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Regular Article

Innovative chemical gels meet enzymes: A smart combination for cleaning paper artworks

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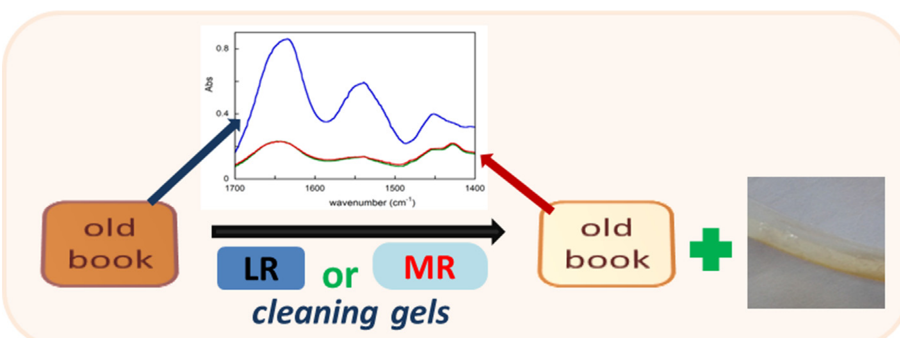
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Due to their highly retentive properties, innovative recently developed, semi-interpenetrated hydrogels made up of poly(vinyl pyrrolidone) (PVP) chains embedded in a poly(2-hydroxyethyl methacrylate) (p(HEMA)) network should be efficiently used as cleaning material for fragile and degraded paper artworks. In restoration practice, indeed the wet cleaning of these artworks is usually performed by immersion of paper in water, a procedure which may lead to several drawbacks, including paper fibers swelling and dissolution of water-soluble original components.
Experiments: This class of gels were yet presented in literature, but their interactions with paper materials and ability to be spiked with active enzymes (as cleaning agents), have not been analyzed. To establish the suitability of these hydrogels as paper cleaning materials, first, a rheological and microstructural characterization of the gels was performed. Moreover, diffusion of macromolecules inside gels was studied using fluorescence microscopy, to check if these innovative hydrogels can be used as carriers for hydrolytic enzymes. Indeed, pastes and glues are usually found in old paper artworks, and their removal is a very delicate operation that requires a selective action, which is granted by specific hydrolytic enzymes. At the same time, spectroscopic analyses on paper samples under investigation before and after cleaning treatment has been performed, thus assessing the capabilty of these gels as cleaning materials.
Findings: With the aim of demonstrating the versatility of these hydrogels, several case studies, i.e., the removal of grime and water-soluble cellulose degradation byproducts, the removal of animal glue and the removal of starch paste from real samples, are presented. Results obtained with these gels have been compared to those obtained by using another gel used for paper artworks cleaning, i.e., Gellan gel.

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1. Introduction

Wet cleaning is a fundamental operation in paper artworks restoration because it allows the removal of grime, dirt and water-soluble substances arising from cellulose degradation. Wet cleaning also allows for the partial dissolution of aged glues and pastes, even if, for a complete and selective removal, specific hydrolytic enzymes are preferred [1–3].

The traditional cleaning procedure implies the immersion of paper artworks in water [3,4], which eventually induces the removal of sizing agents, i.e., gelatine, the spreading of inks and it also leads to the swelling of cellulose fibers, which may cause the deformation of paper after drying, leading to a significant decrease in the mechanical resistance of the cellulosic network [2,5–8]. The usage of hydrogels could overcome the drawbacks induced by this traditional cleaning practice. In fact, when gels are used, the penetration of water into paper is significantly reduced, resulting in minimal damage to the artworks [9–11]. Solvent gels and cellulose derivatives, used as thickening agents for water and solutions, were the first gel-like systems proposed for paper cleaning [12–13]. However, their complete removal from artworks after application is not simple and it often requires mechanical action or the use of solvents, which could be unsafe for the artworks [14]. Recently, physical gels based on natural polysaccharides, such as Gellan gel (Gg), have been proposed for the cleaning of paper artworks. From a rheological point of view, these hydrogels are rigid systems that can be applied and removed from paper in one step, as one body, without leaving residues on the treated surfaces [2,9,15,16]. These materials are also biocompatible (in fact they are widely used in food and medicine), and they are thus safe for operators. However, even if the use of Gg represents a great improvement with respect, to water bath, it has some drawbacks. Indeed, its high rigidity renders it unsuitable for non-flat artworks like backs of books, frayed covers or papers containing both glued and unglued parts because it is not able to adhere uniformly and thus the cleaning process could be not homogenous. Furthermore, the biodegradability of these hydrogels imposes their preparation "in situ", shortly before their application and they can be used only once. In this contest, even if the Gg preparation is very simple, care should be used during the addition (at relatively high temperature) of enzymes [9] to avoid cloths or enzymes denaturation. Moreover, even if the amount of water released by these hydrogels is significantly lower than that used in traditional wet cleaning operations, it is sometimes not sufficiently low to avoid the formation of gores due to the spreading of water on paper samples, thus reducing the possibility of performing a cleaning operation only specific, compromise parts of the artworks.

Finally, highly degraded paper artworks could not usually stand the application of these polysaccharide-based rigid gels. To overcome these drawbacks, making advances in the field of gel for cleaning paper artworks, we have looked for candidates into several materials developed for cultural heritage restoration [17–19]. In particular, a new class of hydrogels proposed for the cleaning of water-sensitive artworks, [20,21] has appeared to be particularly interesting. These hydrogels are based on a semi-interpenetrated network in which chains of poly(vinyl pyrrolidone) (PVP) are embedded in a poly(2-hydroxyethyl methacrylate) (p(HEMA)) structure. The semi-interpenetrated network takes advantages from both the mechanical stability of the p(HEMA) and the high hydrophilicity of PVP. These hydrogels are highly retentive, soft and transparent and can be easily handled. Furthermore, they are stable, not perishable and can be stored in water for months. p(HEMA)/PVP hydrogels can be used with neat water, or loaded with several polar solvents, such as glycerol and ethanol [21]. The properties of the hydrogel mainly depend on the p(HEMA)/PVP ratio and on the amount of water used during gel preparation. In fact, changes in gel composition result in hydrogels with different properties (i.e., the hydrophilicity of the network, pore size distribution and the mechanical properties). This means that, in principle, for example, different gels with different hydrophobic properties could be produced, using simply the same protocol, to clean paper samples with different hydrophobic patinas. In this work, two p(HEMA)/PVP hydrogels were used for the removal of unwanted materials from paper artworks and compared to a well-established gel for paper cleaning artworks, i.e., Gg. Indeed, even if these gels have been reported in literature as highly retentive gels usable for cleaning cultural heritage artifacts, their interaction and compatibility with paper materials, as well as their cleaning ability have not been yet characterized. Moreover, old paper artworks often contain pastes and glues, and their removal is a very delicate operation that requires a selective action, which could be granted by specific hydrolytic enzymes. Therefore, in this work the capability of these gels to carry active hydrolytic enzymes as very specific (and biocompatible) cleaning agents has been also studied. The combined use of retentive gel and enzymes, indeed, allows a localized and selective glue removal, thus minimizing time costs and damages on paper materials The suitability of these gels as cleaning agents, has been established performing experiments concerning both the characterization of their microstructural and rheological properties and about water loss, spreading on paper, mobility of molecules into them. To this end, small angle X-ray scattering (SAXS) and field emission scanning electron microscopy (FE-SEM) measurements, creep recovery tests, and the fluorescence recovery after photobleaching (FRAP) experiments have been carried out on gels.

With the aim of demonstrating the versatility of these hydrogels, several case studies are have been carried out and reported, i.e., the removal of grime and water-soluble cellulose degradation by-products, the removal of animal glue and the removal of starch paste from real samples and tuned specimens.

2. Experimental section

2.1. Materials

α-Amylase [EC-232-560-9; 30,500 U/ml], *Proteinase K* [EC-3.4.21.64, ≥30 U/mg], fluorescein isothiocyanate-dextrans (FITC-dextrans) of different molecular weights (average molecular weights: 10 kDa and 40 kDa), calcium acetate, calcium chloride, 2-Hydroxyethyl methacrylate [HEMA] and poly(vinylpyrrolidone) (PVP) were obtained from Sigma-Aldrich. α,α'-Azoisobutyronitrile (AIBN) and N,N-methylene-bis(acrylamide) (MBA) and Methylene Blue (MB) were purchased from Fluka. Gellan gum is KELCOGEL CG-LA product by CP Kelco (Atlanta Georgia, USA). New cellulosic paper samples (density = 80 g/cm^2, rate of filtration = 1196 s/100 mL) were purchased from ALBET® LabScience. All reagents used were of analytical grade and used without further purification. During all the experiments, ultrapure water obtained from a Millipore system was used.

2.2. Hydrogels preparation

Gellan gum-based hydrogel (Gg) was prepared according to a procedure reported elsewhere [9], using commercial deacylated Gellan gum (20 g/L) and calcium acetate (0.4 g/L). Gg has been stored in refrigerator before use and must be used within few days.

Two semi-IPN hydrogels, based on a polymeric network of p(HEMA) embedding PVP, were prepared. A system is more retentive (MR) while the other one is less prone to retain water (LR).