Journal of Colloid and Interface Science 416 (2014) 205–211

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Gellan hydrogel as a powerful tool in paper cleaning process: A detailed study

Claudia Mazzuca [a], Laura Micheli [a,b,*], Marilena Carbone [a], Francesco Basoli [a], Eleonora Cervelli [a], Simonetta Iannuccelli [c], Silvia Sotgiu [c], Antonio Palleschi [a]

[a] Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00173 Rome, Italy
[b] Consorzio Interuniversitario Biostrutture e Biosistemi "INBB", Viale Medaglie d'Oro 305, 00136 Rome, Italy
[c] Laboratorio di Restauro, Istituto Centrale per il Restauro e la Conservazione del Patrimonio Archivistico e Librario (ICRCPAL), Via Milano 76, 00184 Rome, Italy

ARTICLE INFO

Article history:
Received 5 August 2013
Accepted 21 October 2013
Available online 8 November 2013

Keywords:
Paper conservation
Paper morphology cultural heritage
Gellan gum
FTIR
HPLC
SEM
Gel residues

ABSTRACT

Hypothesis: Wet cleaning of ancient papers is one of the most critical steps during a conservation treatment. It is used to improve the optical qualities of a graphic work and remove dust and by-products resulting from cellulose degradation. Nevertheless, washing treatment usually involves a substantial impact on the original morphological structure of paper and can sometimes be dangerous for water sensitive inks and pigments.
Experiments: The use of rigid hydrogel of Gellan gum as an alternative paper cleaning treatment is developed. The application of a rigid hydrogel minimizes damages caused by the use of water, and therefore is much more respectful for the original integrity of ancient paper.
Findings: Gellan hydrogel has been used to clean paper samples belonging to different centuries (from XVI to XIX) and therefore, characterized by a different story in terms of degradation condition and paper composition. Several techniques, such as high-performance liquid chromatography, Fourier transform infrared spectroscopy, scanning electron microscopy and pH measurements, has been employed to assess the effectiveness and safety of the proposed cleaning method.

1. Introduction

Cleaning is one of the most delicate and important steps in paper conservation. It allows the removal of pollution, deposited on paper surfaces and the partial dissolution of organic substances as a result of cellulose degradation [1]. Washing by immersion – in principle – represents the ideal technique because water can uniformly reach paper artifacts [2]. Nevertheless, such a common cleaning treatment presents several disadvantages: (1) water has to be frequently replaced during the treatment; (2) the prolonged contact with water induces swelling of cellulosic fibers, which, in turn, can cause deformation of paper material after drying. This phenomenon complicates the reconstruction of artworks fragments; (3) water induces a good removal of sizing agents like gelatin [3]; (4) modern paper cannot be cleaned by using this method because of its fragility and sensitivity to water.

In the last years, to confront these issues, innovative cleaning methodologies based on the application of suitable hydrogel have been proposed in the cultural heritage field. Due to their high retention power and their viscosity, the penetration of these liquids into the paper sheets can be significantly reduced, therefore minimizing paper fibers swelling [4–7]. However, a complete removal of these gels often requires an abrasive mechanical action (i.e., removal with a brush or by wet cotton swabs), which is often unsafe for the artwork. At the same time, gel residues can induce dangerous microbial growth [8,9]. To overcome this drawbacks, highly rigid and film forming hydrogels may represent a useful alternative [3,5,7,10], as they can be completely and easily removed in one operation after their application, thus minimizing the side effects already presented. In this contest, a new wet cleaning technique based on the use of a rigid hydrogel of Gellan gum has been recently developed [3,6,11]. Gellan gum is a gelling agent widely used in food, biomedicine and pharmaceutical industry. It is a linear anionic heteropolysaccharide produced by *Pseudomonas elodea* and consists of (1,3)-β-D-Glucose, (1,4)-β-D-Glucuronic acid, (1,4)-β-D-Glucose, (1,4)-α-L-Rhamnose, repeating units [12]. In the native polymer two acyl substituents, L-glyceryl at O(2) and acetyl at O(6) are present at the 3-linked glucose and, on average, there is one glyceryl per repeating unit and one acetyl every two repeating units [13]. Deacylated Gellan gum is obtained by alkali treatment of the native polysaccharide. Both native and deacetylated

* Corresponding author at: Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00173 Rome, Italy. Tel.: +39 0672594420; fax: +39 0672594328.
E-mail address: laura.micheli@uniroma2.it (L. Micheli).

0021-9797/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2013.10.062

polymers form hydrogels [12–18] whose sol–gel transition process is temperature dependent [16,17]; in particular, the deacylated polysaccharide, in presence of calcium salts, forms hard and rigid hydrogel with a slow syneresis rate; moreover, it is homogenous, transparent, and stable to pH variations [14,18]. The pH stability assures that the hydrogel can be safety applied to every paper samples whatever its pH value. Due to these properties, Gellan hydrogel has been selected to perform safer wet cleaning treatments on paper artworks. The present paper will then discuss and compare the results obtained by applying the Gellan hydrogel cleaning method and the traditional cleaning technique (i.e. immersion in a deionized water bath) on different paper samples. Tests for fibers identification and analysis to assess the degradation levels of paper samples have been preliminary carried out using high-performance liquid chromatography (HPLC), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and colorimetric analysis.

2. Materials and methods

2.1. Reagents and materials

The analysis was performed on samples of original papers (50 × 60 mm) without ink color (called blank samples) taken from the following printed books dating respectively to the 16th, 17th, 18th, and 19th centuries:

Virgilius Viridarium Illustrium Poetarum, Venetiis MDVII, Discorso sopra l'iscrittione della Colonna Rostrata in Roma MDCXXXV, Theatrum Veritatis et Justitiae, Venetiis MDCCXXXIV, Ettore Fieramosca o la Disfida di Barletta, Losanna, 1862.

Zinc chloride, aluminum chloride, potassium iodide, calcium acetate, calcium chloride and standard organic acids were obtained from Sigma (Sigma–Aldrich, Mo, St. Louis, USA). Iodine was obtained from Carlo Erba Reagenti (Carlo Erba Reagenti srl, Milano, Italy). Gellan gum was sold under the commercial name KELCOGEL® CG-LA Gellan gum product by CP Kelco (Atlanta Georgia, USA). Whatman paper was purchase by GE Healthcare (Italy). All reagents used were of analytical grade and used without further purification. In all cases, in the preparation of water solutions bidistilled water was used (Millipore, Billerica, MA, USA).

2.2. Methods

2.2.1. Gel preparation

The protocols reported by Iannucelli et al. were followed for hydrogel preparation [13,11]. The weight percentage of the polysaccharide and calcium ion in the hydrogels was selected according to literature [12,17,18] and to the results of several tests like the *contact* angle test, [3] performed in our laboratories on all samples to be treated. To prepare the hydrogel an aqueous solution of Gellan (20 g L^{-1}) and calcium acetate (0.40 g L^{-1} = 2.5 mM) was put for almost a minute in the microwave at 600 W (Mars Microwave, CEM Corporation, Matthews, NC, USA) until it boils and become transparent; then it was left to cool at room temperature on a Petri dish.

2.2.2. Gel application procedure

The samples were divided into four groups each one belonging to a specific century, and subsequently split into two sub-homogeneous samples to be treated respectively by immersion in deionized water and by contact with Gellan gum. In the first case, each sample was placed in a Petri dish containing 40 mL of free deionized water at room temperature. In the second case, 40 mL of Gellan hydrogel was applied to the *recto* of each paper samples and covered with a PET film (Mylar®), uniformly pressed to ensure a contact between the gel and the sample. After treatment, the gel was removed very easily with the use of a spatula. The interval time of both cleaning techniques was one hour.

2.3. Paper samples characterization

2.3.1. Paper composition

Paper fibers composition was estimated by exposing them to graff "C" stain [19]. Briefly, graff "C" was prepared by mixing in 52 mL of a $ZnCl_2$ saturated solution, 0.06 mol of $AlCl_3$ and 0.06 mol of $CaCl_2$, 0.64 mmol of I_2 and 1.4 mmol of KI. To analyze paper materials, a drop of graff "C" stain was applied to a very small portion of each sample, previously chopped with the help of a droplet of water. The sample was then placed on a microscope slide and observed on a Zeiss microscope (mod. Axio Scope. A1, Carl Zeiss AG. Oberkochen, GmbH). The presence of proteinaceous sizing agents was investigated by the Bicinconic acid test (BCA test) [21] on fragments of paper samples and following the procedure reported on the Pierce assay kit.

The presence of carbonates as alkaline reserve or due to the original paper manufacture procedure was investigated by the carbonates test. Few droplets of hydrochloric acid and barium hydroxide were added at the same time, on paper samples fragments. The opalescence due to the formation of barium carbonate indicates the presence of this carbonates salt in the samples [22].

2.3.2. Spectroscopic analysis

FTIR spectra were acquired on a Thermo-Nicolet (mod. Nexus 670) instrument (Thermo Scientific Inc., Madison WI), equipped with an attenuated total reflectance (ATR) ZnSe cell for measurement in the 4000–700 cm^{-1} region, at a resolution of 4 cm^{-1}. Spectra were performed by placing the paper samples directly on the ATR cell. A total of 256 scans were collected for each sample.

To determine the presence of degradation products in the paper samples, a deconvolution of FTIR bands region was done following the algorithm described by Calvini and Gorassini [23]. Briefly, fitting was performed in 1400–1900 cm^{-1} region on normalized absorbance spectra by means of a sum of Lorentzian functions using routines written in-house. The constraints imposed on the fitting algorithm were: the number of fitting bands, the range of allowed full width in half maximum (FWHH) and the range of frequency in which the minima are searched, according to the features of expected products of cellulose and lignin oxidation bands described in literature [23–25].

Scanning Electron Microscopy was performed using a FE-SEM, Field Emission Scanning Electron Microscope (SUPRA™ 35, Carl Zeiss SMT, Oberkochen, Germany). Punched samples were previously metalized to allow electronic conduction on the sample surface in order to obtain high quality images without deteriorating the samples or creating any kind of artifacts. The metallization, 1 min at 25 mA, was performed using a sputter coater (EMITECH K550X, Quorum Technologies Ltd., West Sussex, United Kingdom) with a gold target. The detector used was the SE (Second Electron detector) as the interest was mainly focused on the morphology of the paper fibers and on the presence of residues deriving from the cleaning agents; the main operating parameters of the instrument were 10 kV as gun Voltage and a working distance of about 8 mm.

2.3.3. Chromatographic analysis and pH measurements

The HPLC system consisted of a modular CHROMQUEST spectra system from THERMOQUEST (San Joes, CA, USA), equipped with two LC-10AT Vp pumps, Schimadzu UV–VIS spectrometer model (SPD-10AV) detector. A SCL-10A Vp controller operated the HPLC system working under control of software included in the CHROMQUEST module. The chromatographic separation was performed