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Original article

Measurement of reversible rate of conservation materials based on gel cleaning approach

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ABSTRACT

In this work, a new hydrogel designed for water-sensitive artifacts especially for China Dunhuang mural was synthesized to remove the ineffective conservation materials on mural surface. The reversible rate of each conservation material was measured based on hydrogel cleaning. It was found that the gel filled with cleaning agents showed excellent performance over the empty gel. Besides, it was more environment-friendly without mechanical damage to the sensitive surface and easier to control the cleaning process compared with pure organic solvent cleaning. 3D microscopic system confirmed the cleaning effects both visually and quantitatively. The best "conservation material-cleaning agent" pairs and their reversible rates were obtained, which were "ParaloidB72—P-xylene + ethyl acetate—80%", "polyvinyl acetate—P-xylene + ethyl acetate—40%", "acrylic—P-xylene—44%", "silicone—P-xylene + 1-Pentanol—55%". It was also found that the reversible rates of the conservation materials declined after aging.

1. Introduction

Modern conservation science originated from the 1966 tragic flood that destroyed Florence and Venice, which accelerated the search for new conservation approaches [1,2]. The traditional method for mural protection was applying physical isolation layer such as Paraloid B72, acrylic and silicone-acrylic. For example, some of these materials have been used to consolidate the Dunhuang mural, which is the splendid cultural relic along the Silk Road in northwest China. The conservation materials suffered ageing or other degradations with time, on the other hand, new excellent materials were developed to replace the previous ones. Therefore, the old conservation materials needed to be removed under the premise of not breaking the murals. Cleaning of artifacts is one of the most delicate operations in cultural heritage conservation because not only is it potentially invasive and aggressive for the original materials but also completely irreversible. Traditionally, the cleaning process was carried out through mechanical action or solubilization, mainly done with polar organic solvents. As for murals, the use of neat solvent has two main limits:

- the solubilized polymers may diffuse within the artwork layers with the penetration of organic solvents;
- most solvents are harmful to both environment and operators.

To be environment-friendly and harmless to people, amphiphilic aqueous systems were used [3–8]. However, aqueous systems could not be directly applied on water-sensitive artworks such as easel paintings and Dunhuang murals because the aqueous systems could swell/solubilize the organic binders and induce mechanical stresses on the canvas, the substrate, and the paint layers [9,10]. Recently, gels have been employed to decrease these deleterious effects, offering advantages over liquid systems in the evaporation control of the solvent entrapped in the network, in the minimization of their penetration inside the artworks through capillary action, and in an enhancement of the control of the cleaning action on the surface to be treated. It is worth mentioning that the first application of physical gels and "gel-like" thickeners in the field of conservation science was proposed by Wolbers in the late 1980s, using polymers [e.g., mainly poly(acrylic acid)] as gellants to remove the dirt and coatings from artwork surface (i.e., oil paintings) [11,12]. In this method, the capillary penetration of the solvent into the artifact was reduced by immobilizing the solvent within the gel network. However, the network of these physical

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gels is based on weak interactions (dipole-dipole interactions and/or hydrogen bonding), as a result, the gel residues remained on the artworks after gel application. Additional mechanical action or solvent was adopted to clean these gel residues, but generating the second pollution [13]. Burnstock and Kieslish proved that although a poly(acrylic acid)-based gel was removed from a painted surface through turpentine, residues of gelator still remained [14]. Actually, the high viscous gel distinguished itself in controlling the solvent penetration, which made the removal of gel residues tough. Researchers have made some efforts to solve these problems by developing a new class of rheoreversible organogels [15,16]. The mechanical behavior of this polyamine-based gel can be tuned by switching low-viscosity fluid to normal gel in the presence of CO_2 at room temperature [15,17–19] and back to low-viscosity fluid in a few seconds after weak acid-catalyzed CO_2 displacement.

Hence, it is a graceful method that using chemical gels whose network is formed by covalent bonds to deal with the gel residue issue. Because of the strong covalent bonds, chemical gels show improved mechanical properties compared with physical gels. Besides, they could be shaped in a well-defined form and swell in a liquid medium without gel solubilization. Nowadays, more and more innovative gels with confining systems have been formulated to solve residue issues such as rheoreversible polyallylamine based organogels [20], viscoelastic polyvinyl alcohol-borate based gels [21], and magnetic gels [22,23], etc.

The gels were initially used for aesthetics rather than conservation. Nowadays, with the fast development of technology, the application of gels involves stone preservation [24], cleaning of varnish, grime, stains, and dirt, as well as wood preservation by impregnating silica sol-gel [25]. But the most valuable aspect of gels is the potential in cleaning artworks.

Samai and Biradha [26] found that the pyridine-3,5-bis(benzimidazole-2-yl) ligand (L) with metal salts(Cu(II) or Cd(II)) could form multifunctional metal-organic gels (MOGs) with significantly high mechanical strengths and self-sustainability. Also, the MOGs presented a tendency as potent gas sorption/dye absorption agents, and were found to be responsive with external chemical stimuli (metal capturing agents). Bonini et al. [23] synthesized a new smart gel consisted of a network functionalized with $CoFe_2O_4$ magnetic nanoparticles. The magnetic gel could be loaded with an oil-in-water microemulsion to remove Paraloid B72 coatings selectively. Besides, this responsive system allowed the minimization of the mechanical effect needed to remove them from the treated substrate in cleaning very precious artifacts since they could be easily taken away in the presence of a simple permanent magnet [22]. A new type of aqueous polymeric dispersions with high viscosity based on poly(vinyl acetate) at different hydrolisys degrees (PVAx, where x is the percent of hydrolised acetate monomers) cross-linked by borax was set up by Carretti et al. [21,27,28]. These systems were successfully applied to selectively remove oxidized varnishes coatings from the surface of “Coronation of the Virgin with Saints”, a 15th century egg tempera painting on wood by Neri di Bicci (Florence, 1418–1492) and from the surface of a XVI–XVII century oil-on-wood painting by Ludovico Cardi detto il Cigoli. Domingues et al. [29] synthesized an innovative hydrogels based on semi-interpenetrating p(HEMA)/PVP networks for cleaning water-sensitive artifacts. The gels were transparent, and can be both realized as thin films and shaped freely. It showed that the controlled cleaning process was obtained with a gradual depletion of hydrosoluble grime coating from a Thang-Ka mock-up without color leaching.

Reversibility is referred to that when the material is applied, after a period of natural variation, it can still be removed from the surface without breaking the artworks by means of physical adsorption or chemical reaction. All above cases showed excellent cleaning performance only visually/qualitatively, but our study was focused on quantitative measurement based on gel cleaning, i.e., the reversible rates of conservation materials from the prototype of Dunhuang murals at Mogao Grottoes [30,31]. The reversibility problem of aged Paraloid B72, silicone-acrylic, acrylic and polyvinyl acetate was investigated qualitatively and quantitatively both on glazed tiles and model samples, 3D microscopic system was to observe the removal effect. p(HEMA)/PVP gel was used and assessed based on its mechanical property and operability on water-sensitive substrate. Gels loaded with blends of solvents with different polarity were aimed to control the action of solvents on the water-sensitive substrates and be environment-friendly as well.

2. Materials and methods

2.1. Instruments

Materials and agents weighing were performed using electric analytical balance (FA1004, Shanghai, Hunyuhengping scientific instrument Co., Ltd). Sample drying was carried out with electric heating oven (DH-9070, Shanghai, Jinghong experiment facilities Co., Ltd). UV ageing oven (Common Wealth Industrial Corporation) was used for sample aging and 3D microscopic system (VHX-2000, KEYENCE China Co., Ltd) was used to observe the removal effect. Thermostat water bath (HH-1) and magnetic stirrer (JJ-1 Kanghua) were used in the synthesis of hydrogels.

2.2. Materials

For the preparation of model samples, red lead, azurite and mineral green were purchased from Beijing Tianya Company, lime [$Ca(OH)_2$] was obtained from Sinopharm Chemical Reagent Co., Ltd, gelatin was obtained from Suzhou Jiangsixutang Pigments Company, jute, soil and sand were provided by Conservation Institute of Dunhuang Academy, glazed tiles (10 × 10 × 0.5 cm) and clay blocks (10 × 5 × 1 cm) were purchased from Hangzhou.

Paraloid B72 was obtained from MANUEL RIESGO, S.A., 49% silicone-acrylic, 49% acrylic and 48% polyvinyl acetate (PVAC) emulsion were purchased from Boshijiaofendeli (China) Binder Co., Ltd. Silicone-acrylic, acrylic and PVAC were diluted to concentrations between 15% and 20%, and Paraloid B72 was dissolved in n-butyl acetate to the concentration of 20%.

Ethyl acetate (EA, AR), P-xylene (PX, CP) and 1-Pentanol (1-PeOH, AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. Propylene carbonate (PC, 99%) was obtained from Aladdin Industrial Corporation. All the chemicals were used as received. PX + EA, PX + 1-PeOH, and PX + PC were prepared by mixing them at the ratio of 1:1(w/w).

For the preparation of the gels, 2-hydroxyethyl methacrylate (HEMA) (assay 96%), poly (vinylpyrrolidone) (PVP) (average M_W = 1300 kDa), α,α'-Azoisobutyronitrile (AIBN) (assay 98%) and N,N-methylene-bis (acrylamide) (MBA) (assay 97%) were obtained from Aladdin, AIBN was recrystallized twice from ethanol prior to use.

2.3. Methods

2.3.1. Synthesis of gels

It is a reaction between free radical polymerization of HEMA monomer and the cross-linker MBA in a water solution containing linear PVP. By changing the proportions of monomer, cross-linker, PVP and water, a series of different gels can be obtained. All the reactants and radical initiator AIBN (1:0.01 monomer/initiator molar ratio) were mixed together and the solution was bubbled with nitrogen for 10 min to remove the dissolved oxygen that could