



Original article

Methacrylated gellan gum microgels: A further step in the gel-based cleaning system



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ABSTRACT

Paper has been entrusted with a large portion of humanity's recorded knowledge in recent centuries, therefore its preservation is fundamental for maintaining cultural heritage. Indeed, cellulose—the primary material of these artifacts— goes through irreversible degradation processes as it ages, leading to a weakening of paper stability and color changes. In order to slow down ageing, several restoration strategies involving the use of wet cleaning by hydrogels can be found in literature. Multi-step treatments are often required to complete the cleaning procedure, as the properties of contaminants greatly vary from a chemical–physical point of view (i.e. hydrophilic, hydrophobic or, as for adhesives, polymeric compounds). In this article, we propose a cleaning strategy that accounts for the inherent roughness of paper by developing microgel particles made of methacrylated gellan gum. Microgel particles are smaller than their macroscopic counterparts, hydrogels, and as a result, they can clean paper more quickly, a few minutes as opposed to hours. Moreover, the chemical modification performed on deacylated gellan gum makes the polymer more hydrophobic, as compared to the unmodified one. In this way, the proposed microgels are able to interact with and adsorb not only hydrophilic by-products of cellulose degradation, as gellan gum-based microgels do, but also hydrophobic materials or synthetic adhesives. This procedure represents a valid strategy, safe for operators, for the cleaning of paper artworks as it avoids the use of potentially dangerous organic solvents for hydrophobic material removal.

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1. Introduction

Successful conservation of paper artifacts is of primary importance for human civilization, since most of human knowledge and history is handed down on paper [1]. Preservation is necessary because paper inevitably tends to degrade over time, becoming yellow and very fragile [2–4]. Degradation of paper is the result, from a chemical point of view, of a symbiotic action of acid hy-

drolysis and oxidation on cellulose, which is the main component of paper [5–7]. Oxidation of cellulose is a complex process leading, among other products, to the formation of carboxylic groups that, in turn, catalyze acid hydrolysis by shortening cellulose chains and the production of low molecular weight organic acid compounds [8]. To complicate the scenario, it has to be taken into account that, since the last two centuries, paper is no longer made from rags, but from mechanically or chemically treated wood pulp, and therefore it may also contain hemicelluloses, and lignin [8,9]. Consequently, paper obtained in this way is more susceptible to degradation [3,10]. One restoration step to slow down degradation is water-based wet cleaning [11–13]. For this purpose, cleaning hydrogels have been introduced in recent decades [14–17]. Their use has several advantages: they are relatively inexpensive, easily prepared (or purchased) and applicable, and importantly, they allow to reduce and check the amount of water absorbed

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by the artworks, so as to minimize the impact of this wet cleaning procedure. These cleaning hydrogels can vary in composition (polysaccharides or synthetic polymers) and rheological properties. Regardless of their different features, however, the process of cleaning with hydrogels takes between half an hour and two hours of treatment. Moreover, despite the progress made by these systems, several drawbacks have yet to be addressed in wet paper restoration. Indeed, due to past restorations or poor conservation procedures, artworks may often contain hydrophobic components such as oil, wax or adhesive residues. In detail, oil and/or wax stains can be accidentally transferred to paper sheet through handling, a spill, or close contact with an oily media. The removal of these substances thus requires *ad hoc* restoration work, as they cannot be taken away by simple water-based treatment [18–21]. In this context, it is of fundamental importance to develop compatible restoration procedures, avoiding the use of organic solvents that are toxic for operators.

To this aim, gellan gum chemically modified with methacrylic moieties, with low derivatization degree, has been prepared to obtain methacrylated gellan gum (hereafter called GGMA) [22]. After gelation, this polymer is able to interact and adsorb water-soluble hydrophilic byproducts of cellulose degradation, as unmodified gellan gum-based gels, but also hydrophobic greasy materials or synthetic adhesives, thanks to the presence of methacrylate groups, in a single step application. It is important to underline that, to the best of our knowledge, the authors use this polymer for the first time in the Cultural Heritage field to prepare a physical gel, without resorting to photopolymerization, which is instead widely used in the biomedical field and in 3-D printing [23–26]. The microscopic gelation mechanism of gellan gels, at the conditions used for paper cleaning purposes, has been further investigated theoretically through the use of atomistic molecular dynamics simulations [27]. Furthermore, the use of micro-sized particles, such as gellan microgels recently introduced by some of the authors [28], makes it possible to reduce the wet cleaning process duration to a few minutes. The basic idea behind the use of micro-objects is that paper surface is not flat, but very irregular and rich in micrometric size pores [29]. Colloidal particles are able to adapt easily on this rough surface, thus penetrating inside pores and performing their cleaning action in a much shorter time and with higher efficiency than their macroscopic counterpart, hydrogels [28]. By definition, microgels are units made up of reticulated solvated polymers with diameters ranging from hundreds nanometers to few micrometers [30]. Due to their peculiar viscoelastic properties, microgels are widely used in food, pharmaceutical, biotechnological fields [30]. In the last decade, for example, polysaccharide-based microgels were developed for drug delivery [31]. In this article, the characterization of GGMA microgels and their use as cleaning agent is presented. In detail, the use of these microgels for the simultaneous cleaning of both hydrophilic and hydrophobic components present on paper surface, within just a few minutes, has been described.

The suitability and efficacy of GGMA microgels for paper cleaning were evaluated on contemporary and historical paper samples with different degrees of deterioration and composition. The results were extremely encouraging, as evidenced by spectroscopic, chromatographic, colorimetric, and pH measurements performed both before and after treatment.

Data were also compared with those obtained using microgels made up of unmodified gellan gel (GG), whose paper compatibility and cleaning efficacy as regards hydrophilic compound removal was already tested [28].

1.1. Research aim

Paper materials have an intrinsic roughness and therefore hydrogels applied on them, used for wet cleaning, may not clean ef-

ficiently due to the lack of contact between them. Moreover, paper artworks may often contain components like natural glues, synthetic adhesive or greasy stains that require specific additional wet cleaning. To overcome these drawbacks, tunable modified microgel particles have been developed as cleaning agent. Thanks to their reduced sizes, they are able to penetrate inside paper's pores and carry out a cleaning action in shorter time (few minutes). These microgels were made up by gellan gum chemically modified via methacrylation that render them able to remove in one step, both hydrophilic and hydrophobic components from historical and modern paper samples.

2. Materials and methods

2.1. Materials

Deacylated gellan gum powder Kelcogel was purchased from CP Kelco (San Diego, California). Glycidyl methacrylate, sodium chloride, sodium hydroxide, methanol, sodium phosphate, and Whatman™ n°1 filter paper samples were acquired from Merck (Merck KGaA, Darmstadt, Germany), while linseed oil was purchased from Erboristeria Magentina (Turin, Italy). The 1200014000 Da cut dialysis tubes were purchased from Olinto Martelli srl (Florence, Italy). With the exception of gellan gum, all reagents used were analytical grade and used without further purification. To prepare all the solutions, bi-distilled water (Millipore, Billerica, MA, USA) was used. Historical paper was from “Breviarium Romanum ad usum fratrum” belonging to the 18th century, while modern paper samples are from 1990s notebook paper; both come from a private collection. To soil Breviarium samples with linseed oil, few drops of linseed oil were put by drop casting on Breviarium specimens. Samples were first left to dry at room temperature, and then artificially aged for 21 days at 80 °C [32].

2.2. Methods

2.2.1. Microgels preparation and characterization

2.2.1.1. Microgels preparation. Methacrylated gellan gum (GGMA) was derivatized following the protocol already described [22] and GGMA microgels were prepared through the use of a rheometer detailed in [33]. In detail, a desired amount of GGMA powder was dissolved in ultrapure water at room temperature under stirring in order to obtain different final weight concentrations ($C_w = 0.1, 0.2, 0.3,$ and 0.5%). Then, about 20 mL of the GGMA solution were poured into a home-made bottomless silicone beaker, allowing the sample to be directly deposited onto the MCR102 rheometer plate (Anton Paar GmbH, Santner Foundation, Graz, Austria) and heated up to $T = 80\text{ °C}$ and left in this condition for 10 min. A controlled amount of 1 M NaCl solution was added to the GGMA solution to obtain the desired salt final weight concentration ($C_{\text{NaCl}} = 100\text{ mM}$) necessary to promote the gelation process. Sodium ions (Na^+) are employed in microgel preparation, because they lead to a weak association between polysaccharide helices. Thus, the use of cations favors the control of the needed rheological properties. The GGMA sample was cooled from $T = 80\text{ °C}$ to $T = 25\text{ °C}$ at a cooling rate of 0.5 °C/min keeping the shear rate constant (500 s^{-1}) by means of the rheometer equipped with a Peltier temperature controlling unit. The application of a constant shear during gelation process modifies elastic properties of the polysaccharide solution as a result of microstructure modification leading to the formation of microgels.

Simultaneously, the viscosity of the suspension upon cooling was measured for various GGMA concentrations at 100 mM of NaCl. In detail we measure the normalized viscosity, defined as: $\eta(T)/\eta(80\text{ °C})$ where η_T is the viscosity at a given temperature T (in this case, $T = 25\text{ °C}$) and $\eta_{80\text{ °C}}$ is its plateau value at $T = 80\text{ °C}$.

The rheometer tool, a cone of 50 mm diameter, was used in cone-plate geometry to apply a rotational shear while measuring the viscosity during both the heating and cooling phases. The measuring gap was 3.5 cm.

2.2.1.2. Rheology experiments. Rheological measurements were carried out using the rotational rheometer Anton Paar MCR102 with a cone plate geometry (plate diameter = 49.97 mm, cone angle = 2.006, truncation 212 μm). Temperature was controlled using a Peltier system equipped with an evaporation blocker and an isolation hood to prevent evaporation. Amplitude and frequency sweep measurements were performed on GGMA microgels at different weight concentrations to determine the storage, G' , and loss, G'' , moduli. Amplitude and frequency sweep tests were carried out in the shear strain range (0.01–100) % and frequency range $f = (0.01–100)$ Hz respectively. They provide the moduli $G'(\gamma)$ and $G''(\gamma)$ obtained as a function of strain γ , and $G'(f)$ and $G''(f)$ as a function of frequency f , respectively.

2.2.1.3. Dynamic light scattering (DLS) experiments. The particle hydrodynamic radius has been measured by means of Dynamic Light Scattering as a function of temperature using the Stokes-Einstein relation. A solid-state laser (100 mW) with monochromatic wavelength $\lambda = 642$ nm and polarized beam has been used as optical setup to probe samples in dilute regime. Measurements have been performed in dilute conditions ($C_w = 0.01$ % to be in the single particle regime) at a scattering angle $\theta = 90^\circ$, corresponding to a scattering vector $Q = (4\pi n/\lambda)\sin(\theta/2)$ equal to 0.018 nm⁻¹. The translational diffusion coefficient related to the relaxation time τ has been obtained through the relation: $\tau = 1/(Q^2 D_t)$. The relaxation time (τ) was obtained by fitting the autocorrelation function of scattered intensity through the Kohlrausch-William-Watts expression, $g_2(Q, t) = 1 + b [\exp(-(t/\tau)^\beta)]^2$, where β is the stretching exponent, and b is the coherence factor. The average size was obtained using a Contin algorithm included in the software of the instrument [28,34].

2.2.1.4. Atomic force microscopy (AFM) analyses. The Dimension Icon (Bruker AXS) platform has been used for AFM imaging in Tapping mode, in air and under ambient conditions. RTESP probe with a rotated etched silicon tip (Bruker, Germany) with a nominal radius of curvature $R \leq 8$ nm was used. GGMA microgels at 0.1 % have been diluted up to 0.01 % with MilliQ water and have been deposited on freshly cleaved mica, incubated 1 min and then rinsed with Milli-Q water. Gwiddion 2.56 free software was used for image treatment by background subtraction and levelling.

2.2.2. Paper samples characterization before and after cleaning

2.2.2.1. Microgels application on paper samples. To perform the cleaning process, as schematically described in Figure S1, an adequate volume of microgels was taken from the stock and uniformly spread with the help of a soft flat tip synthetic brush (da Vinci, Künstlerpinselwerk DEFET GmbH) on the selected area. After 2–3 min cleaning occurred and microgels have been removed carefully and extensively with another humid flat tip synthetic brush [28].

2.2.2.2. Hydrogels preparation and application on paper samples. GGMA hydrogel was prepared as reported previously [22]. To perform the cleaning process, a piece of hydrogel, with desired size, was taken from the stock. During the procedure, the paper sample was fully covered with the gel of about 1 cm thickness. A uniformly pressed PET film was applied over it to minimize the evaporation of water and to ensure a close contact between the gel and the sample. After 60 min cleaning was considered finished, and the gel was manually removed in one step.

2.2.2.3. ATR-FTIR analyses. FTIR spectra on samples in Attenuated Total Reflectance (ATR) mode were performed using a Thermo Scientific instrument (model iS50) (Thermo Scientific Inc., Madison WI) equipped with a single reflection diamond ATR cell. Spectra were recorded in the wavenumbers region from 4000 to 600 cm⁻¹, averaging over 32 scans with a resolution of 2 cm⁻¹. All experiments were performed in triplicate in the same points (RSD < 1 %) and in different spots throughout the area of interest, obtaining consistent and repeatable results. The different spots, close together are the same before and after treatment of the paper sample and results are statistically processed, yielding consistent and reproducible results. Spectra are baselined where no absorbance peaks are present (1950 cm⁻¹). The baseline-corrected spectra were normalized to the highest band so that the absorbance of the highest peak is equal to 1.0.

2.2.2.4. HPLC analyses. HPLC experiments were performed using an Agilent 1100 series Autosampler (G1329A), equipped with four pumps (G1311A) and a 1100 Series Diode-array Detector (Agilent Technologies, CA, USA), with column C18 reverse phase (5 μm 250×4.6 mm Pinnacle II, Restek, USA). Analyses were performed on extracts obtained by treating 1 cm² of paper samples with 1 mL of H₂O for organic acids (degradation products of cellulose) [35] or methanol for hydrophobic compounds removal (which are oil residues) [19], stirring on the rotating wheel (Dyna AS, Sweden) overnight at room temperature. Before the analysis, the paper piece was removed, and the final solution was filtered using 0.45 μm PTFE filter. For the determination of hydrophilic compounds (extracted in water, as explained earlier), the chromatographic analysis has been carried out using an isocratic protocol (25 mM phosphate buffer pH 2.4 plus methanol in ratio 90:10 (v/v), flow rate 0.8 mL/min, injection volume 50 μL, wavelength 230 nm (reference wavelength 700 nm), run time 20 min), following, with slight modifications, an established procedure [36]. In the case of hydrophobic compounds determination (extracted in methanol), the chromatographic investigations have been performed using a binary protocol as reported elsewhere [19,37]. All experiments were performed in triplicate and statistically processed, yielding consistent and repeatable results.

2.2.2.5. Surface pH and colorimetry analyses. pH measurements were performed on paper samples surface, before and after every cleaning treatment, using a Crison Instrument (mod. Basic-20, Crison Instrument s.a., Alella, Barcelona, Spain) and a flat-tipped symmetry glass electrode (Hanna Instrument., Woonsocket, RI, USA). Colorimetry measurements to evaluate the variation of optical quality of paper samples due to cleaning were performed using an Eoptis Digital Handheld Colorimeter (mod. CLM-194, Eoptics srl, Trento, Italy). The coordinates in the CIELAB color space (L^* = brightness, a^* = red/green colour component, b^* = blue/yellow colour component) were obtained using a D65 illuminant and a 10° observer. For each sample, at least three measurements were carried out.

3. Results and discussions

3.1. GGMA microgels characterization

As reported in the Methods section (Section 3.2.2.1), the preparation of microgels was achieved using a rheometer. Simultaneously, the viscosity of the suspension upon cooling was measured for various GGMA concentrations at 100 mM of NaCl as reported in Table 1. An abrupt increase of viscosity was observed in correspondence of the gelation point at a temperature T_{gel} , which is found to slightly depend on GGMA concentration, as reported in Table 1. In Fig. 1 the comparison between the normalized viscosity

Table 1

Concentrations, C_w , gelation temperatures (T_{gel}), normalized viscosities ($[\eta(25\text{ °C})/\eta(80\text{ °C})]$), and viscosities at $T = 80\text{ °C}$ ($\eta(80\text{ °C})$), for different GGMA microgels with 100 mM NaCl.

C_w (%)	0.10	0.20	0.30	0.50
T_{gel} (°C)	40.7	41.3	42.3	42.4
$\eta(25\text{ °C})/\eta(80\text{ °C})$	2.4	9.6	13.6	19.7
$\eta(80\text{ °C})$ (mPa·s)	1.5	1.5	1.9	2.8

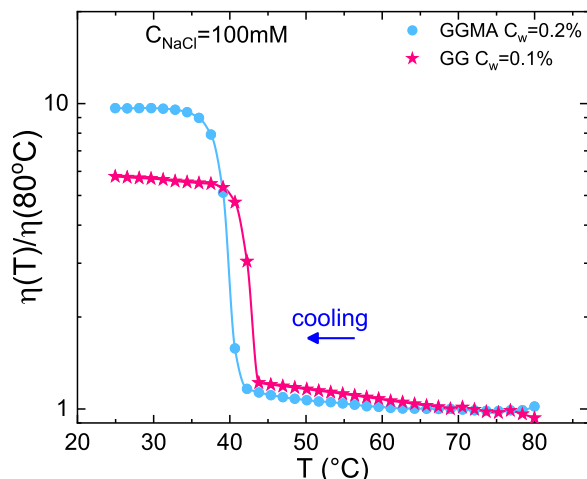


Fig. 1. Normalized viscosity as a function of temperature for GG microgel at $C_w = 0.1\%$ and GGMA microgel at $C_w = 0.2\%$ with 100 mM of NaCl salt, during cooling under a constant shear rate to form microgel particles.

$(\eta(25\text{ °C})/\eta(80\text{ °C}))$ of a gellan gum (GG) microgel at $C_w = 0.1\%$ and a GGMA microgel at $C_w = 0.2\%$ with 100 mM NaCl is reported. The rheological characterization of GGMA microgels at different concentrations with 100 mM NaCl showed that the GGMA microgel at $C_w = 0.2\%$ was the most similar to GG at $C_w = 0.1\%$ (see Table 1). The effectiveness of the latter system as cleaning agent for artworks has been already assessed [28]; this states in turn, that GGMA microgel at $C_w = 0.2\%$ with 100 mM NaCl is a good candidate from a rheological point of view, as potential cleaning materials for paper sample too.

In Fig. 2. A the storage and loss moduli versus shear strain are reported at $f = 1\text{ Hz}$ and $T = 25\text{ °C}$ for GGMA microgels at $C_w = 0.2\%$ and GG microgels at $C_w = 0.1\%$ with 100 mM NaCl. We find that in both cases $G'(\gamma)$ is greater than $G''(\gamma)$ and the two moduli remain constant up to relatively high deformation val-

ues, indicating that the system is an elastic solid at the studied conditions. Indeed, in the linear viscoelastic region (strain range 0.01 %–7 %), $\tan \delta = G''/G' = 0.2 < 1$, signature of a material with tendency to store energy rather than dissipating it, moreover the low value of the zero strain elastic modulus suggests that the system is very soft. Furthermore, as shown in Fig. 2b, frequency sweep measurements performed at constant deformation ($\gamma = 1\%$) indicate that $G'(f)$ and $G''(f)$ are almost parallel and constant at low frequencies, again with $G'(f)$ larger than $G''(f)$ for about three decades in frequency, thus confirming the formation of a gel [38,39]. Additional characterization of the studied system will be reported in a dedicated study, also discussing the different role of added salt ions and GG concentration, as well as a dynamic light scattering characterization. The average radii assessed by DLS data are found to be for the GGMA microgels at $C_w = 0.2\%$ and 100 mM NaCl $324 \pm 50\text{ nm}$, while for GG microgels at $C_w = 0.1\%$ and 100 mM NaCl we find a slightly larger value of $415 \pm 97\text{ nm}$ (the corresponding autocorrelation functions and average size as obtained through Contin Analysis are reported in Fig. S2). The polydispersity index is relatively high, thus indicating that the system is constituted by colloidal particles of different radii, all in the colloidal range. These findings agree with our previous work in which microgels of unmodified gellan gum were found to have similar size and polydispersity [27].

AFM experiments performed in tapping mode on GGMA microgels dried on mica confirm both the heterogeneity of the suspension and their micrometric size (Fig. 3. A). Due to their soft and hydrophilic nature, which favors the interaction with mica, all GGMA microgels become completely flat on the mica support and reach a vertical size of a few nanometers, as it can be inferred also by the false color scale of panel A. At higher magnification, the polymeric nature of these gel particles becomes more evident. Microgels appear as irregular structures with several protrusions and a globular internal structure, well visible in Fig. 3. B-C. The height profile shown in the inset of panel B evidences the homogeneous nature of microgel inner structure and the homogeneity of the nanometric height on the whole particle extension.

3.2. Application on paper samples

3.2.1. Compatibility evaluation of GGMA microgels with paper

First of all, the removability of GGMA microgel residues from paper, as well as pH values and optical properties after paper cleaning, were tested on a reference sample of Whatman paper. This latter reference material has been used because it is made up of new pure cellulose, without any fillers, gluing agents or

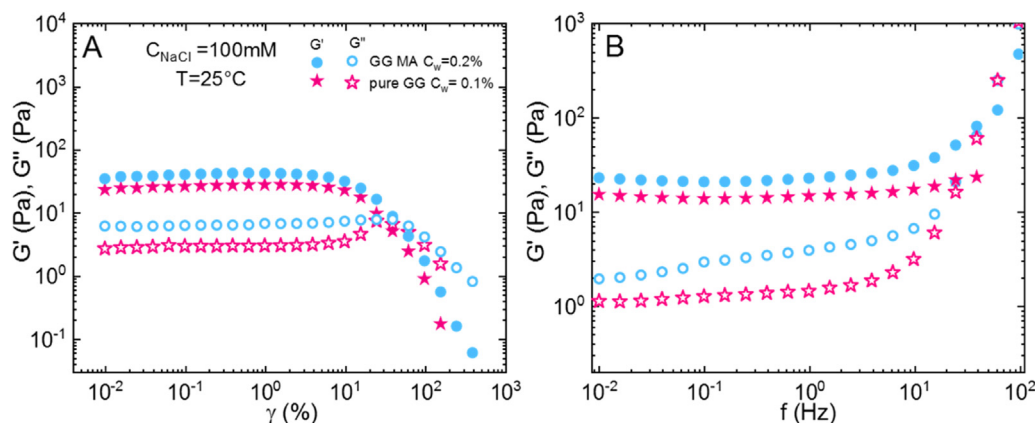


Fig. 2. (A) Storage G' (filled symbols) and loss G'' (empty symbols) moduli as a function of strain at $f = 1\text{ Hz}$ and (B) as a function of frequency at $\gamma = 1\%$ for $C_w = 0.1\%$ of GG microgels (red) and $C_w = 0.2\%$ of GGMA microgel (blue) solution at $T = 25\text{ °C}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

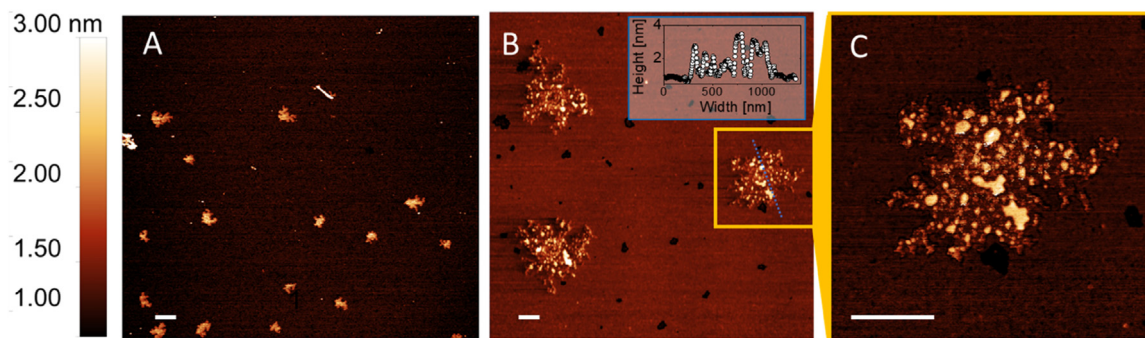


Fig. 3. AFM images (height channel) of GGMA microgels deposited on mica (panel A), where the height profile is traced on the dashed section of a single microgel (inset of panel B) and the magnification of a single microgels is reported in panel C. Bars are 500 nm.

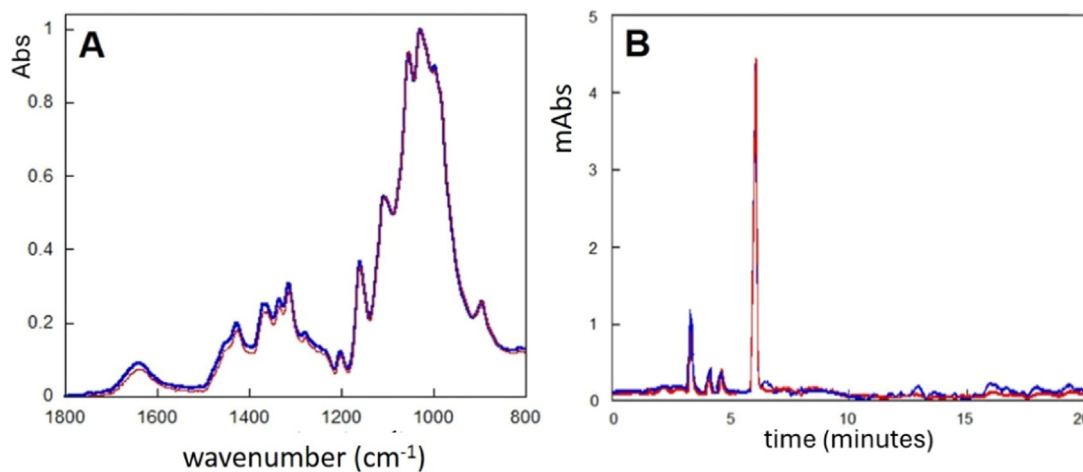


Fig. 4. (A): FTIR spectra of Whatman paper sample before (blue) and after (red) cleaning with GGMA microgels. (B): Chromatographic profiles of water extracts of Whatman paper sample before (blue) and after (red) cleaning with GGMA microgels. FTIR spectra are normalized to the maximum for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

significant concentration of degradation products. If no removable compounds in Whatman paper are present, any variation of its features after treatment is attributable to GGMA microgels application. Absence of detectable residues on paper samples, after GGMA microgel application, has been assessed by performing cleaning procedure on new Whatman paper sheets, and analyzing the water extracts of samples, before and after treatment, by using HPLC. As expected, untreated paper sample showed a pH value equal to 6.3 ± 0.1 and a FTIR spectrum (Fig. 4. A) typical of cellulose in a good state of conservation [40]. Furthermore, HPLC chromatogram of Whatman water extracts highlighted few peaks with very low intensities (Fig. 4. B). Treatment with GGMA does not affect Whatman paper's features. Indeed, FTIR spectra and chromatographic profiles (Fig. 4) of the samples, obtained before and after cleaning, are almost superimposable and the colorimetric and pH variations are negligible ($\Delta E^* = 0.2 \pm 0.1$; pH after cleaning = 6.5 ± 0.1). Crucially, chromatograms of water extracts from cleaned paper samples showed no extra gel-related peaks, indicating no detectable residues attributable to GGMA microgels treatment (beyond the experimental detection limit of this technique). In summary, these results demonstrate that GGMA microgels can be applied and removed without leaving any detectable residues and compromising the structural features of paper.

3.3. Paper cleaning ability

The cleaning ability of microgels was tested on both historical (dated 18th century, made of rag pulp) and modern (dated 20th

century, made up of chemically treated wood pulp) paper [22,29]. This comparison is of fundamental importance because, from the second half of 19th century onwards, the composition of paper has changed considerably, resulting in samples of different stability as well as waterproofing ability.

Cleaning efficacy was tested by characterizing paper samples before and after cleaning through a multidisciplinary approach, mainly using spectroscopic and chromatographic techniques.

As explained above, the aim of this study was to develop an easy to use and rapid tool for an effective one-step cleaning of modern and historical paper artworks, capable of removing simultaneously hydrophilic and hydrophobic contaminants.

3.3.1. Cleaning of historical paper

To start with, the cleaning performances of GGMA microgels on historical samples from *Breviarium* have been tested. Specifically, the removal efficacy of microgels towards hydrophilic contaminants, i.e. low molecular weight acids deriving from cellulose degradation, was tested on *Breviarium* specimens containing no linseed oil (referred to as *Breviarium as is*), while that concerning the cleaning of hydrophobic contaminants (in this case linseed oil degradation products) was studied on *Breviarium* samples opportunistically soiled with linseed oil and artificially aged (referred to as *Breviarium soiled*).

FTIR spectra of *Breviarium as is* samples, before and after cleaning, are reported in Fig. 5. A. The bands in the 1750–1550 cm^{-1} region are attributable to compounds deriving from cellulose oxidation, containing carbonyl and carboxyl moieties [8,9]. As shown

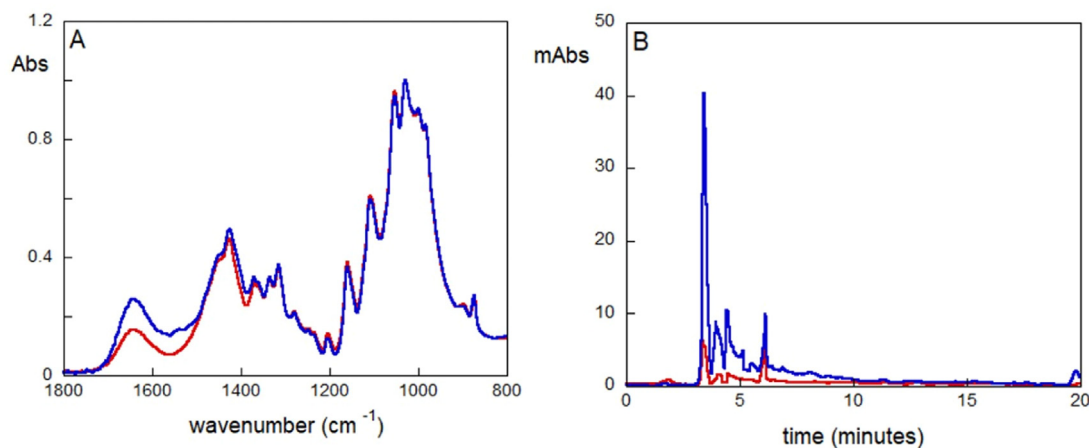


Fig. 5. (A): FTIR spectra of Breviarium as is before (blue) and after (red) cleaning with GGMA microgels. (B): Chromatographic profiles of water extracts of Breviarium as is before (blue) and after (red) cleaning with GGMA microgels. FTIR spectra are normalized to the maximum for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2

pH values of Breviarium samples before and after cleaning, and variation of position in the color CIELAB space^a of samples due to GGMA microgel cleaning.

Sample	pH before cleaning	pH after cleaning	ΔL	Δa	Δb	ΔE
<i>Breviarium as is</i>	6.6 ± 0.1	7.4 ± 0.1	4.6 ± 0.1	-0.5 ± 0.2	-6.6 ± 0.2	8.1 ± 0.2
<i>Breviarium soiled</i>	5.8 ± 0.1	6.3 ± 0.1	5.1 ± 0.1	-2.1 ± 0.1	-8.5 ± 0.1	10.1 ± 0.2

^a Uncleaned paper samples have been used as a reference.

in Fig. 5. A, the intensity of the absorption bands in the aforementioned region decreased (relatively to the band at 1023 cm^{-1} , attributable to the CO and CC stretching and CCH and OCH bending modes of cellulose units and which intensity could be considered constant) [41] after cleaning, thus indicating that the treatment with microgels allows the successful removal of cellulose byproducts. HPLC experiments confirm the cleaning efficiency of the proposed system. Carboxylic acid compounds, resulting from the spontaneous cellulose degradation, may be ascertained by means of HPLC chromatography on water extracts of paper specimens. Here, by comparing the peak heights in the chromatographic profiles of *Breviarium as is* samples before and after treatments, it is possible to evaluate the removal efficiency of these products. As shown in Fig. 5. B, after cleaning the intensity of the peaks corresponding to the acids ascorbic ($t_r = 3.5 \text{ min}$), lactic ($t_r = 4.0 \text{ min}$), malic ($t_r = 4.5 \text{ min}$), and citric ($t_r = 6.0 \text{ min}$) dropped [28,42]. FTIR spectra and chromatograms of the samples after cleaning showed no additional peaks, like those characteristic of microgels (Figure S3), which is noteworthy and confirmed that the treated paper has no detectable microgel residues.

Acids content decreasing, after GGMA microgels action, was confirmed by the increase in pH values of paper samples, as reported in Table 2. It should be highlighted that, as reported in literature [8,9], some cellulose oxidation byproducts (having conjugated carbonyl groups) are chromophores, responsible for the yellowing of paper and thus of a progressive worsening of the optical quality of the artworks. FTIR data indicate, as shown above, that GGMA microgels are able to remove these degradation products and colorimetric measurements confirm this result. Indeed, after cleaning (Table 2 and Fig. S4) there is an increase in brightness and a concomitant decrease of red and yellow tones, resulting in a high chromatic variation ($\Delta E^* = 8.1 \pm 0.2$).

The removal efficiency towards hydrophobic compounds of GGMA microgels was tested on *ad hoc* prepared samples, i.e. aged *Breviarium* samples containing stains made up of linseed oil (see materials and methods section). Linseed oil residues on paper could arise from unintentional contact with oily objects commonly

used for painting, printing and typography through the ages. The drying and oxidative degradation of linseed oil, composed of mixtures of triglycerides, causes macroscopically yellowing and acidity increase, thus constituting a possible additional source for cellulose depolymerization [32,43,44]. In the FTIR spectra of the soiled samples (Fig. 6. A), bands at 1730 cm^{-1} are attributable to stretching mode of carbonyl moieties, deriving mostly from linseed oil and its degradation products (Fig. S5A and for comparison, Fig. 5A) [32]. The treatment with GGMA microgels induced a decrease in their intensity (Fig. 6. A), thus indicating that these materials are capable of removing this coating. The oil content on the paper sheet can be therefore considered proportional to the intensity of the band at 1730 cm^{-1} with respect to that at 1024 cm^{-1} (considered unchanged during the cleaning process, see Section 4.3.1, and assigned to glucose in cellulose). The value of this absorbance ratio, hereafter called hydrophobic ratio ($HR = Abs_{1730} / Abs_{1024}$), decreases from 0.26 ± 0.01 , in the uncleaned sample, to 0.19 ± 0.01 , in cleaned one. The lipid components of linseed oil are responsible for the pattern of peaks shown in the HPLC chromatographic profiles at about 40 min, performed on the methanol extracts of the samples (Fig. 6. B). These peaks decreased in intensity after cleaning; furthermore, no additional peaks related to GGMA are visible. At the same time, the colorimetric results, which indicate a decrease in yellow and red tones and an increase in brightness, reflect an overall improvement of the optical quality of paper thanks to cleaning. The increase in pH (Table 2) resulting from cleaning also ensures the elimination of acid leftovers from paper.

3.3.2. Cleaning of modern paper

Cleaning of modern paper represents an intriguing task, because it is a more degradable sample than the historical one, due to its wood-pulp origin and, in the case of chemically bleached paper, to bleaching treatments [10,45]. This makes the wet treatment of modern paper a more delicate process, with respect to that of historical paper. Moreover, the use of synthetic or natural compounds as gluing agents makes paper sheets difficult to be permeable by water-based cleaning agents. A lot of strategies and

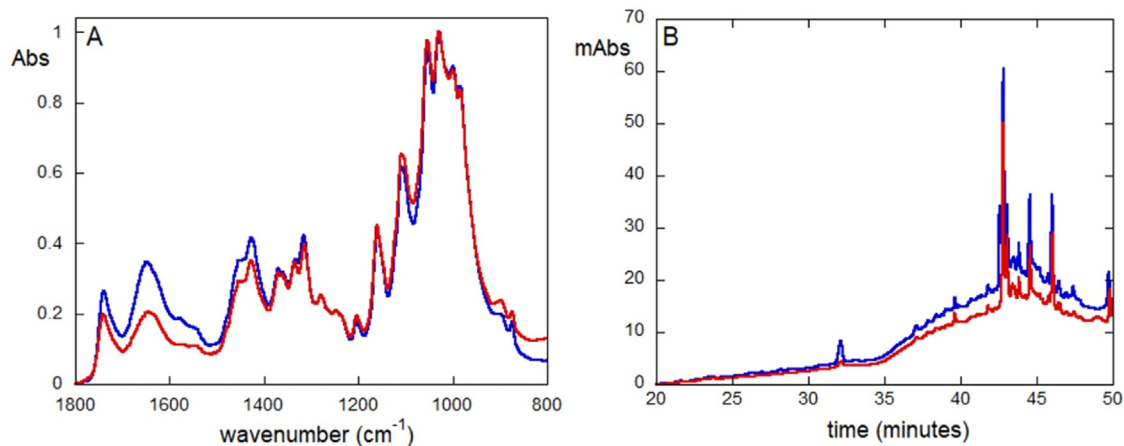


Fig. 6. (A) FTIR spectra of Breviarium soiled sample before (blue) and after (red) cleaning with GGMA microgels (B): Chromatographic profiles of methanol extracts of Breviarium soiled sample before (blue) and after (red) cleaning with GGMA microgels. FTIR spectra are normalized to the maximum for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

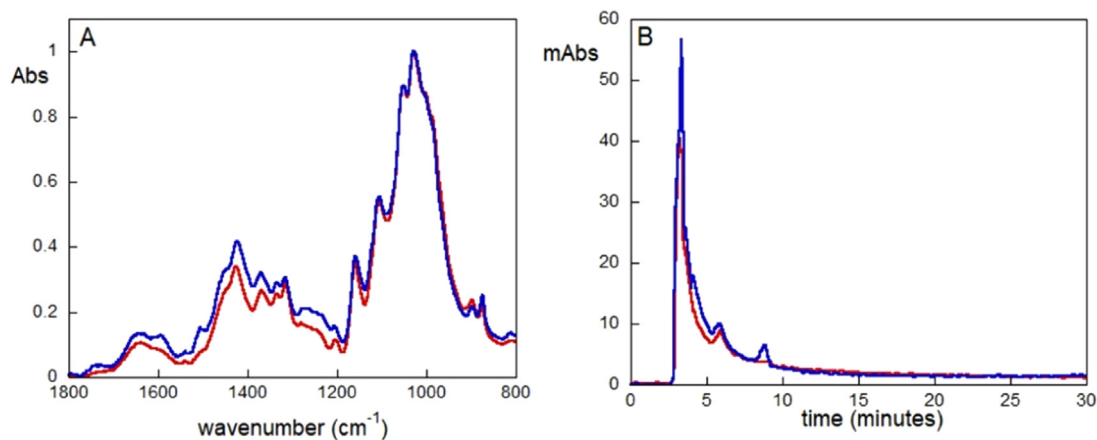


Fig. 7. (A) FTIR spectra of notebook sample without adhesive before (blue) and after (red) cleaning with GGMA microgels. (B): Chromatographic profiles of water extracts of notebook sample without adhesive before (blue) and after (red) cleaning with GGMA microgels. FTIR spectra are normalized to the maximum for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

materials are proposed for the historical paper cleaning [11–13,36], while this is not the case for the modern paper one. Therefore, our aim is to extend the proposed tools for cleaning modern systems and to determine whether GGMA microgels can be generally applicable for cleaning both historical and modern paper. Written notebooks, as well as modern papers containing aged residues of pressure adhesive tapes have been used as samples. Regarding the removal of hydrophilic residues, the intensity of the bands in the 1800–1500 cm^{-1} region was lower in the FTIR spectrum of treated samples with respect to untreated ones, indicating that microgels are able to remove degradation byproducts (Fig. 7. A) without leaving detectable residues. Simultaneously, the intensity reduction in the chromatographic profiles for the peaks at 4, 4.8, and 5.8 min of the treated samples compared to the untreated ones (Fig. 7. B) shows that organic acids (oxalic, lactic, and succinic acid) arising from paper degradation have been removed by GGMA microgels. The 8-minute peak is entirely eliminated by GGMA and remained unidentified. These findings are corroborated by the increase of pH after cleaning, due to organic acids removal, and by the chromatic variation due to cellulose and hemicelluloses oxidized byproducts removal (Table 3).

Importantly, GGMA microgel application did not induce inks spreading or fading, as shown in Fig. S6.

In the modern age, paper tears have often been repaired with pressure adhesive tapes. Unfortunately, these kinds of adhesives tend to become very yellow and brittle over time, further contributing to the deterioration of paper. Thus, once established the ability of GGMA microgels to remove hydrophilic compounds from modern paper, their cleaning efficiency was evaluated on the detachment of aged adhesive tape. FTIR experiments indicate that adhesive residues applied on notebook samples are made of a copolymer of styrene and isoprene (Fig. S5B), a material that tends to oxidize over time and becomes harder and more yellow [46]. After treatment with GGMA microgels, samples appear to be clearer, as shown in Fig. 8. This is also detected by the colorimetric variation reported in Table 2, showing a decrease of the yellow tone on the paper.

FTIR experiments confirm adhesive removal. Indeed, as shown in Fig. 9, the bands at 1730 cm^{-1} , assignable to C = O moieties present in the oxidized adhesive (even if they are present in degradation cellulose byproducts, from comparison of 1730 cm^{-1} bands in Fig. 7. A and 9A, the intensity of this band in the presence of adhesive could be reasonably attributable mainly to adhesive) clearly diminish (with respect to the cellulose band centered at about 1024 cm^{-1}), indicating a decrease of the adhesive content in the sample. It is interesting to note that also in this case the

Table 3
pH values and variation of position in the color CIELAB space^a of notebook samples before and after cleaning with GGMA microgel.

Sample	pH before cleaning	pH after cleaning	ΔL^a	Δa^a	Δb^a	ΔE^a
Notebook	6.7 ± 0.1	7.7 ± 0.1	2.0 ± 0.1	−0.1 ± 0.1	−2.0 ± 0.1	2.8 ± 0.2
Adhesive on notebook	6.6 ± 0.1	7.7 ± 0.1	0.6 ± 0.1	−0.2 ± 0.1	−4.8 ± 0.1	4.8 ± 0.2

^a Uncleaned paper samples have been used as a reference.



Fig. 8. Images of notebook sample with adhesive tape before (A) and after (B) cleaning with GGMA microgels.

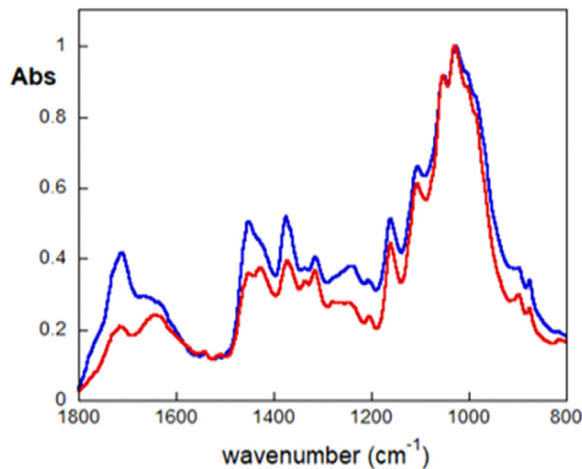


Fig. 9. FTIR of notebook sample with adhesive before (blue) and after (red) cleaning with GGMA microgels. FTIR spectra are normalized to the maximum for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cleaning causes a decrease of the acidity of the sample as the pH value raised from 6.6 ± 0.1 to 7.7 ± 0.1 .

3.4. Comparison between the cleaning ability of GGMA microgels and GGMA macrogels (hydrogels)

Recently, GGMA hydrogels have been proposed as a single component, cleaning tool for both hydrophobic and hydrophilic materials removal from paper [22]. Here, a comparison between the cleaning efficacy of GGMA in macro- (hydrogel) and micro-gel form has been reported. The main hypothesis is that the use of microgels allowed to obtain better performances, in terms of cleaning efficacy and time cost, with respect to hydrogels (i.e. cleaning using microgels takes few minutes, while using hydrogels needs at least half an hour). The innovation of GGMA systems mainly consists in their removal capability of hydrophobic compounds, in addition to the hydrophilic ones. Therefore, the comparison between cleaning efficiency of GGMA hydrogel and GGMA microgels towards hydrophobic materials was addressed. To evaluate the cleaning efficacy, the hydrophobic ratio (HR) was calculated, which is

defined as the ratio between the intensities of the band at 1730 cm^{-1} , related to carbonyl compounds present in oil and in adhesive tape materials, and that at 1024 cm^{-1} , due to cellulose (that is, $HR = Abs_{1730} / Abs_{1024}$). As a consequence, the lower is this absorbance ratio, the higher is the cleaning efficacy. Concerning the oil removal from historical paper, HR is found to be 0.40 ± 0.01 for uncleaned sample, 0.22 ± 0.01 for samples cleaned with GGMA hydrogel and 0.19 ± 0.01 for samples cleaned with GGMA microgels, respectively. In the case of pressure adhesive tape removal, HR is 0.41 ± 0.01 before cleaning, 0.22 ± 0.01 after cleaning with GGMA in hydrogel form, and 0.21 ± 0.01 after cleaning with GGMA microgels. These values demonstrated that the cleaning efficacy of microgels towards historical paper is slightly higher than that of hydrogels towards historical paper, while it is comparable in the case of modern paper. Overall, it should be noted that the use of microgels allows a significant time saving and thus, it is a more convenient and sustainable method with respect to hydrogels.

4. Conclusions

In this work, a tool based on the use of a water-based solution of microgels composed by gellan gum polymer, modified with methacrylated moieties, is proposed for paper cleaning. This cleaning procedure is extremely advantageous from a point of view of health and time costs, thanks to its chemical composition and to the peculiar properties of microgels. The basic idea is that microgels provide fast cleaning, while methacrylation of the polysaccharide makes the system able to remove even oxidized portions of hydrophobic coatings [22]. To this aim, GGMA microgels are prepared with rheological properties comparable to that of GG unmodified microgels and with size of the order of micrometers. GGMA microgels showed, as demonstrated by a multi-technique approach, a satisfactory ability in the removal of cellulose acid/degradation byproducts from both historical and modern paper samples. A similar result has been obtained for the removal ability of two different hydrophobic compounds: aged linseed oil, for historical paper, and pressure adhesive tapes residues, for notebook. These contaminants accelerate the degradation of paper, but their removal is not trivial. Even if the proposed method presents some disadvantages (the synthesis is not easy and the hydrophobic contaminants are not totally removed), the promising results obtained up to now support, on one hand, the use of the hydrophobically modified gellan gum, GGMA, as a valuable material for a water based, safe for operators and single-step wet cleaning tool, thus avoiding the use of time-consuming multi-step treatments and toxic solvents. On the other hand, our findings also support the employment of microgel technology as effective and versatile cleaning agents for paper artwork. Further studies are needed to optimize the proposed method and render it usable also for artifacts of different nature (i.e. wood), however, by exploiting the potentiality of both the *ad hoc* modification of gellan gum and of micro sized soft materials, as tunable cleaning tools, the present results pave the way for the development of materials for a fast cleaning of Cultural Heritage artefacts.

Author Contributions

C.M., E.Z. supervised the research and data interpretation. E.C. experimental investigation, L.S. experimental investigation, data

analysis and interpretation. S.F., R.A. performed the rheology and DLS measurements. S.S. performed the AFM measurements. L.T., L.S. planning experiments and revision of the article. L.M., E.P. performed the HPLC measurements. C.M., E.Z. and L.S. wrote the original draft.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2024.11.008.

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