Chitosan Derivatives as Bio-based Materials for Paper Heritage Conservation

Florin Ciolacu, Raluca Nicu, Tudor Balan, and Elena Bobu *

Three water-soluble chitosan derivatives (ChDs)- carboxymethyl- chitosan (CCh), alkyl-chitosan (ACh), and quaternary-chitosan (QCh)- were evaluated as new materials for paper conservation. Several series of samples were prepared by coating different paper types with ChDs or methylcellulose (MC). The ChDs’ effectiveness were analyzed by their effects on the strength (tensile energy absorption (TEA), double folds) and water barriers (Cobb60, contact angle (CA)). The coatings on laboratory paper showed strength improvements for the CCh/QCh coatings that were consistent with an increase in the coating weight (CW). The ACh had little effect on the strength, but developed an effective barrier to water. The coatings on printing paper were performed at a constant CW by applying two layers of the same ChD or MC, and by combining CCh or QCh in the first layer with ACh in the second layer. Homogenous coatings based on the CCh or QCh resulted in high strength improvements, comparable to MC, but only ACh coatings developed an effective barrier to water. Combinations of the CCh or QCh with ACh provided the best relationship between the strength and barrier properties and proved their effectiveness as strengthening/protective materials in the treatment of natural aged paper.

Keywords: Paper heritage; Conservation; Chitosan derivatives; Water barrier; Strength properties

Contact information: Department of Natural and Synthetic Polymers, “Gheorghe Asachi” Technical University of Iasi, D. Mangeron 71, Iasi -700050, Romania; *Corresponding author: elbo@tuiasi.ro

INTRODUCTION

Archival objects such as manuscripts, books, periodicals, correspondence, and photographs form a large part of our cultural heritage and play a crucial role as the memory of the centuries past. However, paper documents are continuously subjected to degradation processes, together referred to as natural aging, which are responsible for a large loss of paper heritage (Havermans 2002; Stuart 2007). Paper aging involves biological, physical, and chemical processes that are influenced by a complexity of internal and external factors acting simultaneously (Area and Cheradame 2011). Deterioration processes are seen in the relationship with the change of the fiber raw material used in paper manufacturing and especially, with the introduction of an acid sizing method based on rosin and alum. Acid-catalyzed hydrolysis of cellulose, acting primarily by the breakage of cellulose chains by random scission of the hemiacetal links, is seen as the main cause of archival paper deterioration (Baranski et al. 2005). Therefore, deacidification is an important step in paper conservation, which has been demonstrated to greatly reduce the degradation rate (Cheradame et al. 2003). However, deacidification cannot restore the strength lost because cellulose chain deterioration is irreversible. Actually, new studies indicate that aqueous deacidification processes have detrimental effects on the paper strength, and it has been suggested that these processes should be followed by consolidation and strengthening treatments (Zervos 2013).
The resizing of old paper documents is considered a conservation treatment. This consists of the application of film-forming materials on the paper surface, with the aim to restore the barriers to gases and water that were lost by aging, and to limit the interactions between paper and external degradation factors. Resizing also serves frequently as consolidation and stabilizing treatments (Henry 1988). Cellulose ethers are commonly used materials for the resizing/strengthening of aged paper because of their structural compatibility with cellulose and potential to enhance mechanical strength without producing noticeable changes in appearance. Among the cellulose ethers, the methylcellulose (MC) and carboxymethyl-cellulose (CMC) are the most widely used in current practice (Henry 1988; Oprea 2009). However, because of their hygroscopic nature and susceptibility to microbial attack, which favors chemical and biochemical degradation, cellulose ethers have limited effectiveness in the long-term preservation of paper documents (Dobroussina et al. 1996; Ardelean et al. 2011). Films based on synthetic polymers (e.g., polyethylene, polypropylene, etc.), graft-copolymerization (mixture of the ethyl acrylate and methyl methacrylate inserted into paper), and the parylene process (gas phase deposition of the xylylene) are some of the alternative solutions investigated in paper conservation (Anders 2006; Zervos and Alexopoulou 2015). Such materials have proved effective in the resizing/strengthening of aged paper, but they create irreversible changes in paper that are not acceptable in paper conservation (Martuscelli 2008; Baty et al. 2010).

At present, there is a need for an interdisciplinary approach in the restoration processes and new solutions that can produce protective effects, other than restoration. Chitosan, an amino-polysaccharide with a linear structure similar to cellulose and a single biopolymer with a cationic charge, appears as an attractive compound to substitute for cellulose derivatives. The main features of chitosan that express an interest in both papermaking and paper heritage conservation are its structural affinity with cellulose; capacity to form hydrogen bonds and act as a strengthening agent; its high cationic charge, which confers antimicrobial properties without toxicity; and very good film-forming properties (Laleg and Pikulik 1993; Bobu et al. 2002; Ashori et al. 2006; Nicu et al. 2013a).

There are only limited studies on the use of chitosan in paper heritage conservation. Ponce-Jiménez et al. (2002a,b) have shown that the treatment of paper with acid salts of chitosan improves fungal resistance but decreases the paper strength, whiteness, and extract pH, compared with the cellulose derivatives. When the treatment with an acidic solution of chitosan was followed by precipitation with sodium silicate, it was found that the aging resistance of the paper increases due to acidity neutralization (Basta 2003). Both studies concluded that the application of chitosan in paper conservation could be of great interest if it would be available as a water-soluble derivative under a neutral pH. Fortunately, chitosan can be modified at both amino- and hydroxyl- groups to generate new functionalities, including solubility under a neutral/alkaline pH. Early research on the use of water-soluble chitosan derivatives in paper conservation are related to carboxymethyl-chitosan, which has shown it can increase paper strength at the same level as MC (Ardelean et al. 2009, 2011). Fernandes et al. (2010) found that the surface treatment of printing paper with quaternized chitosan produced better optical and printing properties and a higher aging resistance than chitosan. Recent research on the hydrophobization potential of the alkyl-chitosan demonstrated its effectiveness as a water barrier coating, which could be controlled by the length of the alkyl chain and the substitution degree (Nicu et al. 2013b).

The objective of this study is to assess three water-soluble chitosan derivatives (ChDs) with different functionalities as new materials for the sizing and strengthening of old paper documents. First, samples of coated paper were prepared with variable coating
weights (CW) to evaluate the influence of each ChD on the strength and water barrier properties. Second, the ChDs were assessed on commercial printing paper, in comparison with methylcellulose (MC), at a constant coating weight, obtained by the application of two successive layers. Finally, the most effective coating formulas were tested on two different naturally aged papers.

**EXPERIMENTAL**

**Materials**

*Water-soluble chitosan derivatives*

Three chitosan derivatives (ChDs) were lab-synthesized as follows: N,O-carboxymethyl chitosan (CCh) by an alkalization of the chitosan, followed by etherification with monochloroacetic acid (Ciolacu et al. 2003); N-alkyl chitosan (ACh) by a reductive amination of the chitosan using aliphatic aldehydes (Bobu et al. 2011); and quaternized chitosan (QCh) by the O,N-acylation of chitosan with Quat-188 (Lupei 2012). Native chitosan samples and all chemical reagents for the synthesis of the ChDs were purchased from Sigma Aldrich Co., St. Louis, USA.

The main features of chitosan derivatives are as follows: CCh with a degree of substitution (DS) of approximately 0.92, medium molecular weight (MW ≈ 2.4 · 10^5 g/mol), and an amphoteric character that has the potential to improve paper strength and form films with a good barrier to gases and antibacterial activity; ACh with a low DS (~0.04), low MW (MW ≈ 5.5 · 10^4 g/mol), and an alkyl chain of medium length (C8) that can form hydrophobic films on paper surfaces and develop antifungal activity; QCh with a DS of approximately 0.96, high MW (MW ≈ 8.5 · 10^5 g/mol) and a cationic charge across the entire pH range, which has high potential to improve paper strength and develop antibacterial/antifungal activity. The water solubility at a neutral/slight alkaline pH and antimicrobial properties of these chitosan derivatives are documented in a recent publication (Bobu et al. 2016a).

Methylcellulose (MC), which is a conventional material used in paper conservation, was purchased from Glutolin Renovierungsprodukte GmbH, Hann. Münden, Germany (Glutofix 600). The base paper used for coating was laboratory paper, which was obtained via a Rapid-Köthen handsheet former from a mixture of softwood/hardwood kraft pulps (30/70), with 70 g/m² ± 1 g/m², without any additives; and commercial printing paper (80 g/m² ± 2.5 g/m²; 11.5% ash, Cobb60 ~50 g/m²). There were two types of naturally aged paper: A) handmade paper obtained from cotton rags from a religious book that was dated 1884, and B) industrially produced paper of groundwood and bleached sulfite pulp obtained from a math book that was dated 1870. Both of the books are without patrimonial value.

**Methods**

*Obtaining of coated paper samples*

A water solution of the ChD was applied on both paper sides using an automatic applicator with a spiral bar was designed and built at “Gheorghe Asachi” Technical University, Iasi, Romania (Bobu et al. 2016b). The ChD concentration and the number of layers determined the total coating weight (CW). After coating, the sample was first kept in an ambient medium until free water visibly disappeared and then was placed to dry on a photo dryer (Tehnometalica, Arad, Romania) for 5 min.
Series of coating experiments

Lab paper coatings were performed first by applying a single layer of each derivative, at a constant coating weight (CW) of 0.5 ± 0.01 g/m²/side, using different concentrations of the solutions. Second, coated samples were obtained by applying successive layers (1, 2, and 3) using solutions of a constant concentration (5 g ChD/L) to vary the CW. The coatings on the printing paper were performed at a constant CW of approximately 1 ± 0.02 g/m²/side by applying two successive layers. Homogenous coatings consisted of two layers of the same ChD or MC, and the combined coatings were obtained using the CCh or QCh in the first layer and ACh in the second layer.

Characterization of Paper Samples

Before testing, the paper samples were conditioned for 24 h, at 23 °C ± 1 °C and 50% ± 2% relative humidity according to the TAPPI T402-08 (2008).

Tensile strength indexes and double folds

Load-elongation curves were registered on a Zwick-Roell dynamometer (Zwick GmbH & Co., Ulm, Germany), according to ISO 1924-2 (2008). The following indexes were obtained: tensile index (TI), elongation at break (εfmax), and tensile energy absorption (TEA). Double folds were measured on a Schopper apparatus (Werkstoffprüfmaschinen GmbH, Leipzig, Germany) according to ISO 5626 (1993).

Water absorption capacity and contact angle

The water absorption capacity was evaluated via the Cobb method (TAPPI T441-98 (1998)) at a contact time of 60 s (Cobb60). The water contact angle (CA) was measured by the static sessile drop method on an automatic contact angle meter, DCE-1 Kyowa goniometer (Kyowa Interface Science Co. Ltd., Niiza Saitama, Japan), and the CA values of 4-μL droplets were collected at 10 points on each sample.

Surface characterization

Scanning electronic microscopy (SEM) was applied to obtain micrographs of the paper samples using an FEI QUANTA 200 ESEM (FEI-PHILIPS, Eindhoven, The Netherlands).

RESULTS AND DISCUSSION

Evaluation of Chitosan Derivatives (ChDs) on Lab Paper

Single-layer coatings

Paper samples with a single layer of coating were obtained at a constant coating weight of 0.5 ± 0.02 g/m²/side. Mean values (MV) and standard deviations (SD) of the strength indexes and water absorption capacity (Cobb60) are presented in Table 1.

In the case of the CCh and QCh, the TEA values of the coated paper increased by approximately 60%, compared to uncoated paper (reference), primarily because of the increased elongation at break. The improvement in the folding endurance was consistent, but the standard deviation (SD) was unacceptably high, which may have been due to the fast and uneven migration of the polymer into the porous structure of the paper.

The paper properties (high porosity, lack of sizing) and the polymer solution viscosity (at the same concentration, the ChDs’ solution viscosity order was QCh > CCh
ACh) influenced polymer migration. In the case of the coating with ACh, the water absorption capacity decreased slightly (~30%) and was not markedly modified by the CCh and QCh coatings. Other than a fast migration rate, high Cobb$_{60}$ values could have also been due to a low coating weight that did not allow the formation of a continuous polymer layer on the paper surface. For the same reasons, the contact angle could not be measured.

### Table 1. Strength Properties and Water Absorption Capacity of Coated Paper

<table>
<thead>
<tr>
<th>Paper Sample</th>
<th>TI (Nm/g)</th>
<th>$\varepsilon_{f_{\text{max}}}$ (%)</th>
<th>TEA (J/m$^2$)</th>
<th>Double Folds</th>
<th>Cobb$_{60}$ (g/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>57 ± 2</td>
<td>2.4 ± 0.1</td>
<td>63 ± 4</td>
<td>212 ± 34</td>
<td>91 ± 2</td>
</tr>
<tr>
<td>CCh</td>
<td>68 ± 2</td>
<td>3.9 ± 0.1</td>
<td>107 ± 3</td>
<td>487 ± 119</td>
<td>89 ± 2</td>
</tr>
<tr>
<td>ACh</td>
<td>64 ± 1</td>
<td>3.5 ± 0.0</td>
<td>104 ± 3</td>
<td>331 ± 53</td>
<td>63 ± 1</td>
</tr>
<tr>
<td>QCh</td>
<td>61 ± 2</td>
<td>3.9 ± 0.1</td>
<td>105 ± 5</td>
<td>454 ± 132</td>
<td>83 ± 2</td>
</tr>
</tbody>
</table>

Legend: TI – Tensile Index; $\varepsilon_{f_{\text{max}}}$ - elongation at break; TEA – Tensile Energy Absorption.

### Multi-layer coatings

Single-layer coatings showed that the polymer solution migrated partly into the internal pores of the base paper and impaired the formation of a continuous film on the paper surface. Therefore, the next series of samples was obtained with an increased coating weight via multi-layered coatings, using ChD solutions of a constant concentration (5 g/L). The CW after 1, 2, and 3 layers varied as a function of the polymer type (i.e., CCh- 0.79, 1.69, and 2.36 g/m$^2$/side; ACh- 0.71, 1.41, and 2.07 g/m$^2$/side; QCh- 0.79, 1.32, and 1.90 g/m$^2$/side).

The values of the tensile energy absorption (TEA) and double folds after each layer are presented in Figs. 1(a) and (b), respectively. These strength indexes were chosen to evaluate the effects of the ChDs because both are frequently used in assessing paper aging and the effectiveness of conservation treatments (Zervos and Moropoulou 2006).

The carboxymethyl-chitosan (CCh) and quaternary-chitosan (QCh) produced a considerable increase in both strength indexes, which was noticeable with the CW increase; while the effect of the ACh was quite limited and less influenced by the CW. The poor effect of the ACh, especially on double folds (Fig. 1b) could have been explained by its low molecular weight (MW) and low viscosity of its solution. This resulted in a high migration rate of the polymer into the porous structure of the paper. Polymer migration into the internal structure led to a slight increase of the TEA (Fig. 1a), but did not allow film formation on the paper’s surface. The CCh/QCh solutions with high viscosities presented lower migration rates and formed films on the paper’s surface, which resulted in a large increase in the double folds number. However, high standard deviation and an unexpected high number of double folds indicated uneven covering and high local variation of the coating weight. It is also clear that the third layer of the CCh or QCh had little effect on the strength properties.
Fig. 1. Evolution of the (a) tensile energy absorption (TEA) and (b) double folds number with increasing coating weight by application of successive layers of chitosan derivatives

The Cobb60 decreased only slightly when the CW increased for the CCh and QCh coatings. In the case of ACh, it was heavily reduced after the second layer (from 91 to 18 g/m²), and remained about constant after the third layer (Fig. 2a). The contact angle (CA) increased after the first layer for all ChDs and presented small changes after the second and third layers (Fig. 2b). However, only the ACh coating had a hydrophobization effect (CA > 100°).

These results suggest different mechanisms of water barrier development. The CCh/QCh created a slight barrier to water for a short contact time (CA increased) by filling the surface pores of the base paper; however, the paper surface remained sensible to water (high Cobb60 values) because of the hydrophilic nature of these derivatives. The ACh developed a barrier to water because of the hydrophobic groups (alkyl) along the chitosan chain, which is effective for both long contact (reduced Cobb60 from 91 to 18 g/m²) and short contact time (increased CA up to 112°). The ACh was less influenced by the coating weight: the CA increased slightly after the second layer and then remained constant at 112°.

Evaluation of Chitosan Derivatives (ChDs) on Commercial Printing Paper

The coatings on the commercial printing paper were performed by applying two layers of ChDs or MC, at a constant coating weight of approximately 1 g/m²/side, established based on the optimum relationship between the strength and water barrier properties in the case of lab paper (2 layers), and having in view a lower migration rate of the polymer solution in the case of printing paper, which presented a medium sizing level
(Cobb$_{60} \sim 50$ g/m$^2$). Several sets of coated paper samples were prepared: homogeneous coatings by using the same ChD (CCh/CCh, ACh/ACh, QCh/QCh) or MC (MC/MC) in both layers; combined coatings by using CCh or QCh in the first layer and ACh in the second layer (CCh/ACh and QCh/ACh).

**Strength properties**

Figure 3a shows that all of the ChDs coatings produced major improvements in the TEA values in both the machine direction (MD) and cross direction (CD). As was expected, the CCh and QCh gave the highest increases, comparable to those of MC. The folding strength (Fig. 3b) increased more than the TEA (i.e., maximum increases were approximately 2.5 times for TEA and 4 times for double folds, compared with the reference). These results are more consistent than those obtained for lab paper coatings and can be explained by a lower migration rate and more uniform distribution of polymer on the paper surface.

The SEM images in Fig. 4 demonstrate the formation of a continuous film on the paper surface, especially in the case of the CCh and QCh coatings. The low migration of the polymer solution into the internal pores meant reduced inter-fiber binding and less stiffening of the paper structure, which resulted in higher elongation at break and higher TEA, respectively. At the same time, the formation of a continuous film of polymer with a relatively high molecular weight (QCh, MC) or amphiphilic character (CCh) could support improvement in the folding endurance.

The ACh coating had no remarkable effect on the strength indexes because of its low MW and high migration rate, which in fact led to a poor covering of paper surface (Fig. 4). However, it is worth noting that replacing one layer (half CW) of the CCh or QCh with ACh led to higher strength indexes than average of the homogenous coatings, which were comparable with the homogenous coatings. These results suggested synergistic interactions between the ChDs, also reflected in lower standard deviations.

![Fig. 3](image)

**Water barrier properties**

The alkyl-chitosan (ACh) applied alone or as the second layer in combination with other derivatives produced a high sizing level of the base paper (Figs. 5 a/b): Cobb$_{60}$ decreased from 51 to 15 g/m$^2$, and the contact angle increased from 97° to 120°. The homogenous coatings based on the CCh or QCh presented higher hydrophilicity compared with the base paper: Cobb$_{60}$ increased from 51 to 80 g/m$^2$ for CCh and to 69 g/m$^2$ for QCh, and the contact angle decreased from 97° to 75° for CCh and to 83° for QCh.

Fig. 4. The SEM images (x500) of base paper and paper coated with two layers of ChDs

Fig. 5. Effects of two layers of coatings on (a) water absorption-Cobb60 and (b) contact angle at a constant coating weight of approximately 1 g/m²/side

The MC results were similar to that of the CCh and QCh, all being hydrophilic materials. Consequently, hydrophilic coatings could be less stable than hydrophobic ones (ACh) because of moisture absorption and polymer swelling. Also, both Cobb60 and CA reached the same levels, regardless if the ACh was applied as a homogenous coating (ACh/ACh) or as a combined coating (CCh/ACh or QCh/ACh). Therefore, the ACh effectiveness as a sizing agent was only slightly influenced by the support properties and offers many application alternatives in paper conservation, which can be adapted to meet the specific requirements of the paper heritage document.
Assessment of Chitosan Derivatives on Naturally Aged Paper

The tests on printing paper show that two layers of coating, using CCh or QCh in the first layer and ACh in the second, provide the best relationship between the strength and water barrier properties. Consequently, these formulas were tested on naturally aged paper, comparative with methylcellulose (MC). The procedure followed the general steps of the conservation/restoration process for paper heritage objects: dry cleaning, disinfection, wet cleaning, and consolidation/resizing treatments (Zervos and Alexopoulou 2015). All of the coatings were performed via two layers of application on each side, at a coating weight of approximately 1 g/m²/side, in which the two layers were equally weighted. The two types of naturally aged paper (A- religious book and B- math book) were characterized before and after each treatment. Table 2 presents the values of the strength indexes and water contact angle for the following samples: original paper (Reference₀), paper after wet cleaning (Reference₁), and paper after consolidation/resizing with chosen formulas.

First, it should be noted that wet cleaning with slight alkaline solution produced a reduction of TEA and increased the folding strength and surface hydrophilicity. The effects were quite evident for the cotton handmade paper (A) and could be due to the removal of gelatin, which was originally used as the sizing and strengthening agent. The loss of the sizing/strengthening agent could have reduced the TEA by decreasing the tensile strength and could improve the fold endurance by reducing stiffness (Van der Reyden 1992). The paper of book B was produced at an industrial scale, and groundwood and sulfite pulps were used without sizing; consequently, it was less affected by the washing process.

Table 2. Strength Indexes and Contact Angle of References and Coated Papers

<table>
<thead>
<tr>
<th>Coating Formula</th>
<th>Religious book (A)</th>
<th>Math book (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TEA (J/m²)</td>
<td>Double Folds Number</td>
</tr>
<tr>
<td>Reference₀</td>
<td>19 ± 6</td>
<td>14 ± 3</td>
</tr>
<tr>
<td>Reference₁</td>
<td>9 ± 3</td>
<td>22 ± 7</td>
</tr>
<tr>
<td>CCh/ACh</td>
<td>26 ± 5</td>
<td>44 ± 7</td>
</tr>
<tr>
<td>QCh/ACh</td>
<td>31 ± 6</td>
<td>46 ± 10</td>
</tr>
<tr>
<td>MC/MC</td>
<td>26 ± 9</td>
<td>32 ± 10</td>
</tr>
</tbody>
</table>

*Due to book format, the strength indexes were measured for the cross direction (CD) only.

Generally, surface treatments with ChDs or MC improved both strength indexes, but the effect intensity has a strong dependence on the paper type. Strength improvements were evident for the handmade paper (A) because the binding effect of the polymer was well coupled with the length and intrinsic strength of the cotton fibers. For instance, the QCh/ACh coating resulted in increases of 240% for TEA and 110% for double folds. In the case of paper “B,” containing groundwood pulp, the maximum increase in TEA was 90% for the QCh/ACh coating and 60% for double folds for the CCh/ACh coating. Furthermore, the MC was less effective than ChDs, especially in the case of handmade paper. This effect could be explained by the low migration rate of the MC solution because of its much higher viscosity than that of the CCh/QCh solutions. Other than strength...
improvements, the coatings with ACh as the second layer presented hydrophobic characteristics (contact angle between 115° and 120°), regardless of the base paper properties and polymer type in the first layer, which confirmed the results obtained for printing paper.

Generally, the tests on natural-aged papers have shown that conservation treatments cannot be universal and should be adapted to the paper type and its state of conservation. Moreover, the combinations of a strengthening chitosan derivative (QCh or CCh) with a hydrophobic derivative (ACh) in two layers of coatings could offer sustainable solutions to conventional conservation materials based on cellulose derivatives. Furthermore, the design of the conservation treatment could also consider the antimicrobial properties of these chitosan derivatives.

CONCLUSIONS

1. The coatings based on the CCh (carboxymethyl-chitosan) and QCh (quaternary-chitosan) resulted in strength improvements (TEA and double folds’ number) that were consistent with the increase in coating weight, which was achieved by multi-layers’ application. The ACh (alkyl-chitosan) had little effect on the strength indexes, but was the single derivative that developed a good water barrier. Both the strength and barrier properties were strongly influenced by polymer migration into the internal structure of the paper. The results show that the CCh/QCh can provide an increase in strength without paper stiffening (high increases of both elongations at break and tensile index) and the ACh can develop a very good water barrier, which is important in paper heritage conservation.

2. At constant coating weight of approximately 1 g/m²/side, achieved by two-layers application, the homogenous coatings of the CCh and QCh resulted in strength improvements, comparable to a MC/MC coating, and the combined coatings (CCh/ACh and QCh/ACh) led to higher strength indexes than average of the homogenous coatings. It was also shown that the ACh achieved the same levels of the Cobb₆₀ index and contact angle, if it was applied alone or combined with other derivatives. Therefore, an optimum relationship between the strength indexes and water barrier properties was obtained by combining a good strengthening derivative (CCh or QCh) in the first layer with a hydrophobic derivative (ACh) in the second layer.

3. The assessments performed on naturally aged paper showed a higher effectiveness of the ChDs as strengthening materials than that of MC, but the effect intensity presented a strong dependence on the old paper type. Combined coatings with ACh as the second layer presented hydrophobic character, regardless of old paper type. Generally, the tests on naturally aged papers have shown that the chitosan derivatives assessed in this study could be used as multifunctional materials in paper conservation to overcome current limits of the cellulose derivatives.

ACKNOWLEDGMENTS

The authors are grateful for the support of the Romanian Government and UEFISCDI Agency, project “Developing Non-Conventional Materials and Cold Plasma
Technique for Sustainable Solutions in Paper Heritage Conservation- PAPHERCON,” Grant No. 221/2012.

REFERENCES CITED


DOI: 10.1002/9780470060520.ch1

Article submitted: October 27, 2016; Peer review completed: November 21, 2016; Revised version received and accepted: November 22, 2016; Published: December 1, 2016.
DOI: 10.15376/biores.12.1.735-747