

Structural and Mechanical Properties of “Peelable” Organoaqueous Dispersions with Partially Hydrolyzed Poly(vinyl acetate)-Borate Networks: Applications to Cleaning Painted Surfaces

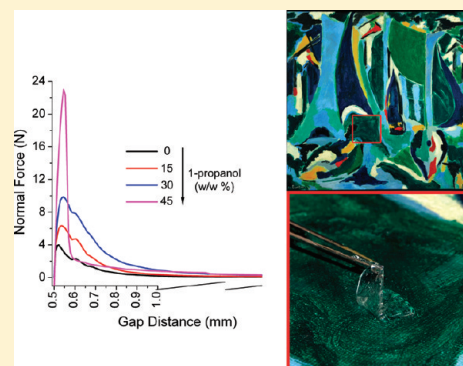
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S Supporting Information

ABSTRACT: The preparation and structural characterization of a family of viscoelastic dispersions of borate cross-linked, 80% hydrolyzed poly(vinyl acetate) (80PVAc) in aqueous–organic liquids are presented. Correlations between mechanical properties (from rheological measurements) and the degree and nature of cross-linking (from ¹¹B NMR spectroscopy) are reported, and the results are used to assess their potential as low-impact cleaning agents for the surfaces of paintings. Because the dispersions can be prepared at room temperature by simple procedures from readily available materials and can contain up to 50% (w/w) of an organic liquid, they offer important advantages over previously described cleaning agents that are based on fully hydrolyzed PVAc (i.e., poly(vinyl alcohol)). The mechanical properties of the various aqueous–organic dispersions, as determined quantitatively by rheological investigations and qualitatively by their ease of removal from a solid surface (i.e., the so-called “peel-off” ability) have been tuned systematically by varying the amount of organic liquid, its structure, and the concentrations of borax and 80PVAc. The ¹¹B NMR studies demonstrate that the concentration of borate ions actively participating in cross-linking increases significantly with the amount of organic liquid in the mixture. The degree of cross-linking remains constant when the 80PVAc and borax concentrations are varied, as long as their ratios are kept constant. Some of the 80PVAc–borax dispersions have been tested successfully as cleaning agents on the surface of a 16th–17th century oil-on-wood painting by Lodovico Cardi, “Il Cigoli”, that was covered by a brown patina and on the surface of a Renaissance wall painting by Vecchietta in Santa Maria della Scala, Siena, Italy, that had a degraded polyacrylate coating from a previous conservation treatment.



INTRODUCTION

Gel technology has grown rapidly during the past few decades, resulting in the use of gel materials as fundamental components of many products and processes. In part, the growing popularity of gels is a result of their controllable physical and chemical properties, including their ability to be applied reversibly or irreversibly to various surfaces, as well as for other applications.^{1–11} Also, sol–gel technology¹² has been used largely for the preparation of many materials with controlled physicochemical properties and performance by means of a combination of microstructural and chemical approaches.^{12–21}

During the last two decades, hydrogels and organogels have been used as low-impact cleaning tools for painted surfaces. Their growing popularity stems, in large part, from the ability of a conservator to exercise much better control of the cleaning action than is possible with neat liquids (i.e., in the absence of the gellants). In this way, problems associated with the penetration of the liquids into the painted layers or the spreading of liquids over the surfaces and even evaporation, can be reduced.²² Thus, painted surfaces of wood and canvas are being treated with increasing

frequency with high-viscosity polymeric cleaning systems^{23–27} because they minimize the impact on both the treated work of art and the environment. One of the polymeric systems, based on aqueous formulations of poly(vinyl alcohol) (PVA), can be highly viscoelastic^{28–30} when cross-links from hydrogen bonds or chemical reactions involving the hydroxyl groups (e.g., complexation of ions such as borate^{31,32} or antimonate³³) are present. Recently, we have explored the ability of mixtures of water and miscible organic liquids, held within PVA–borate networks, to remove foreign materials from the surfaces of easel paintings,³⁴ to remove foreign materials from the surfaces of easel paintings.³⁴ The potential utility of this class of materials is demonstrated by their ability to adapt their shape to establish intimate contact with a surface to be cleaned and their very high shear elastic moduli,³⁵ which allow them to be peeled off of painted surfaces (after they have carried out their cleaning function). Furthermore, tests on the surfaces of paintings coated by aged, natural varnishes

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resulted in good cleaning action without any detectable PVA or borax-derived residue.³⁴ However, the range and amount of organic liquids that can be added to the aqueous PVA–borax systems are limited to ≤ 25 wt % 1-propanol, lesser amounts of other short-chained 1-alkanols, and 10 wt % cyclohexanone and propylene carbonate. At higher concentrations of the organic liquids, macroscopic phase separation (syneresis) occurs and the desired mechanical properties are diminished.

A major goal of this work was to increase the amount and range of organic liquids that can be incorporated into PVA–borax-like systems^{25,34,35} without sacrificing the desired mechanical properties. In addition to being able to prepare highly elastic viscous systems capable of incorporating alcohols, it is desirable to be able to include large amounts of other types of solvents such as ketones, which are commonly used in conservation as cleaning agents.^{36–38} In this way, the range of materials removable from painted surfaces is also broadened.³⁹ As a means to achieve that goal, we have employed a poly(vinyl alcohol-co-vinyl acetate) random copolymer in place of PVA. The ratio of the two monomers can be varied by controlling the degree of hydrolysis of poly(vinyl acetate) (PVAc).⁴⁰ For this study, 80% hydrolyzed PVAc (i.e., containing ca. 20% vinyl acetate and ca. 80% vinyl alcohol groups (80PVAc)) has been selected.

The intrinsic shear elastic modulus—given by the asymptotic value of the shear storage modulus (G') curve at high frequencies—after the loading of the organic solvent was found to be sufficiently high to allow the removal of the cleaning system by peeling it off from a painted surface. A correlation between the macroscopic behavior (performance in the cleaning action and ease of application and removal) and the rheological parameters is presented to establish a rigorous method of predicting how variations of the concentrations of each of the components in these materials affect their ability to be peeled.

The ability of the 80PVAc–borax dispersions with organic–aqueous liquid mixtures to clean a painting was tested on part of the surface of the same wood painting by Lodovico Cardi called “Il Cigoli” (1559–1613), entitled “Santo Stefano”, that was used previously to test PVA–borax systems.³⁵ The target there and here is the removal of a thick layer of oxidized varnishes used in past conservation treatments. To maximize the validity of the comparisons between the 20/80 1-propanol/water PVA–borax and different organo/water 80PVAc–borax systems, proximal surface locations were tested. Another potential application consisting of the removal of aged acrylic organic coatings was explored on wall paintings by Vecchieta in the Santa Maria della Scala Sacristy (Siena, Italy) that had been coated 30 years ago with Paraloid B72.

MATERIALS AND METHODS

Reagents. 80PVAc was supplied by the Kuraray Co., Ltd. as a random copolymer, PVA-424H ($M_w = 47\,300$, 80% hydrolyzed), and was used as received. Poly(vinyl alcohol) (PVA, 99% hydrolyzed, $M_w = 146\,000$ – $186\,000$, Sigma-Aldrich), sodium tetraborate decahydrate (borax, >99.5%, Merck), 1-propanol (certified normal grade, Fisher), 2-propanol (HPLC grade, 99.9%, Fisher), 2-butanone (MEK, >99.5%, Fluka), dimethylsulfoxide (DMSO, >99.5%, Merck), acetone (99.5%, Merck), methanol (HPLC grade, Fisher), *N*-methyl-pyrrolidinone (NMP, 99.0% Merck), ethanol (99.5% anhydrous, Aldrich), D₂O and CDCl₃ (D, 99.9%, Cambridge Isotope Laboratories, Inc.), and chloroform (99%, Carlo Erba Reagents) were used as received. Water was purified by a Millipore Elix3 apparatus ($R \geq 15$ M Ω cm).

Preparation of the Polymeric Dispersions. A weighed amount of polymer was placed in a screw-cap vial and stirred in water at room temperature until the solids had dissolved. An aliquot of a 10 wt % borax solution, prepared by heating the salt in water at 50 °C, was added dropwise with stirring (vortex apparatus) to the polymer solution. The polymeric network became rigid after a few minutes. For those samples containing organic cosolvents, such as acetone and 1-propanol, the same procedure was adopted, but the polymer was solubilized in a liquid mixture that provided the desired organic/water liquid ratio after the addition of the aqueous borate solution. All measurements were performed 1 week after the preparation of the dispersions in order to ensure their equilibration.

Rheological Measurements. Rotational and oscillatory shear measurements were carried out on a Paar Physica UDS200 rheometer working at 25 ± 0.1 °C (Peltier temperature control system) using cone–plate geometry (25 mm diameter and 1° cone angle). The gap between the plates was 0.5 mm. After being loaded, samples were equilibrated for 30 min at 25 °C prior to carrying out the experiments. Rotational tests were performed over a torque range of 10^{-4} to 80 mN·m on samples containing from 0.3 to 7 wt % of polymer and from 0.075 to 1.75 wt % of borax. Viscosity values (η_o) were obtained from the plateau of the curves in the low-shear-rate regime (low Newtonian region). Frequency sweep measurements were carried out within the linear viscoelastic range (5% strain) determined by means of an amplitude sweep test. The storage and loss moduli (G' and G'' , respectively) were measured over the frequency range of 0.005 to 15 Hz.

Extensional rheology measurements were made on an Anton Paar Physica MCR 301 rheometer using flat-plate geometry (25 mm diameter) at 25 °C. The gap between the plates was 0.5 mm. Samples were loaded between the plates and then allowed to equilibrate until the force exerted on the top plate was 0 N. To minimize the evaporation of the liquid, the interfaces of the samples with air (i.e., along the perimeters) were coated with mineral oil. The velocity of the top plate was increased linearly from 0.1 to 10 μ m/s. The data were collected and analyzed using Rheoplus/32 Service V3.10 software.

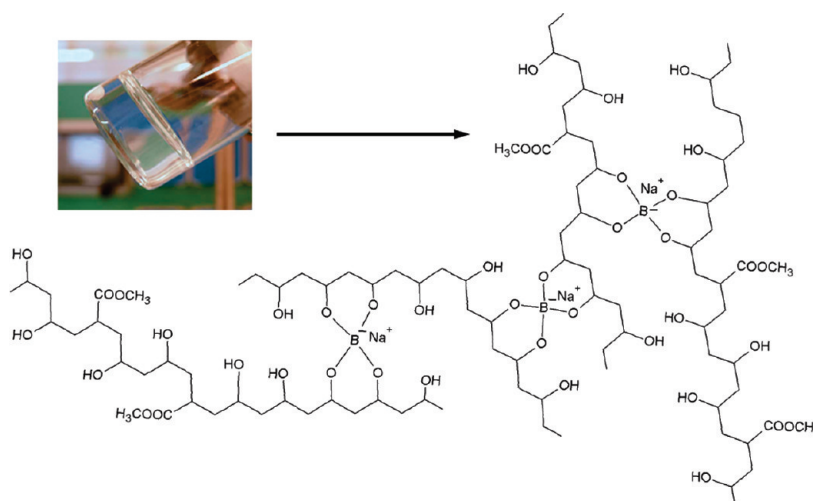
Evaporation Measurements of Dispersions Containing 1-Propanol. A 2 g sample of the dispersion was placed onto a microscope slide so that it covered a ca. 2×2 cm² area and was left in contact with the air for 30 min, during which time the weight decrease was measured on a Mettler AE 163 model analytical balance. The contribution due to the evaporation of water was estimated from experiments with completely aqueous 80PVAc–borax dispersions. The loss of 1-propanol alone was assumed to be the difference between the weight losses over the same time period from nearly equal amounts of dispersions with and without 1-propanol covering the same exposure area.

FTIR Measurements. Fourier transform infrared (FTIR) spectra of dispersions removed with cotton swabs from the surfaces of the paintings were recorded immediately after the cleaning action (vide infra). The swabs were extracted with chloroform, and drops of the obtained solutions were added to premade KBr pellets. Spectra are averages of 32 scans recorded in absorbance mode using a BioRad FTS-40 spectrometer with 4 cm⁻¹ resolution.

HPLC-SEC. A Waters SEC-LS chromatograph with a Waters Alliance 2690 solvent delivery and autoinjector component, a Waters 410 differential refractive index detector, and a temperature-controlled column compartment was used to find the M_w of 80PVAc. Two Tosoh Biosciences TSKGM PW_{XL} columns in series were employed with a mobile phase consisting of aqueous phosphate buffered with saline (PBS). Column calibration was performed with dextran standards. The molecular weight distribution was generated using Empower software from Waters using the M_w data as a function of the elution volume fitted by a linear relation of $\log M$ versus the elution volume.

NMR. ¹¹B NMR spectra were recorded on a Varian 400 MHz spectrometer in 5-mm-diameter quartz tubes from Wilmad Glass with

Scheme 1. Representation of the Structure of the PVAc Network Induced by Borate Cross-Links and (Top Left) an Example of a Cross-Linked Aqueous Dispersion



an external reference capillary containing $\text{BF}_3\text{-Et}_2\text{O}$ in CDCl_3 . A $40\ \mu\text{s}$ observation pulse was found empirically to be sufficient for the relaxation of nuclei in different environments, and 320 FIDs were averaged. Samples were prepared in mixtures of deuterium oxide and nondeuterated organic liquids. A polymer solution was added to a quartz NMR tube, followed by a borax solution, each in the correct amounts to achieve the ratios and absolute concentrations desired. The mixtures were stirred with a long stainless steel needle to aid homogenization. When present, air bubbles were removed from samples by heating or sonicating the tubes.

RESULTS AND DISCUSSION

The structural⁴³ and mechanical^{44,45} properties of viscoelastic solutions of borate and glutaraldehyde cross-linked PVAc with $>88\%$ hydrolysis have been investigated at equilibrium⁴¹ and during the process that leads to the viscoelastic materials.⁴² However, we have not found any studies of the properties of viscoelastic solutions of cross-linked PVAc with lower degrees of hydrolysis, and no materials of this sort are available as cleaning systems for the conservation of cultural heritage. In this work, the properties of a new family of viscoelastic materials based on borate-cross-linked 80PVAc are presented. Attention is focused on the effect on the viscoelastic properties of adding acetone, 1-propanol, methyl ethyl ketone, and *N*-methyl-2-pyrrolidinone (solvents commonly used for the cleaning of paintings) to the aqueous dispersions. Scheme 1 depicts the essential features of the polymeric network, showing how PVAc and borate anions cross-link, and a photograph with a representative sample.

The dispersions based upon 80PVAc–borax were designed to meet three main requirements as cleaning agents of works of cultural heritage: (i) capable of including various solvents for solubilizing/softening quite hydrophobic substances on painted surfaces; (ii) sufficiently viscous to retain organic solvents and retard their evaporation; and (iii) viscoelastic properties that allow them to be peeled off of painted surfaces. The benchmarks for comparison were the rheological and cleaning properties of the previously studied PVA-(2.0 wt %) borax (0.4 wt %) dispersions.³⁵ Unlike the PVA, the 80PVAc could be dissolved in water and some other mixed media at room temperature.

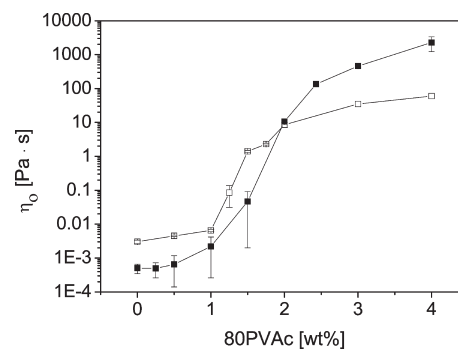


Figure 1. Zero-shear viscosity values for aqueous systems containing 0.4 (□) and 0.6 wt % (■) borax as a function of 80PVAc concentration. The error bars indicate standard deviations.

Although the borax and 80PVAc solutions were added typically at $50\ ^\circ\text{C}$ to increase the rate at which homogeneity is achieved, heating was not necessary. The ability to prepare the dispersions without heating is an important practical attribute of these systems.

Figure 1 shows the trend in the zero-shear viscosity (η_0) as the concentration of 80PVAc is changed whereas the amount of borax is constant at 0.4 or 0.6 wt % (i.e., at lower and higher cross-link densities). In the 0–2 wt % polymer regime, the two curves are similar although the η_0 values indicate that neither is sufficiently viscous to be peelable. Also, the 0.4 wt % borax systems are not suitable for cleaning purposes, even at 80PVAc contents higher than 4 wt %: η_0 reaches an asymptotic value of only $50\text{--}60\ \text{Pa}\cdot\text{s}$. At a borax concentration of 0.6 wt %, the slope of the η_0 curve above the crossing at 2 wt % 80PVAc (viscosity value of $10\ \text{Pa}\cdot\text{s}$, Figure 1) continues to increase dramatically with increasing polymer concentration, by more than 2 orders of magnitude between 2 and 4 wt %.

In Figure 2, the 80PVAc/borax weight ratio has been maintained at 4/1. The 80PVAc concentration range investigated corresponds to 0.08 to 1.7 wt % borax, or in other terms a ratio of hydroxyl groups to borate ions $[\text{OH}/\text{B}(\text{OH})_4^-]$ of almost 12/1 or 3/1 in terms of total number of hydroxyl groups on the

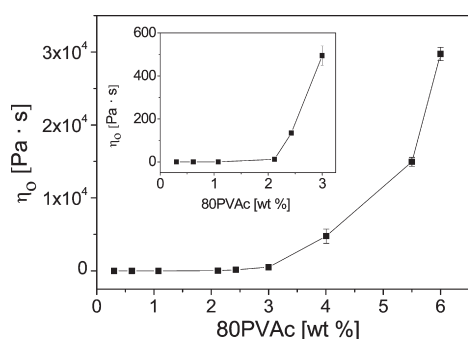


Figure 2. Zero-shear viscosity values for aqueous dispersions of 80PVAc–borax as a function of polymer concentration at a constant 80PVAc/borax weight ratio of 4. The error bars indicate standard deviations. The inset expands the lower concentration region to demonstrate the precipitous increase in η_0 above ca. 2 wt % polymer.

Table 1. Maximum Amounts (wt %) of Organic Solvents That Could Be Mixed with Water in 4 wt % Polymer and 1 wt % Borax Dispersions (i.e., Corresponding to 17/1 and 12/1 [OH]/[B(OH)₄[−]] Ratios for PVA and 80PVAc, Respectively) without Visible Phase Separation

M_w	PVA ³⁵		80PVAc
	146 000–186 000		~47 300
ethanol	30%		50%
1-propanol	25%		50%
2-propanol	25%		50%
acetone	15%		40%
MEK	not measured		20%
NMP	30%		50%

polymer and the potential number of stable cross-links—four hydroxyl groups, two on vicinal carbon atoms of two polymer chains—is necessary to establish a complete cross-link. However, it is known that a significant fraction of the borate ions do not participate in cross-links,^{47,48,52,53} and some hydroxyls of 80PVAc do not have a vicinal partner; the actual fraction that is cross-linked will be estimated later by ¹¹B NMR.

Intramolecular cross-linking predominately occurs when a cross-linker is added to a polymer solution below the critical overlap concentration. To effect a significant increase in viscosity, polymer chains must overlap sufficiently to develop an extended network upon cross-linking. Significant overlap will not occur below the reciprocal of the intrinsic viscosity limit for 80PVAc, estimated to be ca. 1.1 g/100 mL.⁵⁴ The results in Figure 2, showing that η_0 is nearly constant up to ca. 2 wt % polymer, are consistent with this assessment. However, η_0 increases rapidly thereafter and reaches a value of 30 000 Pa·s at 6 wt % 80PVAc. These results and those in Figure 1 demonstrate that it is possible to change the viscosity of the dispersions dramatically by varying the concentration of either the polymer or both the polymer and the cross-linker. This is a very attractive attribute of the 80PVAc–borax systems because it allows a conservator to tune the mechanical properties to fit a specific cleaning task best. The 4 wt % 80PVAc/1.0 wt % borax dispersion was selected for additional study because it was able to accommodate the maximum amounts of organic solvents (vide infra, Table 1).

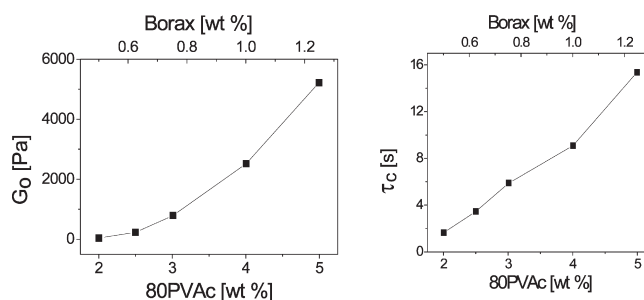


Figure 3. Intrinsic elastic shear modulus and apparent relaxation time as a function of the 80PVAc concentration in water.

Oscillatory shear measurements were also performed to obtain information about the viscoelasticity of the 80PVAc dispersions. As shown in Figure 3, there is an almost linear increase in both the intrinsic shear elastic modulus (G_0) and the apparent relaxation time, τ_c (defined as $1/\omega_c$, where ω_c is the frequency of crossover of the G' and G'' curves⁴⁹), with increasing polymer concentration and consequently borax (keeping the ratio constant). These data indicate, as expected, that the dispersions become stiffer as the polymer concentration increases. Both G_0 and τ_c suggest increasingly elastic behavior characterized by more cross-links. Therefore, there is an absolute increase in the number of cross-links, but the percentage of complexed boron remains constant as long as the ratio of 4/1 is kept constant as demonstrated by the ¹¹B NMR data provided.

¹¹B NMR has been used here to quantify the fraction of borax-derived species participating in 80PVAc cross-links and thus the absolute concentration of those cross-links.^{52,53} Qualitatively, we have noted that the viscosity of the dispersions increases at a constant 4/1 80PVAc/borax weight ratio when the concentration is increased. Materials prepared with polymer concentrations above 3 wt % polymer have the appearance of solidlike gels. However, the integration of the areas under the peaks of the spectra for cross-linked and free boron species shows that the fraction of boron actively participating in cross-links remains relatively low and independent of the polymer concentration when the 80PVAc/borax weight ratio is kept constant at 4/1 (Supporting Information Figure S3). These results indicate that the large change in viscosity is due mainly to the absolute concentration of cross-links and perhaps polymer chain entanglements with attendant hydrogen bonding among the hydroxyl groups of different polymer chains.

A comparison of the ability of the PVA–borax and 80PVAc–borax dispersions to accept different organic solvents (added to the water component) is presented in Table 1. Although the dispersions with PVA³⁵ can accept up to 25 wt % 1-propanol and 15 wt % acetone into their aqueous phase, much higher percentage can be achieved in the 80PVAc dispersions as a result of the presence in the latter of less-polar acetate groups.

As shown previously,^{34,35} the PVA–borax dispersions can be formulated to have high shear elastic moduli. The same is true of the 80PVAc–borax dispersions. Their frequency sweep curves show the typical behavior of polymeric dispersions in which $G' > G''$ at high frequencies and $G'' > G'$ at low frequencies in those samples containing up to 40 wt % 1-propanol. Above this 1-propanol concentration, the crossover point between G' and G'' curves shifts to lower frequencies (Figure 4a,b); in the 50 wt % 1-propanol dispersion, we observed the lack of a crossover within the frequency range investigated ($>2 \times 10^{-3}$ Hz).

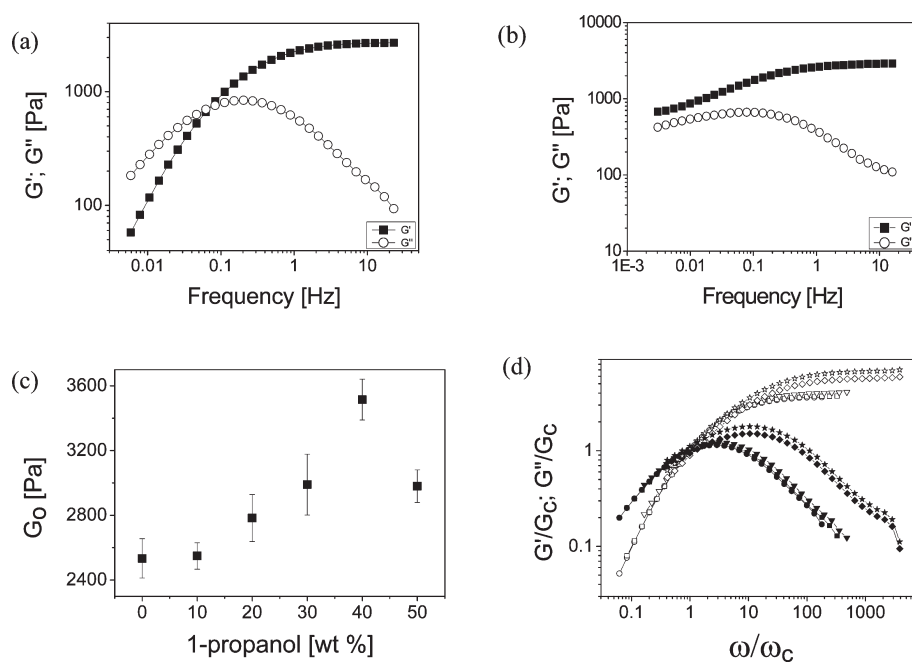


Figure 4. Frequency sweep curves for an 80PVAc-based dispersion containing (a) 10 wt % 1-propanol and (b) 50 wt % of 1-propanol. (c) Intrinsic shear elastic modulus as a function of 1-propanol content. (d) Normalized mechanical spectra at different 1-propanol concentrations. G'/G_c (open symbols) and G''/G_c (closed symbols) data at 0 (○), 10 (□), 20 (△), 30 (◇), and 40 (★) wt % 1-propanol. G_c is the crossover modulus, and ω_c is the crossover frequency.

Thus, the average relaxation times and the solidlike character of the 4 wt % 80PVAc/1 wt % borax systems increase upon the addition of organic solvents. The intrinsic shear elastic modulus, G_0 , of these dispersions, taken as the asymptotic values of the G' curves (and thus the elasticity), also increases with increasing 1-propanol content (Figure 4c). Only at 50 wt % 1-propanol does the elasticity decrease. Analogous behavior was found in samples with added acetone, including the absence of a crossover point in the dispersion containing the highest acetone concentration, 30 wt % (Figure S1a–c in Supporting Information). Overall, this behavior demonstrates that the organic solvents strengthen the cross-linking networks of the dispersions.³⁵

Figure 4d shows the mechanical spectra of samples containing 0, 10, 20, 30, and 40 wt % 1-propanol normalized to the crossover point. The curves of the 0–20 wt % 1-propanol samples overlap within the range of frequencies investigated. Curves of the 30 and 40 wt % 1-propanol systems are almost the same, but they differ from the curves for the 0–20 wt % dispersions; the overall timescale of the relaxations and the distribution of the relaxation times change with the concentration of an organic solvent. With the trends in G_0 shown in Figure 4c, these data suggest that the alcohol molecules induce an increase in the cross-linking in the polymer–borate networks.

To investigate the effect of alcohol content on cross-linking, ^{11}B NMR spectra of aqueous 80PVAc–borax dispersions with varying amounts of 1-propanol were recorded (Figure 5). As the amount of alcohol in the liquid component of the dispersions is increased, the number of borate ions participating in cross-links with the PVAc chains also increases. The noncomplexed boron signal in the ^{11}B NMR spectra shifts further downfield as the organic content in the liquid fraction of the dispersions increases, indicating a decrease in the borate ion/boric acid equilibrium (i.e., an increase in the amount of uncharged boric acid). It appears that the environment created by large concentrations of

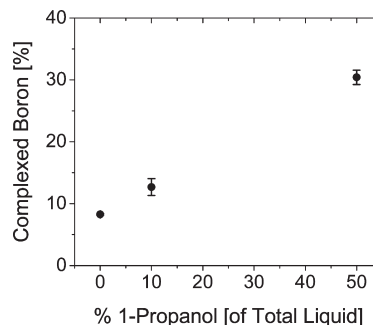


Figure 5. Percent of cross-linked boron from ^{11}B NMR spectra as a function of the fraction of 1-propanol in the liquid component of dispersions with 2 wt % 80PVAc and 0.5 wt % borax.

organic liquids is less attractive to borate ions, forcing them either to become complexed with PVAc chains or to convert to boric acid. The net migration of borate ions toward the polymer chains may also be responsible for the observed decrease in “free” (freezeable) water as the organic component is increased.³⁵

The dependence of the intrinsic elastic modulus of 4 wt % 80PVAc/1 wt % borax dispersions on the amount of an added organic solvent is shown in Figure 6. The moduli increased—leading to stiffer materials—for up to 30 wt % acetone and NMP, 20 wt % MEK, and 40 wt % 1-propanol. Extensional rheology (in which two parallel plates sandwiching a dispersion are moved progressively farther from each other) also shows an increase in the strength of the networks as the amount of organic solvent is increased (Figure 7). Although the error bars in Figure 7b are large, the trend is clear: the maximum force necessary to pull the dispersions apart, a quantitative measure of their “stiffness”, increases. As mentioned before and consistent with these observations as well as the increase in the relaxation time, the

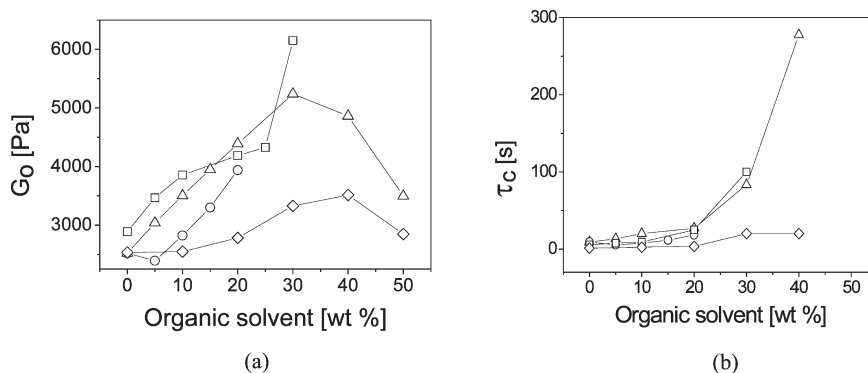


Figure 6. (a) Intrinsic shear elastic modulus and (b) apparent relaxation time as a function of the amount of added (\diamond) 1-propanol, (Δ) NMP, (\square) acetone, or (\circ) MEK in dispersions containing 4 wt % 80PVAc and 1 wt % borax.

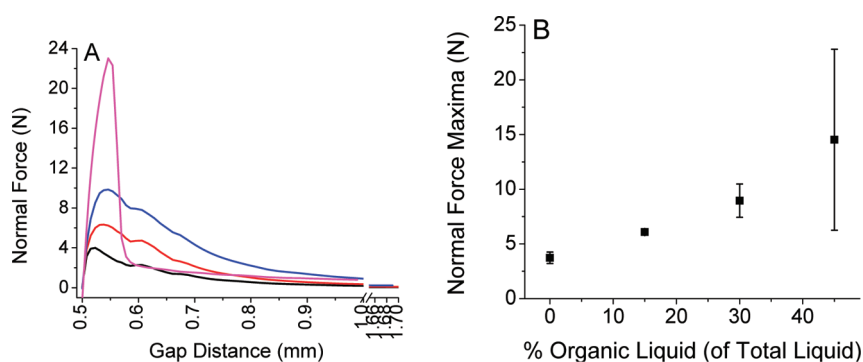


Figure 7. (A) Extensional rheological curves and (B) values of and maximum force for dispersions prepared from 4 wt % 80PVAc, 1 wt % borax, and different fractions of 1-propanol in the liquid: (—) 0 wt %, (red —) 15 wt %, (blue —) 30 wt %, and (purple —) 45 wt %.

organic solvents strengthen and stabilize the cross-links of the polymeric networks.

Application of 80PVAc–Borax Organoaqueous Dispersions for Cleaning Painted Surfaces. As mentioned, the mechanical properties of the PVA–borax and PVAc–borax dispersions are desirable for cleaning works of art²⁵ because the highly elastic character of the dispersions facilitates their removal from surfaces. As explained previously,³⁴ the most important parameter in the rheological behavior that indicates peelability is the intrinsic shear elastic modulus G_0 that corresponds to the asymptotic value of G' at high frequencies. The soft mechanical perturbation during peeling relies upon frequency components in the range from several to hundreds of Hertz. For poly(acrylic acid)-based gels traditionally used in conservation, peelability is not possible because the corresponding G_0 values are ca. 200 Pa; for many PVA systems that are peelable, G_0 values are always larger than 400 Pa.³⁴ Therefore, we conclude that the threshold value for peelability is ca. 400 Pa at frequencies typical of the perturbations commonly induced during the removal of the dispersions from a painted surface (i.e., somewhat more than a few Hz). Also, the high viscosity of these polymeric dispersions should help to control the rate of their cleaning action on a surface and attenuate the evaporation of the solvent. In addition, the PVAc–borax systems offer specific advantages over the PVA–borax dispersions: (1) higher concentrations and wider ranges of organic solvents increase the ability to swell or soften/solubilize several different forms of varnishes and other hydrophobic coatings on the surfaces of works of art and offer better

Table 2. 80PVAc–Borax Dispersions Applied to the Surface of the “Santo Stefano” Wood Panel

	80PVAc (wt %)	borax (wt %)	H ₂ O (wt %)	1-propanol (wt %)
A	4	1	50	50
B	3	0.75	70	30
C	4	1	70	30

control of the cleaning action³⁵ and (2) preparation of the 80PVAc–borax dispersions does not require heating (Materials and Methods section) as a result of the high solubility of 80PVAc in water.⁴⁶

Evidence of these benefits was obtained during cleaning tests performed in cooperation with and under the supervision of conservators at the International University of Art Foundation of Florence (Fondazione Università Internazionale dell’Arte, UIA) on the surface of a wood panel by Lodovico Cardi (called “Il Cigoli”, 1559–1613), entitled “Santo Stefano”. The painted surface was coated with a thick layer of dark, oxidized natural resins that had been applied uniformly for protection during previous conservation treatments. The tests were conducted in an area close to the one already treated by our PVA–borax dispersions containing different amounts of 1-propanol.³⁵ After preliminary cleaning tests with neat liquid solvents, formulations of the 80PVAc–borax dispersions containing two different fractions of 1-propanol in the liquid component were applied to the surface of the painting.

In all cases, the 80PVAc/borax ratio was 4/1 (Table 1). The dispersions were placed onto three adjacent regions of the surface by means of a spatula and kept there for 1 min (Table 2). During this contact period, less than 0.1%



Figure 8. “Santo Stefano” by Ludovico Cardi, called “Il Cigoli”. The black box indicates the area in which tests were conducted. See the text for an explanation of A–C.

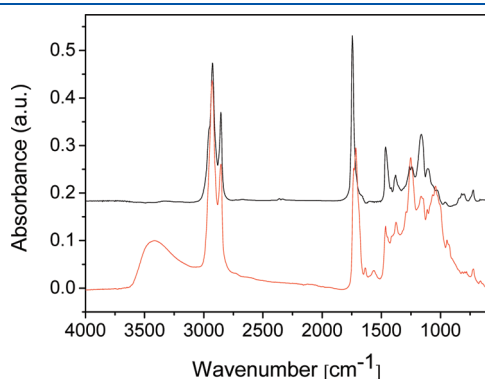


Figure 9. FTIR spectra of the material removed by a cotton swab after treatment with formulation C (red line, reported in Table 2) and of an aged natural resin (black line⁵⁰).

of the liquid evaporated (Figure S2 of the Supporting Information).

The results from the cleaning actions, shown in Figure 8, demonstrate that the cleaning efficiency depends acutely on the composition of the dispersion and can be changed easily by varying the amount of 1-propanol. The dispersion (A) containing 50 wt % 1-propanol was considered to be too aggressive by the conservators: in Figure 8A, the dark coating had been completely removed after 1 min of contact; the cleaning action was not controlled adequately. Reducing the amount of 1-propanol to 30 wt %, as in formulation C (Figure 8B,C) allowed much better control. Qualitatively, the same cleaning action was observed using formulation B, in which 80PVAc is reduced to 3 wt % whereas the 1-propanol concentration is the same as in formulation C; compare Figure 8B,C.

As mentioned, the versatility and ease of changing the cleaning action of the PVAc–borax dispersions by simply tuning the concentrations of the components are important improvements over our previous PVA–borax systems.³⁵ Specifically, the cleaning action of the PVA–borax dispersions was controlled primarily by changing the contact times or by applying more than one dispersion to the same surface area.

Because the mechanical attributes of the PVA–borax dispersions (NB, viscoelasticity) are maintained in the 80PVAc–borax dispersions, it was possible to remove both by peeling them off of a painted surface in a single step using tweezers. However, as observed when the PVA–borax dispersions were employed, after



Figure 10. Wall paintings by Il Vecchietta in Santa Maria della Scala in Siena. The boxed area at left shows where the 4 wt % 80PVAc/1 wt % borax dispersions with 40/60 1-propanol/water were applied.

Table 3. Formulations of and Rheological Data for the Dispersions Applied to the “Santo Stefano” Panel and Comments of the Conservators Who Conducted the Cleaning Tests

formulation	component concentrations				comments			rheological properties
	80PVAc ^a	borax ^a	H ₂ O ^b	1-propanol ^b	ease of application	cleaning action	ease of peeling	
A	4	1	50	50	good	bad	excellent	$G_0 = 2990 \text{ Pa}$ $\tau_c \rightarrow \infty$ $\eta_0 = 12\,800 \text{ Pa}\cdot\text{s}$
B	3	0.75	70	30	excellent	good	excellent	$G_0 = 2760 \text{ Pa}$ $\tau_c = 28 \text{ s}$ $\eta_0 = 13\,700 \text{ Pa}\cdot\text{s}$
C	4	1	70	30	good	good	excellent	$G_0 = 2980 \text{ Pa}$ $\tau_c = 31 \text{ s}$ $\eta_0 = 28\,500 \text{ Pa}\cdot\text{s}$

^a wt %. ^b wt % of the liquid component.

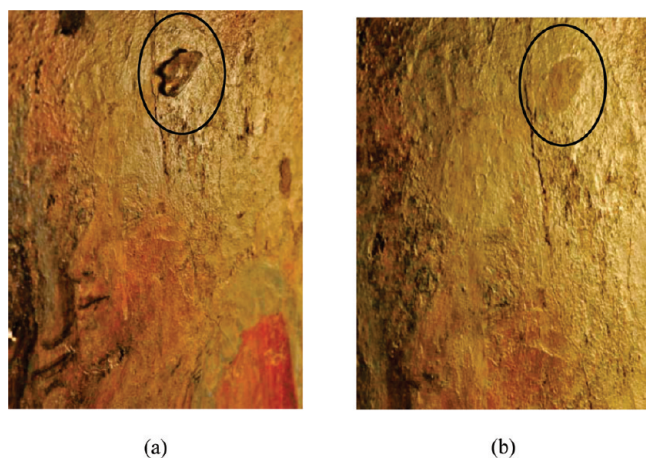


Figure 11. Grazing light images obtained (a) during and (b) after the cleaning test. The black ovals highlight the area at which the cleaning dispersion was applied and from which it was removed.

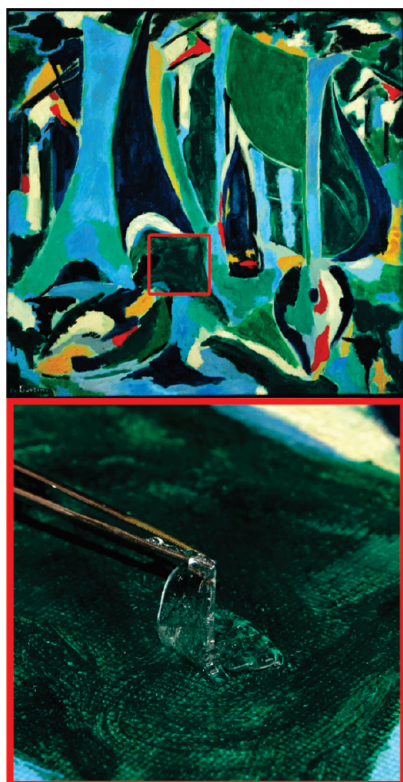


Figure 12. Photograph of the painting oil on canvas “Les Voiles” by Marcel Burtin (1902–1979) with the magnification of the region where the PVAc/borate polymeric dispersion was peeled off from the surface by means of tweezers; 3 wt % 80PVAc/0.75 wt % borax in water.

1 min of contact time and peeling off of the 80PVAc–borax dispersions, some of the brown coating remained but was softened sufficiently to be removed with a cotton swab (NB, a procedure commonly employed by conservators working with poly(acrylic acid)-based gels and other cleaning agents⁵⁵). Figure 9 shows the FTIR spectrum of the material extracted from the cotton swab that was used to remove the coating layer

after the application of formulation C; it is attributed to a natural resin.⁵⁰

Of the 80PVAc–borax formulations tested, C was judged the best by the conservators (Table 2) in terms of the ease of application, removal by peeling action, and cleaning power; it allowed the very gradual and controlled removal of the aged varnish so that the pigment layer could be retained without apparent damage.⁵¹

The ability of the 80PVAc–borax dispersions to remove a layer of an aged acrylic resin, applied almost 30 years ago to the surfaces of wall paintings by Vecchietta in the Old Sacristy of the S. Maria della Scala in Siena (Figure 10), was also tested. In this case, the main challenge was to determine whether the 80PVAc–borax dispersions could clean a vertical surface well while adhering to it with sufficient strength for the period required. After experiments conducted on test panels that were placed vertically in the laboratory, it appeared that 80PVAc–borax dispersions with 40 wt % 1-propanol should meet these requirements. The area tested in the box in Figure 10 has a glossy surface indicative of an organic coating. The polymeric dispersion was applied for 25 min to a portion of the hat of the man portrayed with his arms crossed and then removed with metal tweezers. The grazing light image after the cleaning procedure (Figure 11) clearly shows the absence of the organic coating in the area where the 80PVAc–borax dispersion was applied.

CONCLUSIONS

The mechanical and rheological properties of viscoelastic dispersions comprising mixtures of water and organic liquids in matrixes of 80% hydrolyzed poly(vinyl acetate) cross-linked by borate ions have been correlated with the structures of the cross-linked networks and the influence of the concentration and structure of the organic liquid on them. The stiffness of the dispersions can be increased or decreased, as desired, by varying the concentrations of the polymer, borax, and organic liquid. These correlations can be related principally to the degree of cross-linking by the borate ions. The stiffness is strictly correlated to the intrinsic shear elastic modulus, G_o : we showed that when $G_o > 400$ Pa the rheological behavior allows the peelability of the cleaning system from the surface of the painting by a simple one-step soft mechanical action such as that realized by tweezers as well visualized in Figure 12.

The dispersions are better cleaning agents than the analogous dispersions composed of fully hydrolyzed poly(vinyl acetate) in several important ways: (1) they can be made without heating; (2) they can incorporate a much wider range of organic liquids; and (3) they can incorporate much larger quantities of the organic liquids. Tests performed on two different types of painted surfaces demonstrate the attributes of these dispersions. The correlation of the structural and rheological characteristics of the dispersions with their ability to clean works of cultural heritage is an important step in ensuring that such treatments will be effective and cause minimal collateral damage.

The trend, that increasing the fraction of retained acetate side chains of poly(vinyl acetate) increases the amount and range of organic liquids that can be retained in a dispersion with borate cross-links, is demonstrated. However, there must be an optimal compromise among some competing factors that control the strength of the dispersions—the fraction of sites with vicinal hydroxyl groups (needed for cross-linking), the solubility of the aqueous borate portion of the liquid in the polymer matrix, and

the stabilizing influence of interchain H-bonding—and the amount of organic liquid that can be incorporated. At some point, the cross-linking efficiency will become too low and it will not be possible to prepare dispersions that are peelable and good surface cleaning agents. In future work, we will explore these aspects of the dispersions.

■ ASSOCIATED CONTENT

S Supporting Information. Frequency sweep curves. Weight loss as a function of time. Percent of cross-linked boron calculated from ^{11}B NMR spectra of aqueous samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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