based materials (e.g. chitosan and micro/nanocellulose), which can provide good barrier and strength properties for packaging paper.

Chitosan and chitosan derivatives

Chitosan is an *N*-deacetylated derivative of chitin, a copolymer composed of 2-amino-2-deoxy-β-D-glucose and *N*-acetyl glucosamine units linked by β(1-4) bonds (Figure 1a).[8] As a potential papermaking additive, chitosan displays several advantages: has cationic charge and good film forming properties, presents structural affinity for cellulose and can develop hydrogen bonding. The chitosan could be also an environmentally attractive solution to synthetic polymers due to its biodegradability and biocompatibility.[9,10] Furthermore, it displays antibacterial and antifungal activity.[11,12] These features are important for potential applications of chitosan as surface coating or wet end additive in the papermaking processes.

In spite of the benefits that chitosan could provide as a papermaking additive, its large scale application is greatly limited due to the lack of water solubility under neutral/alkaline conditions. However, the amino ($-NH_2$) and hydroxyl (-OH) groups present on the chitosan backbone offer alternatives for chemical modification in order to obtain water soluble derivatives with various functionalities.[13] Few studies are currently available on the application potential of chitosan derivatives in papermaking. Nevertheless, several papers demonstrate the efficiency of water soluble chitosan derivatives as process and functional additives. Quaternary chitosan was investigated as retention, drainage and flocculation aid.[14] It was proved the carboxymethylchitosan and *N*-alkyl chitosan derivatives have high potential as dry strength and sizing additives when are applied in surface coating formulas.[15,16] Although scarce, the experimental data available on this subject provide promising results, which validate the versatility and multifuntionality of chitosan derivatives as papermaking additives.

Micro/nanofibrillated cellulose (MFC/NFC)

The MFC and NFC are materials produced generally by chemical or biochemical pretreatments of the cellulosic fibre pulp (e.g. carboxymethylation, enzyme treatment), followed by disintegration into micro/nanofibrils with the aid of high pressure homogenization. The nanofibrils are typically 5-15 nm in diameter, up to 1 µm long, and the microfibrils are of several micrometres long and 20-60 nm in diameter.[17,18] The pretreatments lead also to an increase in the content of carboxylic acid groups on the fibre surface. The MFC/NFC is obtained as a viscous, aqueous gel, consisting of cellulose micro/nanofibril aggregates.

The micro/nanofibrillated celluloses present high intrinsic tensile properties and high aspect ratio, which result in good reinforcing potential when used in composite materials.[17,19] Furthermore, they have the ability to form dense films, with nanoporous structures, which can provide gas barrier effects similar to those of synthetic polymer films. In dry athmosphere, the oxygen permeability of neat MFC films is comparable to that of ethylene co-vynil alcohol (EVOH) copolymer, but it is subtantially lower than that of polyvinilidene chloride (PVDC) or polyethylene terephtalate (PET) films with the same thickness.[17,20] Therefore, further development in obtaining and application of nanocelluloses could offer alternatives to synthetic polymer films for barrier properties of packaging paper, along with mechanical strength improvement.

Research aim

This study is aiming at evaluating three water soluble chitosan derivatives (ChDs) and microfibrillated cellulose (MFC) as barrier and mechanical strength additives in coating formulas for packaging paper grades. Three types of water soluble chitosan derivatives, namely alkyl-chitosan (ACh), carboxymethyl chitosan (CCh) and quaternary chitosan (QCh) were obtained in laboratory for these investigations. Particularly: the ACh derivative has an amphiphilic character (contains hydrophilic and hydrophobic groups), which can develop hydrogen bonds on fibre surface and can reduce the substrate

hydrophilicity;[21] the CCh has amphoteric character, presents anionic and cationic charged groups with complexation potential[22,23] that lead to very uniform films with low porosity and bonding potential; the QCh has permanent positively charged ammonium groups that increase its antibacterial and antifungal efficiency, and can also improve paper strength due to hydrogen bonding potential.[24]

The MFC was investigated in coating formulas as additive to supplement different polymers, including chitosan, for the improvement of barrier and strength properties. However, water soluble chitosan derivatives were never investigated in such coating formulas. With this consideration, the experiments were designed to allow us to evaluate the synergic effects of the chitosan derivatives and MFC in different coating formulas on the packaging board properties.

EXPERIMENTAL
Materials
Synthesis of water soluble chitosan derivatives
Alkyl chitosan (ACh) synthesis was performed by Schiff reaction with an aliphatic aldehyde at the primary amino groups of chitosan followed by a reduction with sodium cyanoborohydride, which yielded the N-alkyl derivative with a low substitution degree (Figure 1b).[16,21]

Carboxymethyl chitosan (CCh) synthesis was conducted under alkaline conditions by the etherification of chitosan with monochloroacetic acid using water/isopropyl alcohol as solvent system. The reaction pH and temperature were adjusted so both N- and O- substitutions could take place, yielding the N,O- carboxymethyl chitosan with medium substitution degree (Figure 1c).[23]

Quaternary chitosan (QCh) synthesis was achieved by a heterogeneous process using N (3-chloro-2-hydroxy-propyl) trimethylammonium chloride (commercially available as Quat188), under alkaline conditions. The corresponding epoxide of Quat188, generated in the presence of sodium hydroxide (NaOH), reacts with the primary amino groups of chitosan following a nucleophilic addition pathway (Figure 1d).[24]

The synthesis of chitosan derivatives was performed at the "Gheorghe Asachi" Technical University of Iasi.

Coating substrate: Ensocoat 190 g/m^2 bleached sulphate board with light pigment coating on reverse side. The solidboard sheets used in the experiments were provided by CTP Grenoble.

MFC suspension: with 20 g/L solids content, prepared at Centre Technique du Papier Grenoble, through enzymatic pretreatment and mechanical shearing on a microfluidiser.

Methods and analyses
Preparation of coating formulas
Single-component coating formulas were prepared by dissolving ChDs into water at neutral pH. A concentration of 10 g/L was established for all chitosan derivatives, based on solubility tests. Two-component coating formulas with total solids content of 1.33% were prepared by mechanical dispersion of the MFC suspension into ChD-solution, at MFC:ChD ratio of 1:1.

Coating method
Coating formulas were applied with a spiral bar using an Elcometer 4340 automatic film applicator. Spiral bar size and coating speed were adjusted to allow a total solid deposition of 2 g/m^2 in 5 passes for each coating formula. Coated samples were dried at 70 ºC in a contact drier after each pass. Three series of coating experiments different by composition and layer structure (Figure 1) were performed as follows:

a) *Single-component coatings*: ACh, CCh and QCh (Figure 2a) and MFC films (Figure 2b);

b) *Composite coatings* consisting of the ChD:MFC mixtures (1:1): ACh:MFC, CCh:MFC and QCh:MFC (Figure 2c);

c) *Successive coatings*, consisting of a 1 g/m^2 MFC base layer and a 1 g/m^2 ChD top layer: MFC-ACh, MFC-CCh, MFC-QCh (Figure 2d).

Characterisation of board samples
Sample conditioning: All paper tests were carried out under conditioned atmosphere (23 °C and 50% relative humidity) according to Tappi Standard T 402 sp-08. All samples were exposed to conditioned atmosphere for 24 hours prior to testing.

Wettability and water absorption capacity: Paper surface wettability was evaluated through water contact angle (CA) measured by the static sessile drop method on a DCE -1 Kiowa goniometer. The CA values for 2.5 µL droplets were collected on ten different points for each board sample. Water absorption capacity was evaluated by Cobb method, according to Tappi Standard T-441 om-98, at 60 seconds contact time between the paper surface and water (Cobb$_{60}$ Index, g/m^2).

Water vapour transmission rate (WVTR) is defined as the amount of water vapour transmitted from one face of the sample to the other per unit time and unit area, under specific conditions. In these experiments, the WVTR was measured by a gravimetric method, according to ISO 2528 standard. The samples were sealed with paraffin wax on top of aluminium cups containing anhydrous CaCl$_2$. The cups were exposed to conditioned atmosphere (23 °C and 50% RH) for 96 hours and weighed at regular time intervals. The mass uptake was used to calculate the WVTR. Five samples were tested for each coating type.

Tensile strength properties: The load–elongation curves of coated solid board samples were registered at constant strain gradient (according to ISO 1924-2-1994) on a Zwick-Roell dynamometer with a 500N

load cell. The clamp separation was 100 mm and the strain rate was 10 mm/s. Tests were carried out in machine direction only. Ten samples were tested for each coating type. The following strength indexes were obtained: tensile index, elongation at break and tensile energy absorption.

Surface characterization: SEM micrographs of coated surfaces were obtained on a Quanta ESEM using secondary electron analysis – SE and backscattered electron analysis – BSE.

The water vapour transmission rate measurements and the surface characterization by SEM were performed at CTP Grenoble. The contact angle, water absorption capacity and tensile strength measurements were performed at "Gheorghe Asachi" Technical University of Iasi.
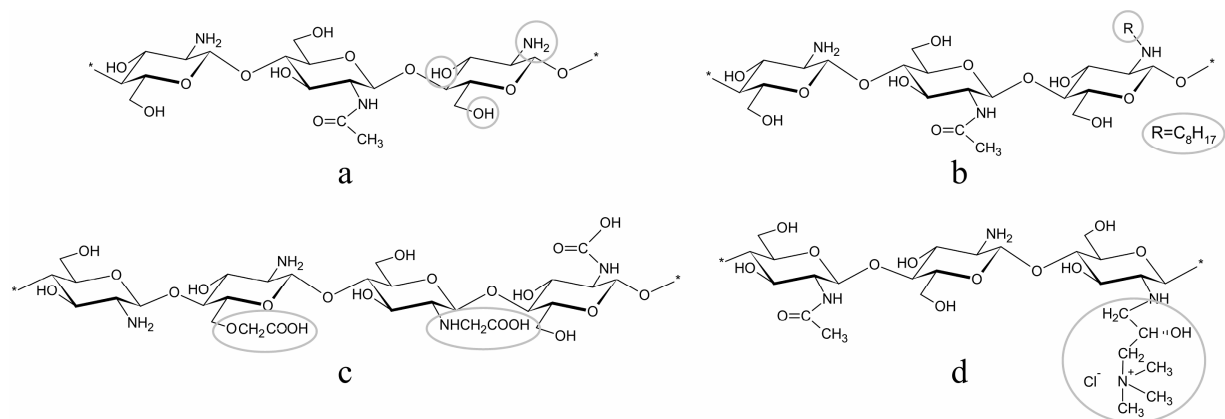
Figure 1: Chemical structure of unmodified chitosan (a), alkyl chitosan (b), carboxymethyl chitosan (c) and quaternary chitosan (d)
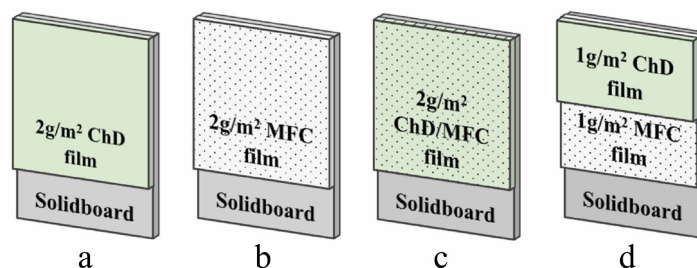

Figure 2: Design of coating series – single component (a, b), MFC:ChD mixtures (c), successive coating of MFC-ChD (d); (all surface coatings were applied at CTP Grenoble)

RESULTS AND DISCUSSION
Contact angle and water absorption capacity

Based on the contact angle against water on different surfaces, the materials are classified as hydrophilic for contact angle values lower than 90º or hydrophobic for values higher than 90º. In this study, the reference solid board is characterised by a contact angle of 100.6 ± 0.6º and a water absorption capacity of 25.7±1.91 g/m^2, which practically represent a medium sizing degree. Therefore, the migration of aqueous coating colours inside the solid board structure is limited, favouring film formation at low solids deposition (total coating weight was around 2 g/m^2).

Figure 3 illustrates the contact angle values of board samples coated with single-component films (series a and b – ChDs or MFC) and with bicomponent films in two variants (series c – ChD:MFC composite coatings, series d – MFC-CHD successive coatings).

When it is applied as a single component coating, the alkyl-chitosan derivative (ACh) leads to a slight increase of the contact angle value (+1.7º) and, in both composite and successive coatings, it changes the hydrophilic character of MFC to hydrophobic, increasing the CA value by up to 85º, compared to single-component MFC coatings. On the opposite side, all carboxymethyl chitosan (CCh) based coatings show hydrophilic

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character and compared with the reference sample, the contact angle decreases by 73-80º, being close to the values registered for the MFC film coatings. The coatings based on quaternary chitosan (QCh) present intermediary hydrophilicity, their contact angle values ranging between 81º and 86º, which could be explained by the short alkyl chains ($-CH_3$) introduced to chitosan through quaternisation. It can be noticed that in the case of the two-component coatings the MFC has no significant influence on the contact angle value. This leads to the conclusion that the chitosan derivatives are adsorbed on the surface of cellulose microfibrils at a high coverage level, producing a slight reduction of surface hydrophilicity in the case of QCh coatings and conferring hydrophobic character in the case of ACh coatings.

The values of $Cobb_{60}$ index for solid board samples treated with ChDs and MFC coating formulas are shown in Figure 4. Except for the ACh coatings, all other formulas lead to an increase of water absorption capacity, in relation with their hydrophilic character. As the water absorption decreases with contact angle increase, the water absorption indexes are a kind of reflection in the mirror of the contact angle (see Figure 3). This behaviour is also influenced by the relatively high sizing degree of the reference sample, which reduces the migration of the polymer and water from coating colour and thus, the characteristics of board surface are governed by the coating composition. A significant influence on surface properties comes from the MFC content. The water absorption capacity increases in the case of the ACh and QCh coatings with MFC addition, while a reverse effect is observed for the CCh with MFC.
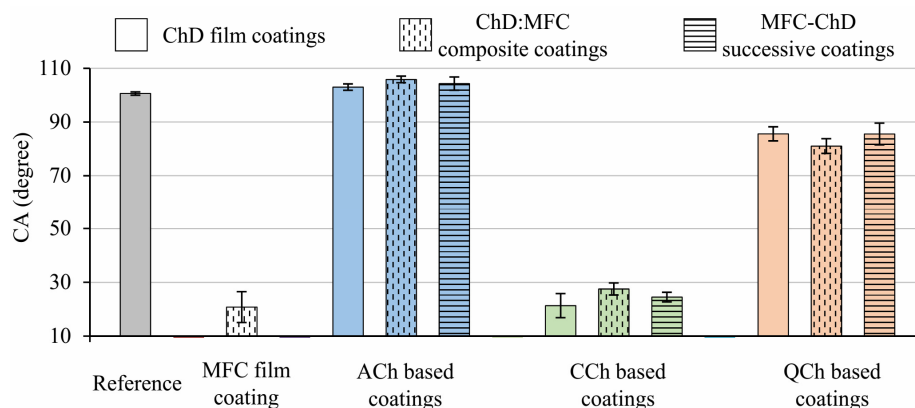

Figure 3: Contact angle of board samples coated with ChDs, without and with MFC
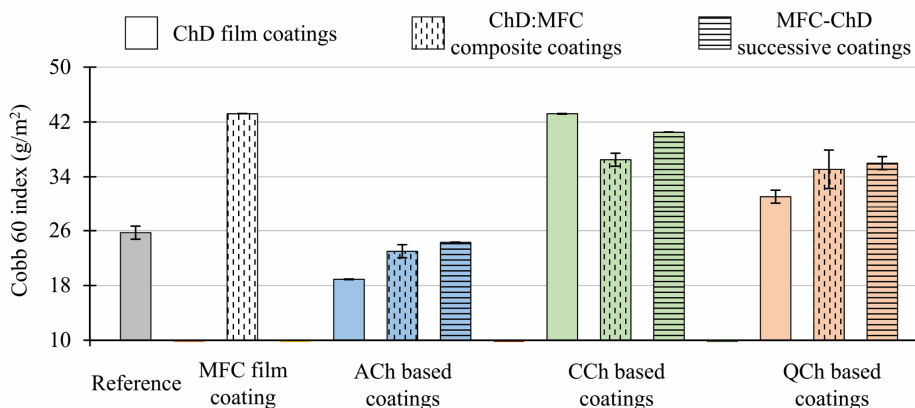

Figure 4: $Cobb_{60}$ index of board samples coated with ChDs, without and with MFC

As expected, the $Cobb_{60}$ index values are in accordance with CA values for all three ChDs' with a significant influence coming from the MFC content. In the case of the ACh and QCh based coating, the water absorption capacity increases with the addition of MFC. A reverse effect is observed in the case of CCh, which could suggest that composite formula consisting of the MFC dispersed in CCh solution gives a more closed structure of the coating.

Water vapour transmission rates

The WVTR values show wide differences among coating formulas, which are related to the chitosan derivative type and MFC presence (Figure 5). Single-component coating formulas based on the ACh and CCh give the lowest WVTR values, with a reduction of about 30% compared to the reference, but no significant reduction is registered in the case of QCh coating. Therefore, the CCh and ACh derivatives have the ability to generate uniform films, with compact structures at relatively low coating weight (2 g/m^2). Unlike CCh coating, the MFC coating had no significant influence on the WVTR, though both are hydrophilic and have similar values of the contact angle and $Cobb_{60}$ index. In fact, all coatings containing MFC (mixture or separate layers) have higher WVTR values than individual ChD coatings. This could be explained by the differences of surface structure observed by SEM analysis. For example, the micrographs of Figure

6 reveal uneven fibre coverage and distribution of cellulose microfibrils in the CCh/MFC coatings, comparatively with that of the CCh coating.

The efficiency of the studied ChD coatings in the reduction of WVTR is not significant, but appears promising considering the results for coatings based on chitosan combined with other polymers. A few examples are the following: Reis *et al.*[25] reported a 51% reduction of the WVTR for Kraft paper coated with 1.8 g/m^2 chitosan and palmitic acid films; Despond *et al.*[26] obtained an excellent water vapour barrier effect with two-layer coatings consisting of a bottom layer of 7 g/m^2 chitosan and a top layer of 2 g/m^2 carnauba wax; and Fang *et al.*[27] reported 98% reductions of WVTR for 7.4 g/m^2 two-layer coatings based on chitosan and poly(vinyldene chloride).

Tensile strength properties

The tensile index (TI, Nm/g), elongation at break ($\varepsilon Fmax$, %) and tensile energy absorption (TEA, J/m^2) were registered for all coating types in machine direction. As Figure 6 illustrates, CCh film coatings led to a slight increase in TI (3% higher than the reference), while none of the other coating types produced changes beyond the standard deviation of measured values. This is consistent with the results obtained by Bordenave *et al.*,[28] Kjellegren *et al.*[29] and Reis *et al.*,[25] who reported little or no influence of chitosan based coatings on the tensile strength of paper substrates.
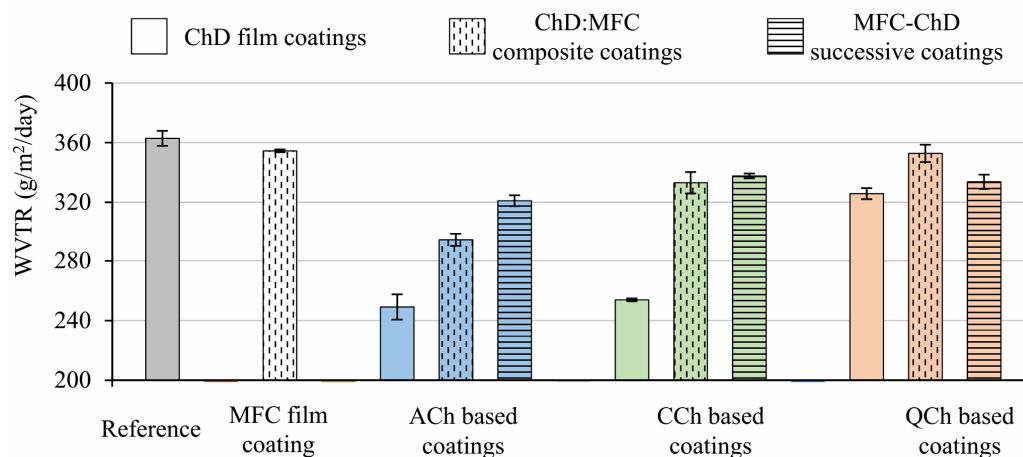

Figure 5: Water vapour transmission rates of board samples coated with ChDs, without and with MFC
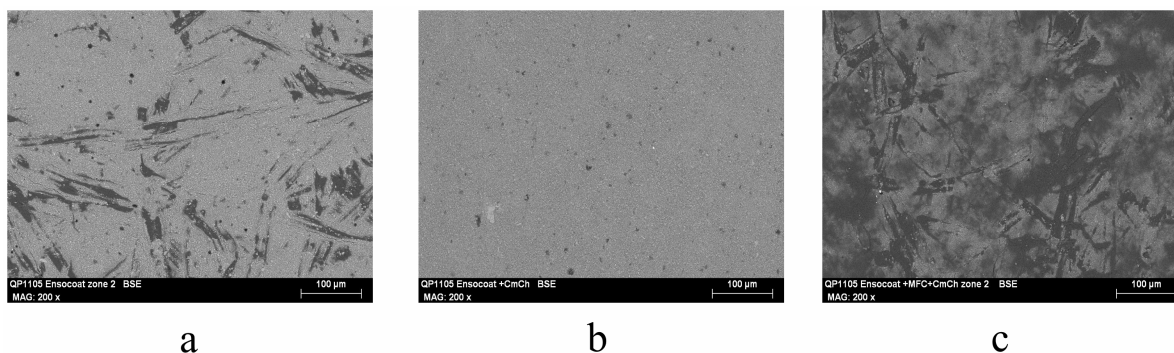
Figure 6: SEM images of: a – reference sample; b – CCh coating; c – CCh/MFC coating
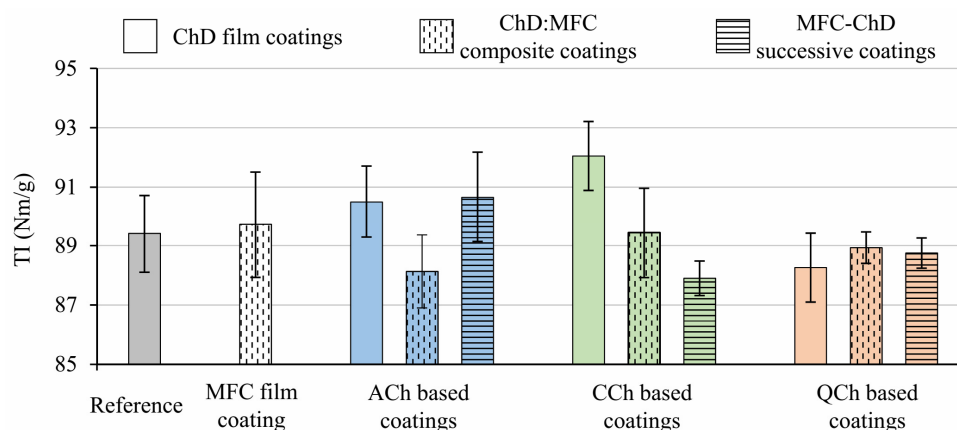

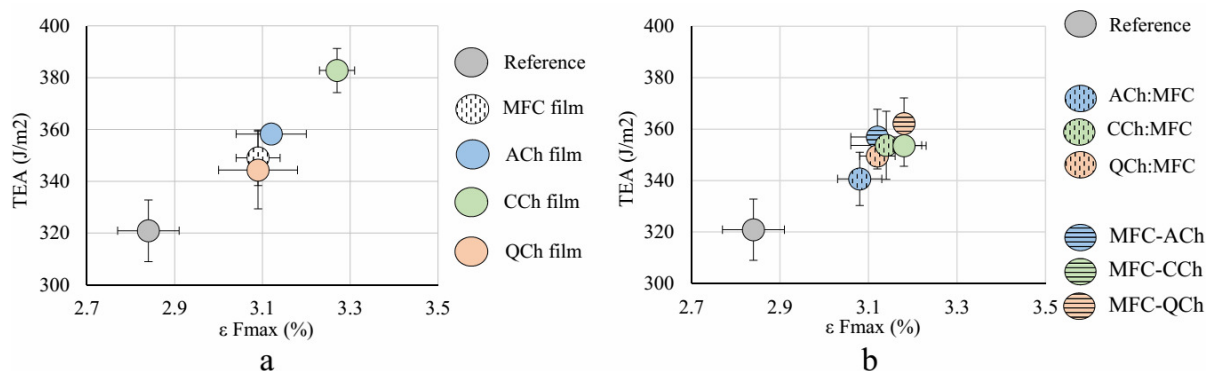Figure 7: Tensile index of board samples coated with ChDs, without and with MFC

Figure 8: Tensile energy absorption *vs.* stretch for samples with: single-component coatings (a) and composite and successive coatings (b)

However, the results of different studies cannot be compared because of substantial differences regarding the type of chitosan derivatives used, the type of cellulose substrate and the method of application. As an example, Vartiainen *et al.*[30] reported a 15% improvement in TI for copy paper sheets coated with 4.7 g/m² chitosan films. Considering the high relative porosity characteristic of copy paper sorts, this substantial improvement of tensile properties could be due to the high migration of chitosan into the internal structure of the substrate. M. S. Jahan *et al.*[31] observed a 40% increase in TI for laboratory sheets obtained from acacia and bamboo pulps, using chitosan as dry and wet strength additive, demonstrating that the presence

of chitosan in the internal structure provides significant improvements of strength properties.

Therefore, the efficiency of ChD based coatings in improving the TI of solid board samples in this study is greatly limited by the hydrophobic character and low water absorption capacity of the substrate, which greatly reduces the amount of polymer that migrates into the internal structure of paper. Furthermore, the reduction of inter fiber bonding caused by repeated wetting and drying has an overall negative influence on the mechanical resistance properties. This effect was previously demonstrated by Lavoine *et al.*[32] in their study on the effects of MFC surface coatings on paper.

Figure 8 illustrates an overall increase in paper stretch (εFmAx) values for all coating types. The highest effect corresponds to the CCh derivative, which leads to a 15% increase of the elongation in single-component coatings (Figure 8a). On average, the CCh based coatings show higher elongation values than the QCh and ACh based counterparts. Though, the MFC as single component improves the elongation at a level comparable with the ChDs, there is no a cumulative effect in the case of the two-component coatings (Figure 8b).

A more consistent improvement of tensile strength properties is illustrated by the 20% increase of tensile energy absorption (TEA) in the case of CCh film coatings. The TEA value is an indication of the ability of paper and paperboard to withstand repetitive stress and strain, a very important feature for packaging applications. The TEA values obtained for surface coatings based on ChD and MFC combinations are narrowly distributed between 362 and 340 J/m^2 (Figure 8b) and are inconsistent with their single component counterparts. The results show that more investigations are required to find out solutions for a more uniform distribution of the cellulose microfibrils in a polymer matrix.

CONCLUSION

Chitosan derivatives (ChD) and microfibrillated cellulose (MFC) show wide differences in water barrier properties when applied as single-component coating. Alkyl chitosan (Ach) increases the hydrophobicity while MFC, carboxymethyl chitosan (CCh) and quaternary chitosan (QCh) coatings increase the hydrophilicity of paper surface, these effects being clearly evidenced by the values of contact

angle and Cobb index; the WVTR drops by 30% for the CCh and ACh coatings, due to the presence of hydrophobic groups in the case of the ACh and due to a compact and uniform film structure in that of the CCh (proved by SEM images). However, the combinations of MFC with ChDs in composite coatings led to poorer water barrier properties than individual ChD films; one can suppose the effect is caused by uneven covering and lower ChD content in the coating layer (1 g/m^2 instead of 2 g/m^2).

When applied as single-component coating, both ChDs and MFC have positive influence on the mechanical strength properties (e.g. tensile energy absorption – TEA increases by 19% for the CCh and by about 10% for MFC, QCh and Ach). However, like in the case of water barrier, composite coatings produce a lower improvement in strength indexes than individual coatings, confirming that MFC impairs the uniformity of coating layers.

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