U.P.B. Sci. Bull., Series B, Vol. 80, Iss., 2, 2018 ISSN 1454-2331

NEW APPROACHES IN CELLULOSIC ETHERS ANALYSIS USED IN OLD PAPER RESTORATION

Nicoleta MELNICIUC PUICĂ[1], Elena ARDELEAN[2], Dana Ortansa DOROHOI[3]

This study deals about the efficiency of some consolidation agents on paper restoration treatment. As consolidation agents were used aqueous solutions of methyl cellulose MC and carboxymethyl cellulose CMC with 0.5% concentration. Samples of old handmade paper and old industrial paper were consolidated and then submitted to a thermal aging treatment and analysed by spectral means (Fourier Transform Infrared Spectroscopy) and Atomic Force Microscopy, in order to obtain information about surface and structural modifications. This kind of study is important because it contributes to the choice of adequate methodology for old paper restoration.

Keywords: aging process, FTIR, AFM, methyl cellulose, carboxymethyl cellulose

1. Introduction

The structure and composition of materials components of documents and books are affected by the environment factors such as humidity, temperature, light, oxygen, reactive vapour, etc. The damages are produced more or less quickly according to relative stability of cellulosic fibres and auxiliary materials to the actions of different external factors.

Among auxiliary materials and used additives for paper fabrication, the sizing, as well as filling materials have the biggest influence on degradation resistance.

In the manufacture of paper, the sizing agent has a definite purpose: improving resistance to wetting and penetration by liquids [1]. Throughout time, the starch, gelatine, rosin and recently, synthetic resins as alkenyl succinic anhydride (ASA) and alkyl ketene dimers (AKD) have been used as paper sizing agents.

Most old paper partially loses their sizing agents under the action of biological agents, atmospheric humidity and other microclimate conditions.

[1] Prof., Dept. of Sacred Art, Faculty of Orthodox Theology, “Alexandru Ioan Cuza” University, Iasi, Romania, mail: nicoletamelniciuc@yahoo.com
[2] Lecturer, Dept. of Sacred Art, Faculty of Orthodox Theology, “Alexandru Ioan Cuza” University, Iasi, Romania, mail: elardelean@yahoo.com
[3] Prof., Faculty of Physics, “Alexandru Ioan Cuza” University, Iasi, Romania, mail: ddorohoi@uaic.ro

In time, the paper whose sizing agent has been aging becomes absorbent and fragile; its mechanical properties are diminished and it is more exposed to physical, chemical and biological degradation factors.

Consolidation (sizing) of paper is achieved by allowing the consolidant to deposit in the fibre structure. The consolidants are frequently used in suspension or barely soluble [2]. Consolidation by the resizing represents a stage of old document and book conservation and restoration processes. Its purpose is to improve the paper physical mechanical properties by replacing the lost consolidation agent by materials compatible with original consolidation agents.

Among materials currently used for traditional treatment of resizing cellulosic supports are cellulose ethers (methyl cellulose MC and carboxymethyl cellulose CMC). These sizing agents must meet certain criteria: compatibility with the original medium, high capacity impregnation, lack of toxicity, resistance to oils and grease, aging resistance and to form solid and transparent film [3].

In conservation science, Fourier Transform Infrared Spectroscopy (FTIR) analysis is often used for the monitoring of chemical reactions, the determination of chemical changes and degradation, the ascertaining of damage from specific conditions, and the evaluation of material stability [4, 5]. This is very useful in the field of studies on degradation process of old paper constitutive of books and manuscripts. The Atomic Force Microscopy (AFM), a new technique used in the investigation of works of art, has many applications in the field of conservation and restoration science; new researches [6, 7] use AFM in the study of the cellulose substrates undergoing an ageing process.

The paper aims to highlight, by spectral means (FTIR) and AFM, the influence of consolidation treatment on stability of two types of old paper (handmade paper) obtained from textile fibres and industrial paper made from chemical pulp and sizing with rosin.

2. Materials and Methods

Cellulosic supports

Two types of paper: a paper from the mid XIX century, without patrimonial value, handmade obtained from textile fibres and sizing with gelatine (samples M) and a 1980 paper industrial made from paste chemical, sizing with rosin (samples I) were used in this study.

Agents of consolidation

As consolidation agents were used aqueous solutions of methyl cellulose MC (GmbH Germany) and carboxymethyl cellulose CMC (CPR Rome) with 0.5% concentration.

The cellulosic supports and consolidation agents’ solutions are presented in Fig. 1.

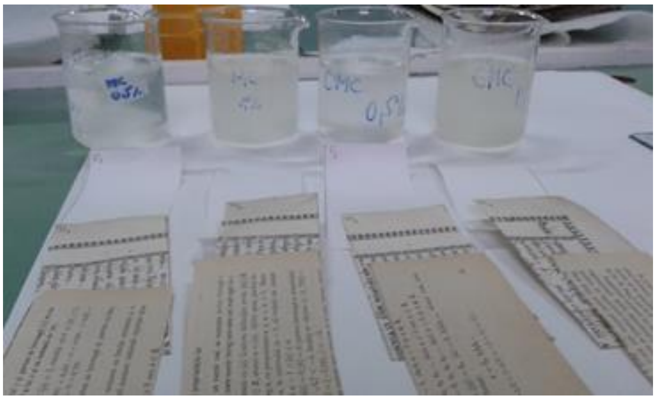


Fig. 1. The cellulosic supports and consolidation agents solutions

Methods

The sheets of paper were covered with protective films: methylcellulose and carboxymethyl cellulose. Methods have been done similarly for the two types of supports. The technique frequently used by old book restorers is also applied here: the one side brushing samples, free drying, brushing and free drying the other side of sample.

Paper samples were initially analysed, after consolidation with different agents and also after accelerated ageing heat treatment. Exposure for six days to 105^{o}C temperature was chosen as accelerated ageing treatment, which produces almost the same effect as natural ageing of 50 years [8].

Further on, the samples have been jarred and KBr-pelleted. ATR-FTIR was measured using VERTEX 70, Bruker. The spectral measurements have been processed with the Spectra Manager. Normalization of the spectra was based on an internal standard. In order to obtain information regarding the surface stability of the treated paper and then subjected to accelerated ageing paper, atomic force microscopy (AFM) was used. For this study, the analyses were performed with a SOLVER PRO M microscope; the cantilever was NSG10-Si/Au, NT-MDT; the analysis mode was the intermittent contact type; analyses were performed on (3x3) μm surfaces. 2D images and 2D profile images of paper surfaces were made, the surface roughness was measured and 3D images of the paper were made. The whiteness of the studied samples was then determined using Wsb-1 Portable Digital Leucometer, Wb = r457.

3. Results and Discussions

As known, in time, paper suffers degradation processes. Such a phenomenon, involving the degradation of cellulose, consists in the oxidation and hydrolysis of the various functional groups from natural polymer structure. In the

IR spectra of paper, characteristic bands of these functional groups may be observed [9, 10]. The most important ones appear in the following domains [11, 12]:

- 3600–3300 cm^{-1}, valence vibrations of OH groups (νOH).
- 3000–2800 cm^{-1}, valence vibrations of CH groups from $–CH_3$, $–CH_2–$ and CH (νC–H).
- 1760–1650 cm^{-1}, valence vibrations belonging to the carbonylic and carboxylic groups C=O (νC=O).
- 1500–1300 cm^{-1}, a series of IR bands, mainly corresponding to the C–O and CH bonds deformation vibrations of the $–CH_2–OH$ primary alcoholic groups.
- 1200–900 cm^{-1}, valence vibrations of the C–O, C–C bonds, of the piranosic cycles (1050 cm^{-1}), etc.
- 900–400 cm^{-1}, deformation bands of the $–CH_2–OH$ groups and piranosic cycles.

There have been extracted only four IR spectra of the industrial paper samples unaged and industrial paper thermic aged, subjected to a temperature of 105 ^{o}C, for 6 days (Fig. 2).

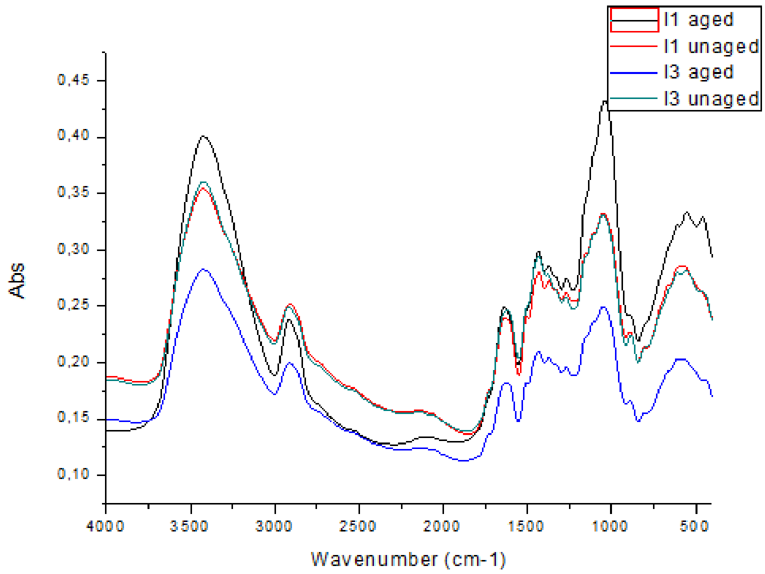


Fig. 2. IR spectra of the industrial paper samples treated with MC 0.5% (I1 aged and I1 unaged) and CMC 0.5% (I3 aged and I3 unaged)

The spectral shift of the maximum at 1650 cm^{-1} and the presence of maximum situated around 1740 cm^{-1}, caused by transformation of carboxylic groups into diketones, according to the mechanism suggested by Lojewska [13], demonstrate that the analysed samples suffer chemical transformation by heating. This observation may be proved by spectra shown in Fig. 3.

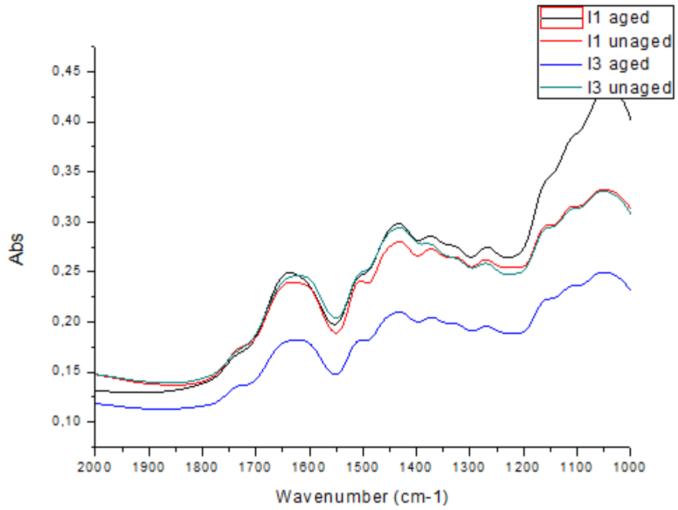


Fig. 3. Evolution of the absorption maxima as a function of aging process of the industrial paper samples treated with MC 0.5% (I1 aged and I1 unaged) and CMC 0.5% (I3 aged and I3 unaged)

A small modification can be observed to the maximum situated around 1480 cm^{-1}, corresponding to the deformation vibrations of some primary alcoholic groups (-CH_2OH), which are subjected to oxidation processes at thermal degradation. IR spectra for handmade paper treated with CMC 0.5% is shown in Figure 4.

Fig. 4. IR spectra of the handmade paper samples treated with CMC 0.5% (M3 aged and M3 unaged)

It was observed that handmade paper is less affected by oxidation process at thermal degradation, when the support is treated with CMC 0.5%.

Figs. 5 to 7 present the 2D images and 2D profiles of the paper samples' surface, studied by AFM, after thermal ageing.

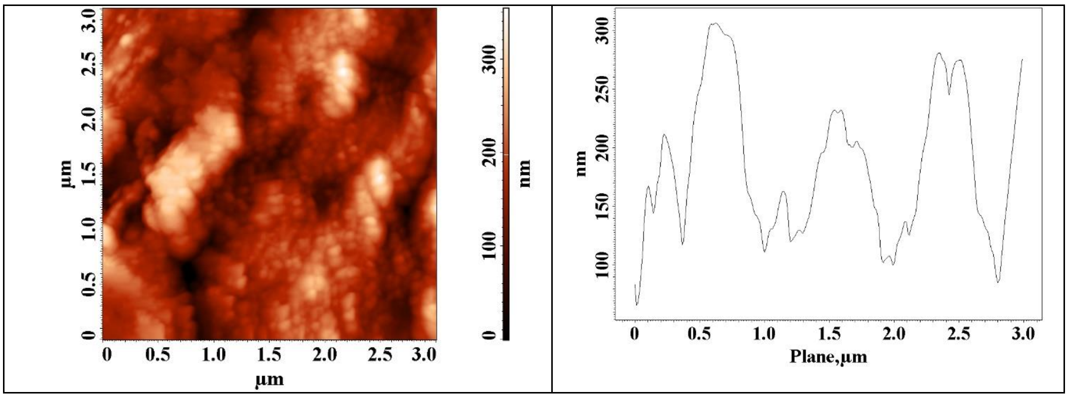


Fig. 5. 2D image of the control industrial sample surface – view of the tested area (left); 2D profile (right).

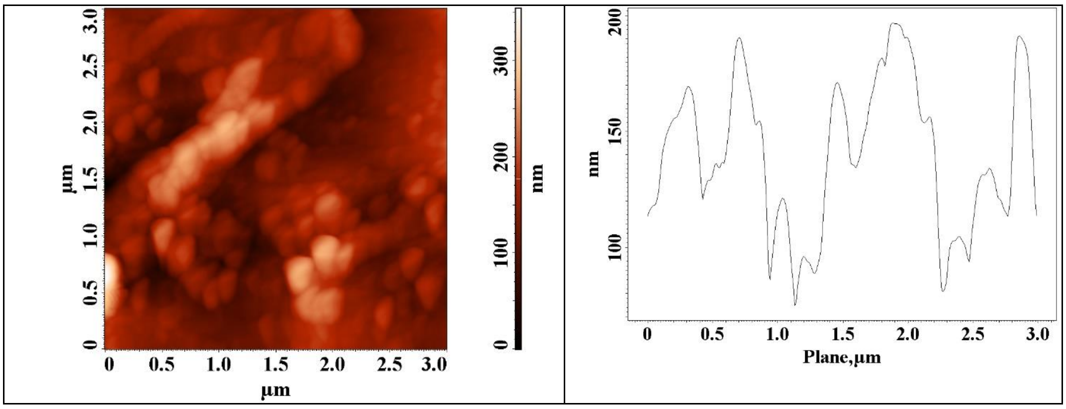


Fig. 6. 2D image of the 0.5% MC treated industrial sample surface – view of the tested area (left); 2D profile (right).

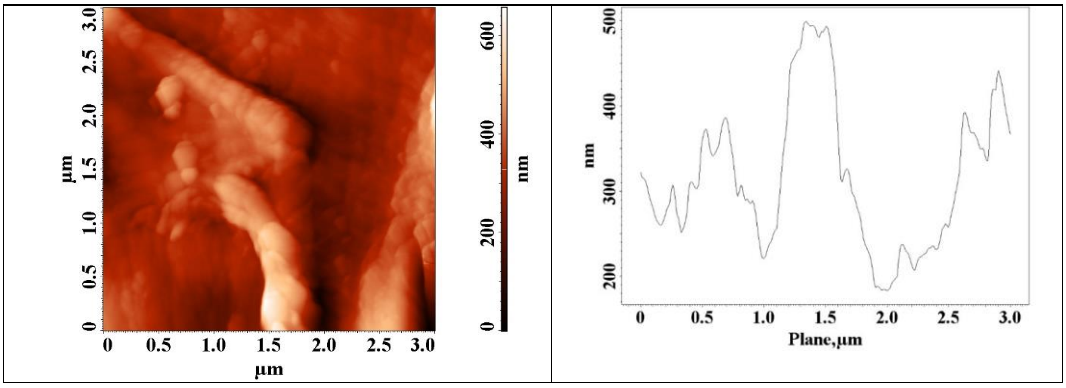
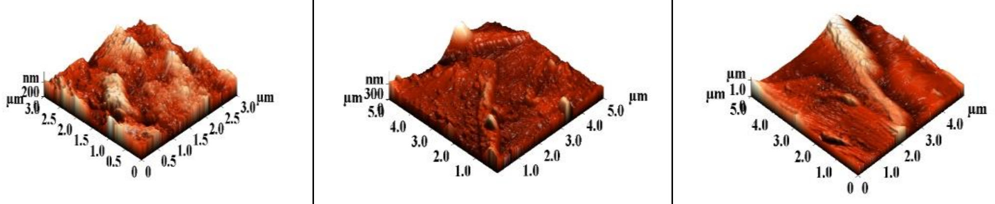


Fig. 7. 2D image of 0.5% CMC treated industrial sample surface – view of the tested area (left); 2D profile (right).

The AFM images of the paper samples treated with MC show a more uniform morphology, indicating a better preservation effect of the consolidation treatment for industrial paper. This conclusion is confirmed by 3D image of the treated and heat – aged industrial paper (Fig. 8).



a b c

Fig. 8. 3D image of the surface-treated and heat-aged industrial paper: control sample without treatment (a); paper coated with a film of 0.5% MC (b); paper coated with film of 0.5% CMC (c)

In Table 1 are presented the values of average roughness for aged old paper consolidated with MC 0.5% and CMC 0.5%.

Table 1

The values of average roughness for aged old paper consolidated with MC 0.5% and CMC 0.5%

Average roughness, nm	Not treated Paper	Paper aged and treated with MC 0.5%	Paper aged and treated with CMC 0.5%
Handmade paper	71.95	89.16	39.85
Industrial paper	39.43	31.94	65.98

The calculated roughness of the analysed samples proves that, in comparison with control sample, for industrial sample treated with methyl cellulose, calculated roughness decrease (31.94 nm) and for the handmade sample treated with carboxymethyl cellulose the calculated roughness decrease (39.85 nm).

It is noted that the carboxymethyl cellulose treatment better preserves the morphological characteristics of the original handmade paper, being less affected by thermal ageing. The surface 2D profile and its roughness prove it. The handmade paper treated with methylcellulose is affected by thermal ageing, the surface profile showing great irregularities. The 3D images are suggestive, proving that the carboxymethyl cellulose film is more resistant to thermal degradation in the case of handmade paper, but methyl cellulose film is more resistant to thermal degradation of industrial paper. The determined values of the whiteness of the studied samples are shown in Fig. 9.

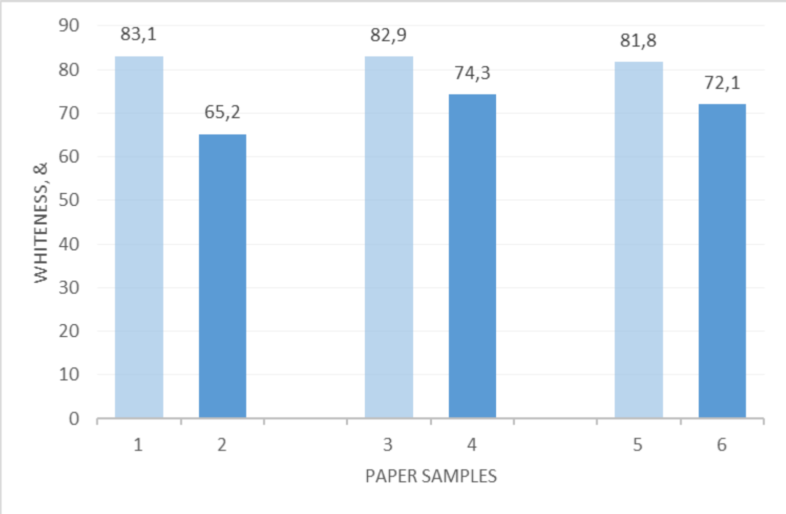


Fig. 9. The values of whiteness of studied industrial paper samples: 1- unaged control sample; 2- aged control sample; 3- unaged sample treated with 0.5% MC; 4- aged sample treated with 0.5% MC; 5-unaged sample treated with 0.5% CMC; 6 aged sample treated with 0.5% CMC.

It is observed that MC consolidation treatments lead to a decrease in whiteness with 10.3% after treatment and thermal aging, while CMC consolidation treatments produce 11.8% decrease in whiteness.

4. Conclusions

Small modifications of two maxima observed in FTIR spectra confirm the idea that the old industrial paper under analysis suffers oxidation processes, handmade paper being more durable, especially when is consolidated with CMC 0.5%.

AFM analysis proves that the carboxymethyl cellulose film is more resistant to thermal degradation in the case of handmade paper, but methyl cellulose film is more resistant to thermal degradation for industrial paper.

The AFM analysis on paper surface shows that MC film applied on industrial paper during the consolidation treatment is recommended in the case of thermal degradation, according to recent thermogravimetry analysis [3].

On the other hand, CMC film is more appropriate for handmade paper, as confirmed by our FTIR analysis. The comparison of whiteness values confirms the fact the consolidation with 0.5% MC offers a better protection to thermal aging for industrial paper than 0.5% CMC treatments.

Spectral study of old paper consolidated with methyl cellulose and carboxymethyl cellulose is important because it contributes to the choice of adequate methodology for old paper restoration.

R E F E R E N C E S

[1]. *P. Obrocea, E. Bobu*, Bazele fabricării hârtiei (The Basics of Paper Making), vol I, Ed. U.T. Gh. Asachi, Iași, 1993.

[2]. *C.V. Horie*, Materials for Conservation: Organic Consolidants, Adhesives and Coatings, Second Edition, Elsevier, Oxford, UK, 2010.

[3]. *E. Ardelean, G. Lisă, I. Rusu, N. Melniciuc Puică*, Considerations about Old Paper Consolidation with Cellulose Ethers, in vol. „ESRARC 2016. 8th European Symposium on Religious Art, Restoration & Conservation. Proceedings book" (C. Pelosi, G. Agresti, L. Lanteri, C. Parisi Eds.), Kermes Quaderni, Nardini Editore, 2016, pp. 55-57.

[4]. *M. R. Derrick, D. Stulik, J.M. Landry*, Infrared Spectroscopy in Conservation Science, The Getty Conservation Institute, Los Angeles, 1999.

[5]. *L.M. Proniewicz, C. Paluszkiewicz, A. Weselucha-Birczynska, H. Majcherczyk, A. Baranski, A. Konieczna*, FT-IR and FT-Raman Study of Hydrothermally Degradated Cellulose, Journal of Molecular Structure, **vol. 596**, 2001, pp. 163-169.

[6]. *E. Ardelean, N. Melniciuc Puică*, The Evaluation of Paper Consolidation Treatments using Atomic Force Microscopy, Conservation Restoration Bulletin „Restitutio", **vol. 7**, 2013, pp. 158-161.

[7]. *E. Ardelean, E. Bobu, Gh. Niculescu, C. Groza*, Effects of Different Consolidation Additives on Ageing behaviour of Archived Document Paper, Cellulose Chemistry and Technology, **vol. 45**, no. 1-2, 2011, pp. 97-103.

[8]. *V. Lasheva, M. Karsheva*, Investigation on the Thermal Ageing of Printing Paper, J. Univ. Chem. Technol. Metallurgy, **vol. 43**, no. 4, 2008, pp. 394-398.

[9]. *Th. Malutan, A. Pui, P.P. Obrocea*, Spectroscopia IR a celulozelor obţinute prin procedeul sulfat cu aditivi (IR Spectroscopy of Celluloses Obtained by the Sulphate Process with Additives), Revista de Celuloza si Hârtie, **vol. 51**, no. 4, 2002, pp. 17–20.

[10]. *C.M. Popescu, Z. Sakata, A. Osaka, C. Vasile*, Degradation of Lime Wood Painting Supports, e-PRESERVATIONScience, **vol. 2**, 2005, pp. 19–29.

[11]. *B. Stuart*, Infrared Spectroscopy: Fundamentals and Applications, Wiley, 2004, 184.

[12]. N. *Melniciuc Puică, A. Pui, D. Cozma, E. Ardelean*, A Statistical Study on the Thermal Degradation of some Paper Supports (Old Documents), Materials Chemistry and Physics, **vol. 113**, no. 2-3, 2009, pp. 544-550.

[13]. *J. Lojewska*, *P. Miskowiec*, *L.M. Proniewicz*, Oxidative and Hydrolytic Path Of Paper Degradation Studied By In-Situ FTIR Transmission Spectroscopy, Proceedings of the International Conference on Durability of Paper and Writing, Ljubljana, Slovenia, 2004, pp. 24–25.