

ALKYL-CHITOSAN AS PAPER COATING MATERIAL TO IMPROVE WATER BARRIER PROPERTIES

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The aim of this study was to obtain and evaluate alkyl-chitosan derivatives as paper coating materials in developing water barrier properties. Three alkyl-chitosans, differing by alkyl chain length and at two substitution degrees each, were tested in two coating formulas – polymer and polymer/CaCO₃. Water barrier properties of paper were evaluated by contact angle (CA), water absorption capacity (Cobb₆₀ index) and water vapour transmission rate (WVTR). The polymer formula based on alkyl-chitosans improved consistently water barrier properties, which were positively influenced by substitution degree and negatively by alkyl chain length: the alkyl-derivative with the shortest alkyl chain and the highest substitution degree led to the highest increase of CA (82.1%) and the highest decrease of Cobb₆₀ index (82.6%). The WVTR, which depended less on surface hydrophobicity, showed only a slight reduction (only 20.3%) when using the polymer formula. Coating formulas based on alkyl-chitosan/CaCO₃ were more effective than the polymer formula in reducing Cobb₆₀ index and WVTR, suggesting a more uniform film formation, with lower porosity.

Keywords: chitosan, alkyl-chitosan, functional coating, barrier properties

INTRODUCTION

Paper is a porous structure network made up of cellulose micro-fibrils, which are composed of long-chain cellulose molecules in a crystalline state, with amorphous regions regularly disrupting the crystalline structure. Due to the free hydroxyl groups from the amorphous fraction and from the surface of the crystalline area, the hydrophilic nature of cellulose, along with the fibre network porosity, limit the barrier properties of paper. Paper can easily absorb water from the environment or from the products that come into contact and lose its physical and mechanical strengths. Moisture migration can occur in paper by diffusion of water or water vapours through the void spaces, as well as in condensed form through the fibre cell walls.¹

Paper is often associated with other materials, such as plastic materials and aluminium, for their good barrier properties that could be advantageously combined with paper stiffness for developing different barrier properties.^{2,3} The barrier properties are important because during processing and use, paper and cardboard come in contact with different fluids, which can penetrate the surface by various mechanisms and at diffe-

rent rates. Some areas of paper and paperboard application, such as packaging, require a wide range of barrier properties, depending on the nature of the packaging content, storage conditions and transport. Frequently, packaging paper and board must provide barrier properties to water, gases, greases or flavours, depending on the composition and properties of the products that come into contact.⁴ The treatment of the paper surface in order to control its surface properties, such as surface energy, smoothness, porosity or specific barrier properties to different agents, has been thoroughly explored.⁵ Currently, the coating formulas used to improve the barrier properties of paper and board are mainly based on synthetic polymers: non-polar hydrocarbon polymers, such as polyethylene, have excellent water vapour barrier properties; polyolefins are generally chosen as paper coating materials to overcome porosity and hygroscopicity of paper; aluminium or ethylene-vinyl alcohol copolymers (EVOH), polyesters or polyamides are used to laminate paper-based packaging materials to obtain a low oxygen and a low water vapour transmission rate.^{6,7} Some of the disadvantages of

these treatments are low recyclability, decreased biodegradability and, in some cases, limited use of packaging supposed to come into contact with foods.⁸

Current trends in functional coating aim to develop green solutions for barrier properties to allow the replacement of synthetic polymers with biopolymers, originated from naturally renewable resources, such as polysaccharides, proteins and lipids.⁷ Biopolymer-based packaging materials offer favourable environmental advantages of recyclability and reutilization, compared to conventional petroleum-based synthetic polymers. Biopolymer films and coatings may also serve as gas and solute barriers and complement other types of packaging by minimizing food quality deterioration and extending the shelf life of foods.^{9,10} Moreover, biopolymer-based films and coatings can act as efficient vehicles for incorporation of various additives, including antimicrobials, antioxidants and colouring agents.¹¹ The association of biopolymers with paper provides interesting functionalities, while maintaining the environment-friendly nature of the material and its recyclability. They can be applied in-line and the coated material can easily be re-pulped.¹²

Chitosan can be considered an alternative for the development of paper barrier properties, as it is a polymer that is obtained from renewable resources and features a number of important properties for applications in paper industry, as follows: it is a cationic biopolymer, containing free hydroxyl groups, which are able to develop hydrogen bonds like cellulose fibres; it has the ability to form films with antimicrobial properties; it is biodegradable and non-toxic. Chitosan has been reported to be used as a wet end additive in paperboard to improve the mechanical properties of the product or in the development of paper barrier properties or bending strength by its inclusion in paper coating formulas.^{12,13} Moreover, studies on chitosan used in combination with poly(lactic acid),¹⁴ poly(ϵ -caprolactone)¹⁵ or clay micro/nanoparticles¹⁶ have shown to improve the water vapour barrier and mechanical properties of chitosan films. Although various studies of chitosan coatings on paper have been reported, there are no practical applications since the use of chitosan in coating formula is limited by the low water solubility under neutral pH and by the hydrophilic character of its films.^{17,18,19} However, different studies focused on other applications of chitosan show that the

introduction of alkyl chains into the chitosan structure allows obtaining water soluble derivatives under neutral/slightly alkaline pH, which could be compatible with the formulas for surface treatment of the paper and board.²⁰

Considering these aspects, the objective of this study was to evaluate alkyl-chitosan derivatives as paper coating material for developing water barrier properties.

EXPERIMENTAL

Materials

Paper sheets, with 65 ± 1 g/m² grammage, obtained from bleached softwood and hardwood Kraft pulp mixture (20:80, w:w), were used as the base paper for surface coating.

Chitosan (Ch) of low molecular weight (supplied by Sigma Aldrich Co.), with a molecular weight of 77 kDa and 85.7% deacetylation degree, was used in the alkyl-derivatives synthesis and as reference in surface coating formulas.

Chemicals for the synthesis of alkyl-chitosan derivatives: aldehydes with different alkyl chain length – octanal, decanal and dodecanal (all aldehydes supplied by Sigma Aldrich Co.); sodium cyanoborohydride reagent grade 95% (Sigma Aldrich Co.); glacial acetic acid 99.5% (Chemical Company S.A.), hydrochloric acid 37% (Sigma Aldrich Co.), sodium hydroxide (pellets for analysis, Merck KGaA), ethanol 96% (Chemical Company S.A.) and methanol 99% (Chemical Company S.A.).

Calcium carbonate powder (commercial product Omya Hydrocarb®), with 98% purity and 1.40 μ m median diameter, was used as pigment in coating formulas.

Analysis methods and procedures

Modification of chitosan by alkylation

Alkyl-chitosan derivatives were synthesized using a previously developed method²¹ by the reductive amination reaction, which allows the selective introduction of an alkyl substituent on the amino groups of chitosan. Three alkyl-chitosan derivatives with different alkyl chain lengths (octyl-ACh8, decyl-ACh10 and dodecyl-ACh12) were synthesized. Each alkyl-chitosan was obtained at two different substitution degrees (e.g. alkyl-chitosans with C8 chains: ACh8.1, ACh8.2; alkyl-chitosans with C10 chains: ACh10.1, ACh10.2 and alkyl-chitosans with C12 chains: ACh12.1, ACh12.2) by varying the ratio between glucose-amine units of chitosan and aldehydes (Table 1).

Characterisation of chitosan and alkyl-chitosan derivatives

The FT-IR and ¹H-NMR spectroscopy was used to characterise the chitosan and alkyl-chitosan derivatives in order to establish the deacetylation degree (DD) and

substitution degree (SD). The FT-IR analyses were carried out with Digilab FTS 2000 Fourier transform spectrometer, domain 4000-400 cm^{-1} , resolution 4 cm^{-1} , 32 scans. The $^1\text{H-NMR}$ spectra were obtained by a Bruker Avance DRX 400 spectrometer, at a frequency of resonance of 400 MHz and temperature of 27 °C, in D_2O . The deacetylation degree (DD) was calculated from the FT-IR spectra by applying the method provided by Brugnerotto *et al.*²² and the substitution

degree (SD) was calculated by the method proposed by Bobu *et al.*²¹, using Equation 1:

$$\text{SD} = (\text{DD}_1 - \text{DD}_2) \quad (1)$$

where DD_1 and DD_2 are deacetylation degrees of chitosan and alkyl-chitosan, respectively.

The values of SD measured by $^1\text{H-NMR}$ and FT-IR spectra are very similar, demonstrating the validity of calculating the SD based on FT-IR spectroscopy, which is an easier and more accessible method than those based on $^1\text{H-NMR}$ spectra (Table 1).

Table 1
Substitution degree of alkyl-chitosan derivatives by FT-IR and $^1\text{H-NMR}$ methods

Polymer type	SD by FTIR, %	SD by $^1\text{H-NMR}$, %
Chitosan (Ch)	-	-
ACh8.1	2.38	2.17
ACh8.2	4.11	3.74
ACh10.1	3.00	3.11
ACh10.2	3.97	3.51
ACh12.1	3.07	2.94
ACh12.2	3.60	3.35

Preparation of surface coating formulas

Polymer solutions: chitosan was dissolved in 0.1M acetic acid solution (final pH of the stock solution was 4.05) and alkyl-chitosan derivatives were dissolved in distilled water (final pH of the stock solutions was in the range of 6.80-6.95).

Coating formulas: two types of formulas were used in surface coating: one coating formula based on polymer solution (5 g polymer/L) and another formula based on polymer/ CaCO_3 dispersions (15 g/L). The latter formula was obtained by mechanical dispersion of calcium carbonate powder into polymer solutions, with a polymer: CaCO_3 ratio of 30:70 (w/w). The concentrations of the coating formula were tested in order to achieve an average coating weight of $0.98 \pm 0.2 \text{ g/m}^2$ for the polymer solution and $2.87 \pm 0.28 \text{ g/m}^2$ for the polymer/ CaCO_3 dispersions, respectively.

Surface coating application method

The Meyer-Rod method was used for surface coating of paper sheets, which consisted in the application of a thin layer on one side of the sheet, using a glass rod for uniform distribution. The coated sheets were dried first under ambient conditions and then in a lab dryer with steam pressure (5 min).

Evaluation of water barrier properties of coated paper

Water barrier properties were evaluated by contact angle, water absorption capacity and water vapour transmission rate (WVTR).

Contact angle was measured with a Krüss DSA 10Mk2 goniometer (Krüss, Palaiseau, France) equipped with a camera and a recording system. The

contact angle was calculated from 10 measurements, for each of the three typical test liquids (two polar – water and ethylene glycol, and one non-polar – diiodomethane for which the polar component is zero).²³ The surface free energy (SFE) and its components were calculated from the measured parameters of contact angle against polar and non-polar liquids by applying the Owens and Wendt computing model.²⁴

Water absorption capacity, which represents the amount of absorbed water by unit area of paper in a defined period of time (60 s in this study), was evaluated by Cobb₆₀ index, according to TAPPI Standard T-441 om-98 method.²⁵

Water vapour transmission rate (WVTR) was evaluated using test dishes, as described in TAPPI Standard T-448 om-09 method.²⁶ WVTR represents the mass of water vapour transmitted per unit time and per unit area, from one face of the sheet to the other, under specific steady conditions. The standard unit is $\text{g/m}^2\text{-day}$ and the specimen is subjected to an atmosphere approaching 0% relative humidity (RH) on one face and 50% RH on the other, at a temperature of 23 °C.

RESULTS AND DISCUSSION

Contact angle and surface free energy of paper surface treated with different coating formulas

The measurement of contact angle against water is the most widely used tool to evaluate paper surface hydrophobicity, being an accurate method for determining the interaction energy between a liquid and a solid.²⁷ The results for

water contact angle and the components of surface free energy are presented in Table 2.

From the definition of contact angle, the wetting occurs when the contact angle value of water to the paper is below 90° . In the case of surface paper treated with the chitosan solution, the contact angle is lower than 90° , which is not unexpected because chitosan has hydrophilic nature. But, all alkyl-chitosan derivatives give coatings with contact angles higher than 100° , demonstrating a consistent increase of the paper surface hydrophobicity. Comparatively with chitosan, the alkyl-derivatives lead to an increase of water contact angle between 40 and 70% (between 33.1° and 59.8°), depending on the alkyl chain length and substitution degree.

The decrease of surface free energy is well correlated with the contact angle increase for all alkyl-derivatives (Figures 1a, 1b, 1c). It is interesting to remark that the decrease of surface free energy is due to the reduction of both non-polar and polar components (see Table 2), but the intensification of the hydrophobic character could be associated with a higher ratio of the non-polar component (γ_s^{LW}), which is around 99% for all

alkyl-chitosan derivatives, while it represents only 93% for chitosan films. The changes of surface free energy components indicate inter- and intra-molecular interactions of functional groups, which reduce the surface free energy of chitosan films.

The hydrophobic character of coated paper increases with the substitution degree and decreases with alkyl chain length: the paper treated with derivative ACh8.2, with the shortest alkyl chain and the highest substitution degree (Figure 1a) has the highest contact angle (133°) and the lowest surface free energy, respectively; a reversed situation can be observed for paper treated with derivative ACh12, with the longest alkyl chain and the lowest substitution degree (Figure 1c). A negative influence of long alkyl chain on surface hydrophobicity would not be expected when considering the current hydrophobization agents used in papermaking, like alkyl ketene dimer (AKD) having C14-C16 alkyl chain. Of course, the mechanisms of interaction with cellulose fibre surface are totally different for the AKD and alkyl-chitosans, respectively.

Table 2
Water contact angle and surface free energy and its components for paper surface treated with different polymer formulas

Polymer	Water contact angle, $^\circ$	SFE- γ_s , mN/m	γ_s^{LW} , mN/m	γ_s^p , mN/m
Ch	73.5 ± 2.6	54	50.4	3.6
ACh8.1	126.3 ± 1.9	50.5	49.2	1.3
ACh8.2	132.6 ± 1.9	27.6	26.6	1.0
ACh10.1	116.5 ± 2.7	50.9	49.7	1.2
ACh10.2	125.3 ± 1.1	26.8	25.5	1.3
ACh12.1	105.9 ± 1.2	50.9	50.0	0.9
ACh12.2	106.7 ± 1.8	50.3	49.3	1.0

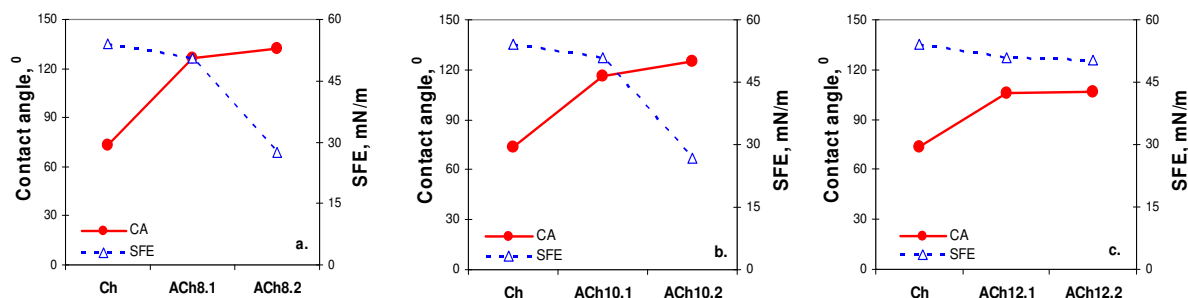


Figure 1: Contact angle (CA) against water and surface free energy (SFE) as a function of substitution degree of chitosan derivatives, for treated paper surface with polymer formula

Water absorption capacity for paper surface treated with different coating formulas

In the case of the polymer coating formula (Figure 2), the water absorption capacity ($Cobb_{60}$ index) decreases only slightly (15.6%) for chitosan, mainly due to the filling of surface pores; while the treatments with alkyl-chitosans lead to consistent reductions from 26.6% up to 82.6%, as a function of substitution degree and alkyl chain length. These evolutions clearly demonstrate the improvement of water barrier properties of paper samples treated with alkyl-chitosans. Water adsorption capacity values are in agreement with the changes of water contact angle values: water absorption capacity increases with alkyl chain length and decreases with substitution degree.

Figure 3 presents the water absorption capacity vs. water contact angle of paper surface treated with different polymer formulas. As expected, there is a good correlation between these two parameters: the lowest decrease of water absorption capacity (15.6%) was registered for chitosan with the lowest increase of water contact angle (0.96%); while for alkyl-derivatives with the shortest alkyl chain and the highest substitution degree (ACh8.2), a 82.6% decrease in water absorption capacity for an increase of

82.1% in water contact angle was recorded. The alkyl-derivatives with longer alkyl chain (ACh12.1 and ACh12.2), for which the increase of water contact angle ranged between 45-46%, produce only 26-34% reduction of water absorption capacity. In these cases, the lower correlation between water contact angle and water absorption capacity indicates a modification of the film structure with chain length increase. The influence of the substitution degree is easy to understand because of the increase of the hydrophobic sites, but the influence of the alkyl chain length is more complex and could be correlated mainly with the film properties. The alkyl-derivatives with short alkyl chains (ACh8.1 and 8.2) lead to more compact and wrapped films with hydrophobic alkyl chains oriented toward film surface and low water absorption capacity. The increase of alkyl chain length (ACh10 and ACh12) produces probably more open structures of the polymer film with less orientation of the chain length and higher water absorption capacity. Thus, the lowest water absorption capacity of the film based on derivative ACh8.2 is the consequence of the highest degree of substitution among the alkyl-chitosans tested and of the more compact and uniform film formation.

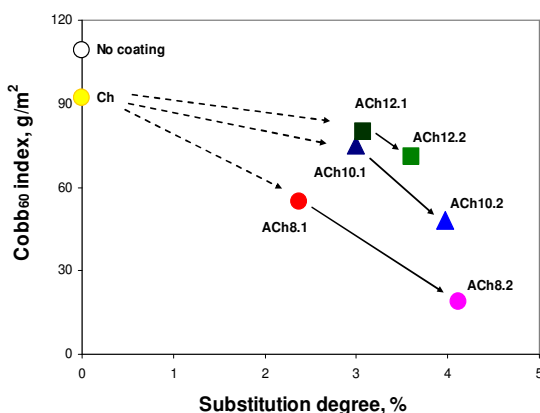


Figure 2: Water absorption capacity of paper surface treated with polymer formulas

The water absorption capacity of the paper samples decreases more significantly (about 80-84%) when the alkyl-chitosan/ $CaCO_3$ coating formula is applied (Figure 4), while the decrease is of only about 16% for the chitosan/ $CaCO_3$ coating formula. Moreover, there are no evident differences among alkyl-derivatives, concerning

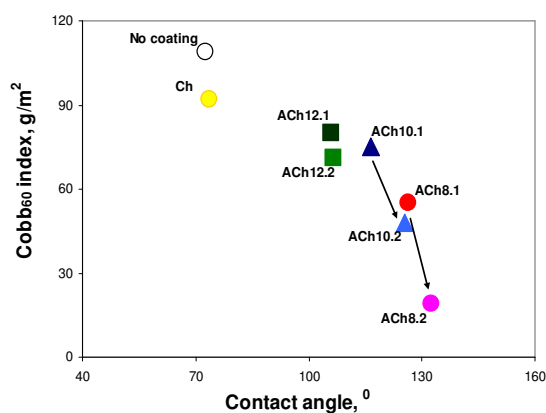


Figure 3: Water absorption capacity vs. contact angle of paper surface treated with polymer formulas

the alkyl chain length or degree of substitution. In this case, the strong reduction of water absorption capacity, regardless of the alkyl-chitosan type, indicates a completely different mechanism of film formation: the mechanical distribution of calcium carbonate powder into alkyl-chitosan neutral solution results in a stable dispersion in

which pigment particles are covered by a polymer film; when alkyl-chitosan/CaCO₃ dispersion is applied on paper surface, particles covered by a polymer film fill the surface pores and thus, less polymer migrates into the internal pores of paper, leading to a more uniform and well-structured

film. This hypothesis is supported by the absence of a significant decrease of water absorption capacity in the case of chitosan, when less stable dispersions are obtained since chitosan is dissolved in acetic acid and a partial solubilisation of calcium carbonate particles could take place.

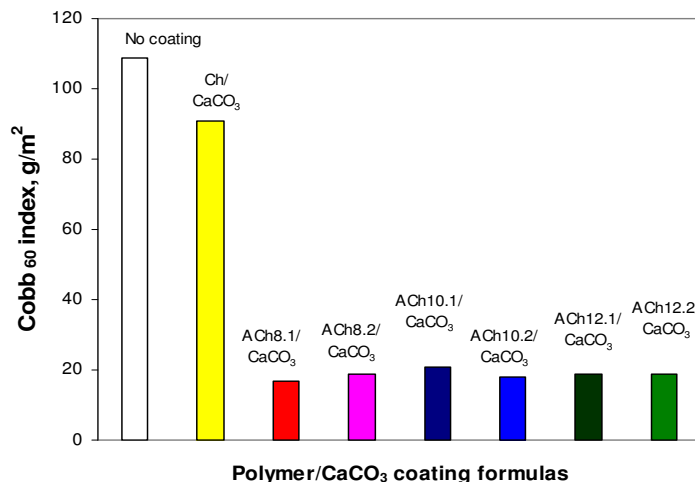


Figure 4: Water absorption capacity of paper surface treated with polymer/CaCO₃ formulas

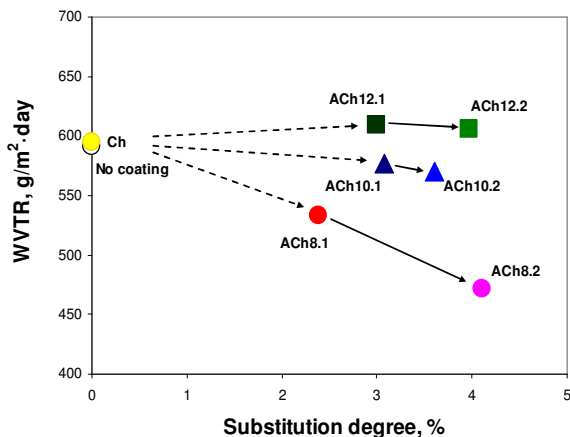


Figure 5: Water vapour transmission rate of paper surface treated with polymer formulas

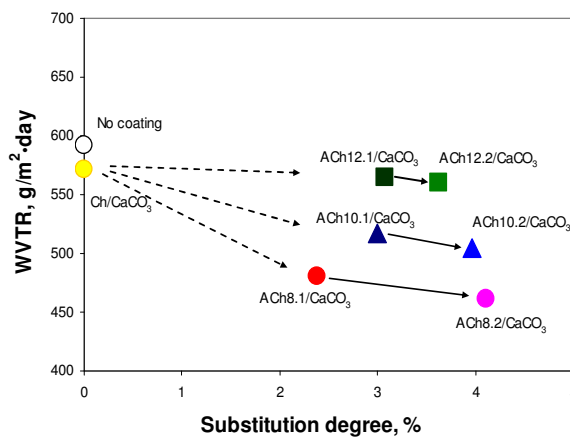


Figure 6: Water vapour transmission rate of paper surface treated with polymer/CaCO₃ formulas

Water vapour transmission rate for paper surface treated with different coating formulas

Figures 5 and 6 present the water vapour transmission rate (WVTR) of the paper samples treated with polymer and polymer/CaCO₃ coating formulas, comparatively with paper without coating. No influence on the WVTR can be observed in the case of the polymer formula based on chitosan (Figure 5). Though the water barrier is slightly improved due to surface pore filling, it appears that chitosan films were more sensitive to water vapour due to their strong hydrophilic

character.²⁸ In the case of alkyl-derivatives, the WVTR evolution as a function of the substitution degree and alkyl chain length presented the same trend as water absorption capacity: the alkyl-derivative with the shortest alkyl chain and highest SD (ACh8.2) led to the lowest WVTR value, which was the combined effect of the lower porosity and higher hydrophobicity of these films, comparatively with the film based on longer alkyl chains. Therefore, the decrease of WVTR was lower compared to water absorption capacity decrease, because of the two different agents,

liquid water and water vapour, which imply different mechanisms of interaction with the paper surface. Unlike water absorption, the water vapour transmission rate was controlled mainly by gas diffusion through the surface and internal pores, being influenced strongly by the paper porosity and only partially by surface hydrophobicity.

In the case of the polymer/CaCO₃ formula, the WVTR decreased only by 3.4% for chitosan, while the decrease was between 4.6-22.1% for alkyl-derivatives, depending on the alkyl chain length and substitution degree (Figure 6). The WVTR presented clear differences as a function of alkyl chain length, the alkyl-derivative with the shortest alkyl chain (ACh8.1 and ACh8.2) leading to the lowest WVTR values, being slightly influenced by the substitution degree. This is sustained by the previous explanation, regarding the different ways of action of liquid water and water vapour, the latter being influenced mainly by the surface porosity (pore number and size) and less by surface hydrophobicity.

CONCLUSION

In this study, the application of alkyl-chitosan derivatives as additive in developing water barrier properties was approached for the first time. The alkyl-chitosans were tested comparatively with chitosan in two paper coating formulas, in order to improve the paper water barrier properties, such as water contact angle and surface free energy, water absorption capacity and water vapour transmission rate.

◦ *Polymer coating formula*: In the case of the polymer coating formula, the hydrophobic character of treated paper surface (water contact angle increase and surface free energy decrease) was intensified with the substitution degree and was decreased slightly with alkyl chain length. The negative influence of long alkyl chains on surface hydrophobicity could be caused by an increase in polymer film porosity, which was confirmed also by the water absorption capacity measurements. When it was compared with chitosan coated paper, the alkyl-derivative with the shortest alkyl chain and the highest substitution degree (ACh8.2) led to the highest increase of contact angle (82.1%) and the highest decrease of water absorption capacity (82.6%). The WVTR evolution presented the same trend as water absorption capacity but, in all cases the decrease was lower (the highest decrease was only 20.3%) because the two agents (liquid water

and water vapours) imply different mechanisms of interaction with paper. WVTR is controlled mainly by gas diffusion through the surface and internal pores and is influenced strongly by paper porosity and only partially by surface hydrophobicity.

◦ *Polymer/CaCO₃ coating formula*: In the case of the alkyl-chitosans, the water absorption capacity decrease was between 80-84%, regardless of the derivative type, while the decrease was only 16% in the case of the chitosan/CaCO₃ formula. This totally different evolution from that of the polymer coating formulas indicates that, in the case of the alkyl-chitosan/CaCO₃ formulas, less polymer migrates into the internal pores of paper, forming more uniform and compact films on paper surface. This hypothesis is supported by the lack of a significant decrease of water absorption capacity in the case of chitosan, when less stable dispersions are obtained since calcium carbonate is partly dissolved in acetic acid. Moreover, the evolution of the WVTR, which is influenced more by paper surface porosity than by surface hydrophobicity, confirmed a better structured film in the case of the alkyl-chitosan/CaCO₃ formula, comparatively with the chitosan/CaCO₃ formula.

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