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# ALKYL CARBONATE SOLVENTS CONFINED IN POLY (ETHYL METHACRYLATE) ORGANOGELS FOR THE REMOVAL OF PRESSURE SENSITIVE TAPES (PSTS) FROM CONTEMPORARY DRAWINGS

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## Abstract

The removal of aged pressure-sensitive tapes (PSTs) from contemporary drawings is a frequent and challenging task for paper conservators: in this work an innovative method to overcome this issue is presented. Aged PSTs are largely found on paper artworks due to their use for mending, mounting and framing operations. Nevertheless they may provoke several drawbacks on artworks (e.g. media bleeding and adhesive mass migration): the necessity of their removal promoted the development of several methodologies, but they all pose risks to both artifacts and conservation professionals. We propose a method involving polymeric gels able to load a “green” solvent, pertaining to the class of alkyl carbonates, which efficiently interacts with PSTs components; the embedment of the solvent into the gel network allows a feasible and effective intervention where the gel is directly applied on the top surface of the PST: the solvent gradually penetrates through the plastic layer of the PST (as proved by Laser Scanning Confocal Microscopy measures), swelling the underlying adhesive. In this way, the solvent-artwork contact is minimized. In order to optimize the processing costs and final properties of the gels, three formulations of poly (ethyl methacrylate)-diethylcarbonate (PEMA-DEC) organogels were synthesized, using different diluents and additives. A thorough physico-chemical investigation of the systems was performed by means of rheology, gravimetric analysis, thermogravimetry, and IR Spectroscopy. After assessment on representative mock-up

samples, the developed systems were successfully used for the removal of six aged PSTs from a drawing on paper by Keith Haring.

## Introduction

Adhesives, both natural and synthetic, are widely used in the restoration practice, yet in many cases their aging produces aesthetic alterations, or the formation of volatile and acidic compounds that are detrimental to the artefacts [1–3]. Following their invention in 1845 (attributed to Dr. Horace Day) for medical purposes, Pressure Sensitive Tapes (PSTs) were industrially developed in the 1920s, and largely exploited in different applicative fields [4]. PSTs were also extensively used on artworks, especially on paper, for framing and mounting, repairing lacerated pages, or holding together different parts of the artifacts. PSTs present a multi-layered structure, composed of a pressure-sensitive adhesive (PSA) and its carrier (backing). Minor components include a release coat, ensuring an easy unrolling of the tape, and a primer, that enhances adhesion between the backing and the adhesive layer. Backing materials comprise paper, fabric, cellophane, cellulose acetate, oriented polypropylene, etc. The most common PSAs are composed of either rubber, acrylic co-polymers, styrene or silicone, and are either solvent or water-based [5]. The aging of PSTs, primarily due to oxidation processes of the adhesives, leads to changes in adhesiveness and color (yellowing) with loss of structural function, or to disfiguring and damaging effects on artworks such as media bleeding, stains, plasticizer migration, and cockling of paper [5]. Therefore, in order to preserve the integrity of artworks, aged PSTs need to be removed. Depending on the artistic substrate on which they are applied, current strategies for PSTs removal include mechanical methods, immersion, the use of poultices and suction tables. However, each method involves some risks, which often result in undesired damage to the artwork: mechanical removal may cause skinning of the paper [6], suction techniques or poultices can lead to formation of tidelines or media bleeding, immersion treatments tend to cause media solubilization, especially on contemporary artworks where highly water or solvent-sensitive materials are frequently used (e.g. inks of ball-point or felt-tip pens). Wet methods often involve the use of volatile and toxic organic solvents, such as tetrahydrofuran, toluene, xylene, acetone, and *N,N*-dimethylformamide, considerably hazardous for conservation professionals. Here we propose an innovative approach using polymeric organogels based on a poly (ethyl methacrylate) (PEMA) network, aimed at minimizing the risks to artworks and conservators in the removal of aged PSTs from contemporary drawings. A polymeric organogel consists of two phases, i.e. a solid polymeric network and a liquid organic solvent embedded in the network. Alkyl carbonates, in particular diethyl carbonate (DEC), were selected

owing to their low eco-toxicological impact and the ability to swell/solubilize most of the PSAs [7]. Extensive solubility tests proved that these solvents are inert towards the most common contemporary artistic media, such as ball-point and felt-tip pens. As described in previous works, the confinement of cleaning fluids in polymeric gel networks allows to control their spreading, penetration, and evaporation rate, as opposed to the use of non-confined fluids [8–11]. Here, further minimization of the intervention invasiveness was achieved thanks to the possibility of applying the gels directly on the top surface of the PSTs; Laser Scanning Confocal Microscopy (LSCM) measurements showed the penetration of the solvent into the polypropylene backing layer of a model PSTs (PP-PST), providing insights in the mechanism of interaction with the adhesive.

Polymeric organogels based on poly (methyl methacrylate) (PMMA) networks were previously successfully used for the removal of unwanted materials from artistic substrates [10,11]. In our case, the polymerization of ethyl methacrylate (EMA) using DEC as diluent was preferred to MMA, in order to reduce the eco-toxicological impact also during processing. Furthermore, the possibility to reduce processing costs using a different diluent (2-propanol) or additives (polyethylene glycol, PEG<sub>1000</sub>) was also explored.

The equilibrium solvent content and the release rate (on model paper samples) of the PEMA-DEC gels were measured. The evaporation kinetics of the confined solvent was investigated, because reducing the solvent's volatility is essential to grant prolonged contact with the PSTs. The study of the swelling kinetics and mechanical properties of the gel (by means of rheological measurements) permitted to evidence structural changes induced by the use of different diluents or by the addition of PEG<sub>1000</sub>.

Finally, applicative tests were carried out on representative mock-up samples, before using the developed PEMA-DEC systems for the removal of six aged PSTs from a drawing by Keith Haring (*Untitled* – ink on paper – 46,5 x 34,5 cm, signed and dated 'K. Haring May 10-83 Napoli'), belonging to the *Naples Series* and realized on the occasion of the artist's first European exhibition in May 1983 at the Lucio Amelio Gallery in Naples,. ATR-FTIR analysis was used to assess the removal of the PSTs and the absence of gel residues after treatment.

## **Experimental**

### Materials

Ethyl 2-methylprop-2-enoate (EMA) (Sigma-Aldrich, purity  $\geq$  98.5%), 2-(2-methylacryloyloxy)ethyl 2-methylacrylate (EGDMA) (Sigma-Aldrich, purity  $\geq$  99%), 2,2'-Azobis(2-methylpropionitrile) (AIBN) (Fluka, purity  $>$  98%), polyethylene glycol (average Mw  $\approx$  1000 kDa)

(PEG<sub>1000</sub>), diethyl carbonate (DEC) (Sigma-Aldrich, purity  $\geq 98.5\%$ ), and 2-propanol (CTS, denatured isopropyl alcohol, 4% 2-methyl-1-propanol) were used for the syntheses of gels. Fluorescent probes used for Laser Confocal Scanning Microscopy (LCSM) experiments were Coumarin 6 (Cou6) (Sigma-Aldrich, purity  $\geq 99\%$ ) and Rhodamine B Isothiocyanate (RhBITC) (Sigma-Aldrich, purity  $> 99\%$ ). All chemicals were used as received. Pressure sensitive tape with polypropylene backing (PP-PST) was purchased from Tesa<sup>®</sup> (product code 56100), blue ball-point pen ink was from Bic<sup>®</sup>.

### Synthesis of Organogels

PEMA-based organogels were prepared by radical polymerization of EMA solubilized in different organic solvents (i.e. DEC, 2-propanol), using AIBN as initiator and EGDMA as cross-linker (both 1% w/w as compared to EMA). PEMA/PEG organogels were prepared by adding PEG<sub>1000</sub> to the reaction solution. Syntheses were carried out in glass moulds, in order to obtain gel sheets of 1-2 mm thickness. The polymerization reaction was carried out at constant temperature (55°C) for 6 hours, as described in previous works [10,11]. After gelation, the gel films (5 g each) were immersed in DEC (20 mL) for 24 h, to extract possible unreacted monomer. After the first extraction, the solvent was refreshed. Before characterization, organogels were let to equilibrate with DEC. Table 1 lists the name of the gels, and the composition of the solutions used for the polymerization reaction.

	<b>MONOMER</b> (w/w %)	<b>SOLVENT</b> (w/w %)		<b>PEG<sub>1000</sub></b> (w/w %)
<b>ED50</b>	50	DEC	50	-
<b>EI50</b>	50	IP	50	-
<b>EI50P10</b>	40	IP	50	10

Table 1 - Compositions (w/w) of the pre-gel solutions of the organogels (i.e. monomer, solvent, and additives).

The presence of monomer in the refreshed solvent was checked with FT-IR measurements: a BioRad FTS-40 spectrometer recorded spectra from 4000 to 400 cm<sup>-1</sup>, at 4 cm<sup>-1</sup> spectral resolution, averaging 32 scans, after a delay-time of 300 s. For the analysis 20 µl of the exchange solvent were put on a KBr pellet (about 200 mg; KBr, Sigma-Aldrich, FT-IR grade  $\geq 99\%$ , trace metal basis).

The reaction yield was calculated as the ratio between the mass of the dried organogels,  $W_d$ , and the mass of the monomer in the initial mixture,  $W_0$  (in the case of PEMA/PEG systems the weight of both the monomer and PEG<sub>1000</sub> was considered):

$$\text{yield (\%)} = \frac{W_d}{W_0} \cdot 100 \quad (1)$$

$W_d$  was obtained by placing swollen gels under nitrogen flux at 30°C for 2 hours and then under a fume hood overnight, until a constant weight was reached.

### Physico-chemical characterization

The equilibrium solvent content,  $ESC\%$ , was obtained by means of Differential Thermogravimetry (DTG) using a SDT Q600 (TA Instruments) apparatus. Fully swollen gel samples of 2-3 mg were placed in aluminium pans and subjected to a temperature scan from 20 to 500 °C (10 °C/min) in a nitrogen atmosphere (100 mL/min). The temperature range for solvent removal is 20-150°C (the boiling point of DEC is 125.8°C).  $ESC\%$  was calculated as follows:

$$ESC\% = \frac{W_s}{W_g} \cdot 100 \quad (2)$$

where  $W_s$  is the amount of solvent loaded in the sample as determined by DTG, and  $W_g$  is the mass of the fully swollen gel.

The quantity of released solvent,  $SR$ , on a model porous substrate was assessed by gently drying the surface of the swollen gels, and then placing them on Whatman® filter sheets ( $\varnothing = 55$  mm) for 15 minutes, a representative time of real applications in cleaning interventions. During tests, the gels were covered with plastic foils to prevent solvent evaporation. The amount of released solvent was measured gravimetrically and normalized by unit area.

The dynamics of interaction between the solvent-loaded polymeric gels and a model polypropylene backing PST were studied by means of Laser Scanning Confocal Microscopy (LSCM), using a Leica TCS SP2 instrument equipped with a 20x air objective. The fluorescent probes Cou6 and RhBITC were respectively excited with 488 and 561 nm laser lines. The fluorescence signals were acquired in the ranges 498–539 nm for Cou6 and 571–636 nm for RhBITC. The acrylic adhesive of PP-PST was labelled by simple immersion of the sample in an aqueous solution of RhBITC (20 mM). For LSCM measurements, the gels were equilibrated in DEC previously marked with Cou6 (20 mM). The experimental setup was designed in order to mimic a real application: a labelled PP-PST was attached on a coverglass, and a gel sample loaded with Cou6-labelled DEC was layered on it. To study the interaction between the solvent and the PP-PST, the samples were visualized through confocal microscopy for a period of 20 minutes.

Field Emission Gun Scanning Electron Microscopy (FEG-SEM) on the polypropylene backing was carried out with a FEG-SEM SIGMA (Carl Zeiss, Germany) using an acceleration potential of 25 kV and a working distance of 1.8 mm. For the analyses, a gold-metallization of the sample was performed with an Agar Scientific Auto Sputter Coater.

The evaporation rate of both confined and bulk DEC was assessed gravimetrically by exposing the swollen gels and bulk solvent to room conditions ( $T = 25^\circ\text{C}$ ,  $\text{RH} = 65\%$ ) and normal air circulation

(no ventilation/aspiration) within 60 minutes. Approximately 0.30 g of swollen gels was compared to an amount of DEC equal to the  $ESC\%$ . The residual solvent fraction at time  $t$ ,  $F_s$ , is defined as follows:

$$F_s = \frac{M_t}{M_{inf}} \quad (3)$$

where  $M_t$  is the mass of residual solvent at the given time, and  $M_{inf}$  is the total amount of solvent in the fully swollen gels, as derived by calorimetric analysis.

Solvent uptake kinetics were evaluated by immersing the completely dried gels (as previously described) in DEC; the gels were then weighted at given time intervals, up to complete swelling.  $F_s$  values, as defined in (3), were reported.

Rheological measurements were performed on a TA Instrument Hybrid Rheometer DISCOVERY HR-3, using a plate-plate geometry (diameter 20 mm) with a maximum axial force of 1 N; all the measurements were carried out at 25°C (Peltier temperature control system). Silicon oil was used during analysis in order to prevent the evaporation of DEC. Oscillatory shear measurements (shear strain between 10<sup>-3</sup> and 80%, oscillation frequency 1 Hz) were carried out in order to determine the linear viscoelastic region and the critical oscillation strain. Frequency sweep tests for the determination of the frequency dependence of the storage and loss moduli  $G'$  and  $G''$  were carried out within the linear viscoelastic range (shear strain 0.1%) over the frequency range 0.1 - 100 Hz.

#### Removal of PSTs from paper artifacts

Before application on the real case study, the removal of PSTs from cellulosic substrates using the PEMA-DEC organogels was assessed on Whatman® filter paper and on printing paper/ink mock-up samples.

Mock-ups were prepared by covering part of the ball-point pen inked area of printing paper with a polypropylene backing PST and an acrylic copolymer adhesive (i.e. PP-PST). The excess of solvent was removed from the gels surface with absorbent paper; then the swollen gels were shaped with a scalpel to match the dimension of the PST, and applied on the samples. ATR-FTIR spectroscopy was performed on samples treated with the gels to assess the gels' cleaning effectiveness; further analyses were carried out on Whatman® paper samples to investigate the presence of gel residues on the treated substrates. A Thermo Nicolet Nexus 870 FTIR spectrometer equipped with a Golden Gate diamond cell was used; spectra were collected with an MCT detector (sampling area of 150 μm<sup>2</sup>), averaging 128 scans in the 4000-650 cm<sup>-1</sup> range, with a spectral resolution of 4 cm<sup>-1</sup>. The possible presence of gel residues was double-checked performing 2D FTIR imaging on the Whatman® samples, using a Cary 620-670 FTIR microscope, equipped with an FPA 128x128 detector (Agilent Technologies). The spectra were recorded directly on the surface of the samples

(or of the Au background) in reflectance mode, with open aperture and a spectral resolution of 4  $\text{cm}^{-1}$ , acquiring 128 scans for each spectrum. A “single-tile” analysis results in a map of 700 x 700  $\mu\text{m}^2$  (128 x 128 pixels), and the spatial resolution of each Imaging map is 5.5  $\mu\text{m}$  (i.e. each pixel has dimensions of 5.5 x 5.5  $\mu\text{m}^2$ ). “Mosaics” of 1400 x 2100  $\mu\text{m}^2$  were acquired to observe a larger field of view.

The removal of PSTs from the Keith Haring artwork was performed using the ED50 gel, following the procedures implemented on mock-ups. The solubility of the artistic media in DEC was previously assessed by micro-solubility tests. After the removal of PSTs from the original drawing, ATR-FTIR analysis was used to assess their chemical composition.

## **Results and Discussion**

To be suitable for cleaning sensitive artworks, a gel must allow the gradual release of the solvent on the artwork’s surface avoiding possible damages due to uncontrolled solvent spreading. Moreover, the mechanical properties of the gel must allow its easy handling and removal, without leaving polymer residues on the artworks. Finally, optical transparency of the gel is desirable, since it helps the conservator to follow the cleaning process during gel application.

The studied PEMA gels are obtained as 1-2 mm thick films after radical polymerization of EMA, using DEC as diluent, as described in the experimental section. Since DEC is an expensive solvent, the possibility to reduce the processing costs by replacing it with 2-propanol was explored and the potential changes in the gels properties were studied; moreover the effects of the addition of PEG, used as a plasticizer, were also investigated.

All the three formulations are characterized by optical transparency and good mechanical stability, i.e. they can be cut to shape using a scalpel, and are easily manipulated and applied.

Figure 1 shows the FTIR spectrum of DEC that was let exchange with the gel for 24 h (20 mL of solvent for 5 g of gel), after the first extraction of monomer had been carried out (also using 20 mL of solvent for 24 h). The spectrum was compared to that of pristine DEC, and of pure EMA. No detectable bands of the EMA monomer (1140-1180  $\text{cm}^{-1}$  region, stretching of C–O–C in ester groups [12,13]) were found in the spectrum of the exchange solvent. The instrumental detection limit for EMA, 0.5 g/L in DEC, was determined experimentally by collecting the spectra of a range of reference EMA/DEC solutions with decreasing EMA concentrations.

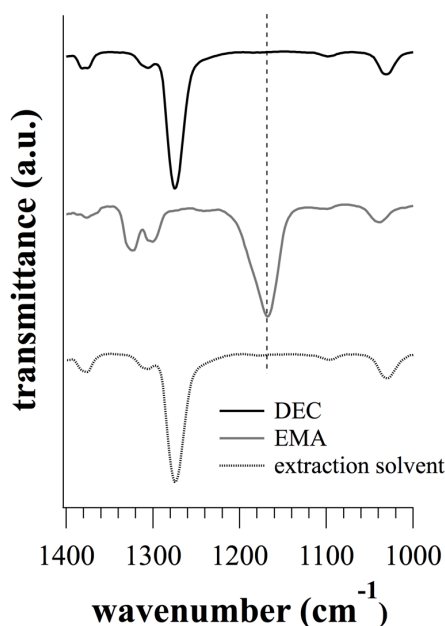


Fig. 1 - FT-IR spectra (1400-1000  $\text{cm}^{-1}$ ) of DEC, pure EMA monomer, and DEC used as exchange solvent (24 h) after preparation of the gels and extraction of 24 h in DEC.

As reported in Table 2, the solvent used in the reaction mixture does not affect the reaction yield, which is between 70-75% for polymerization in both DEC (formulation ED50) and 2-propanol (formulation EI50). A reaction yield below 100% can be due to the volatility of the monomer, which leads to its evaporation in the early stages of the polymerization reaction. On the other hand, the addition of PEG<sub>1000</sub> into the reaction mixture noticeably reduces the reaction yield (down to 65%), probably due to the lower amount of monomer used, and to possible interference of PEG<sub>1000</sub> with the gelation process; moreover, not all PEG<sub>1000</sub> might be efficiently embedded into the PEMA polymeric network.

	<i>Yield (%)</i>	<i>ESC (%)</i>	<i>F<sub>s</sub> (60 min)</i>	<i>t<sub>f</sub> (h)</i>	<i>SR (mg/cm<sup>2</sup>)</i>
<b>ED50</b>	73% ± 3%	76% ± 3%	0.70 ± 0.03	5	1.7 ± 0.4
<b>EI50</b>	72% ± 2%	79% ± 2%	0.44 ± 0.04	4	1.4 ± 0.1
<b>EI50P10</b>	65% ± 3%	86% ± 2%	0.53 ± 0.03	4	1.8 ± 0.6

Table 2 – Reaction yield, equilibrium solvent content (*ESC%*), residual solvent fraction (*F<sub>s</sub>*) after 1 hour evaporation, time required to reach *ESC%* for completely dried gel samples (*t<sub>f</sub>*), and solvent release (*SR*) after 15 minutes contact on Whatman® filter paper for the three PEMA gel formulations. Presented data are the mean of at least three measurements.

Table 2 also summarizes some parameters related to the affinity of the PEMA networks to the solvent (DEC), their ability to reduce its evaporation, and to deliver the solvent in a controlled way on a porous substrate such as paper. The equilibrium solvent content (*ESC%*) gives a measure of the capacity of the polymeric network to swell in a specific solvent. As shown in Table 2, *ESC%* is higher than the percentage of solvent used during the synthesis for all selected formulations, indicating a strong affinity of PEMA-based gels to DEC. As expected, at equilibrium ED50 and EI50 have an *ESC%* of 75-80%, indicating that the solvent used for preparation does not significantly affect the swelling of the network in DEC. The EI50P10 formulation exhibits higher *ESC%* (86%). In fact, according to the literature, a lower initial monomer concentration in the pre-gel reaction mixture leads to decreased chain interpenetration and reduced efficiency of the cross-linking reaction in the resulting gel network, overall leading to enhanced swelling [14].

Besides the total amount of solvent retained within the polymeric matrix, the rate of solvent release is also an essential parameter from an applicative standpoint: the quantity of released solvent should be neither too high, nor too low, so as to obtain effective cleaning without spreading of the solvent across the artwork surface. The amount of DEC released on Whatman® paper samples within 15 minutes (a time length representative of real applications) normalized by unit area (*SR*) is reported in Table 2 for the three gels: regardless the *ESC%*, *SR* is around 1.5 mg/cm<sup>2</sup>. This value indicates that the PEMA gels are highly retentive, and are thus suitable for the treatment of highly solvent-sensitive surfaces.

The proposed methodology for removing the PSTs consists in the application of the DEC-swollen gel on top of the PST backing, so as to minimize the impact of the cleaning intervention. The effectiveness of this method depends on the ability of the solvent to penetrate the backing of the PST. To allow sufficient interaction between the solvent and the backing layer, the PEMA-DEC gel must be able to release the solvent while reducing its evaporation. LSCM measurements were performed using an experimental setup that mimics the real application. Figure 2 shows the dynamic interaction between the PEMA-DEC gel ED50 and the polypropylene PST backing. The DEC liquid phase was marked with the fluorescent dye Cou6 (in green), and the adhesive layer of PP-PST with the RhBITC dye (in red). At  $t = 0$  the two dyes are well separated by the polypropylene backing layer (not marked, black) showing no interaction between the solvent and the PP-PST components (Figure 2a). After 20 minutes the RhBITC marked adhesive layer loses its initial homogeneous appearance with a decrease of fluorescence intensity (Figure 2b). The interaction between the solvent and the PP-PST components does not occur through the penetration of a homogeneous solvent front moving from the upper PST surface towards the adhesive layer. DEC is a good solvent for the acrylic adhesive, but not for polypropylene; indeed, no direct

solubilization of the PP backing by the solvent was observed. Instead, as shown by the LSCM images (Figures 2c-d), the solvent penetrates the backing through conduits in the plastic film (all across the surface, not just close to the gel lateral edges), reaching the adhesive layer. The FEG-SEM images of the backing show that the PP surface is altered after the interaction with DEC, and exhibits swollen areas (see Figure 3). No pre-existing micron-sized conduits were observed in the backing cross-section before treatment with the PEMA-DEC gel. Thus, we concluded that the solvent, gradually released by the gel, is able to partially swell (rather than solubilize) the PP backing, forming conduits up to reach the acrylic adhesive layer.

When the same quantity of solvent is applied as non-confined on top of the PST backing, no interaction between DEC and the PST components is observed: in this case the volatility of the non-confined solvent (vapour pressure of free DEC is  $1.5356 \cdot 10^3$  Pa at 298.2 K [15]) is high enough to cause fast evaporation before any interaction with the PST takes place.

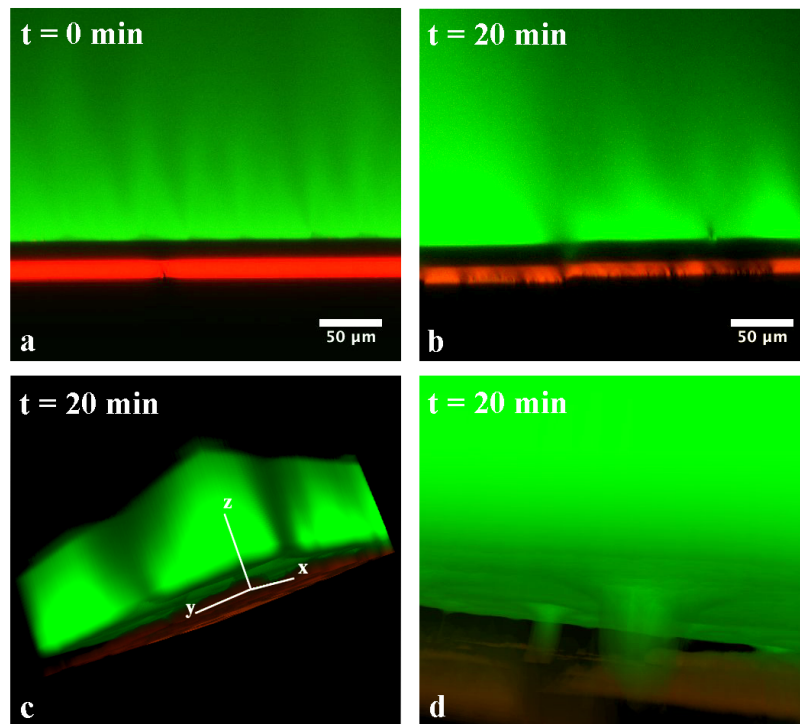


Fig. 2 - LSCM measurements on the ED50 gel loaded with DEC (solvent marked green with Cou6) and applied on a PP-PST (acrylic adhesive marked red with RhBITC); the black layer corresponds to the polypropylene backing of the tape (not marked). At  $t = 0$  the two fluorescent probes are well separated (2a) while after 20 minutes an evident penetration of the Cou6 dye through the PP-PST backing is visible (2b,d); Figure 2c shows the 3-D reconstruction of the a portion of gel lying on the PP-PST (2c-d). The images 2a,b,d were collected on internal planes (parallel to plane  $yz$ ) along the  $x$  axis.

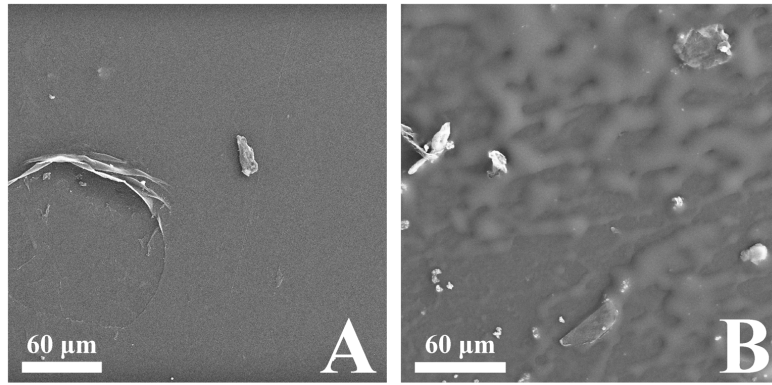


Fig. 3 – FEG-SEM images of the polypropylene backing of a PST, before (A) and after (B) treatment with a PEMA-DEC gel (20 minutes application).

Thus, the use of gels is necessary to decrease the evaporation of DEC, and promote its interaction with the PST, even when limited amounts of solvent are used. Figure 4 shows the solvent loss of the PEMA gel gels and of bulk DEC, up to 1 hour at 25°C and 65% RH. The residual solvent fraction ( $F_s$ ) after 1 hour for the bulk solvent is  $0.33 \pm 0.03$ ; on the other hand,  $F_s$  is higher for all the gel formulations, proving their ability to retain the solvent. The experimental data in Figure 3 show that the evaporation of both confined and bulk solvent occurs according to a zero-order kinetic: since the evaporation of solvents from a polymer network can be compared to a drying process, the constant evaporation rates (assuming a constant drying area) reveal that the process is fully governed by the rates of external heat and mass transfer, and that a film of free solvent is always available at the evaporating surface after 1 hour [16].

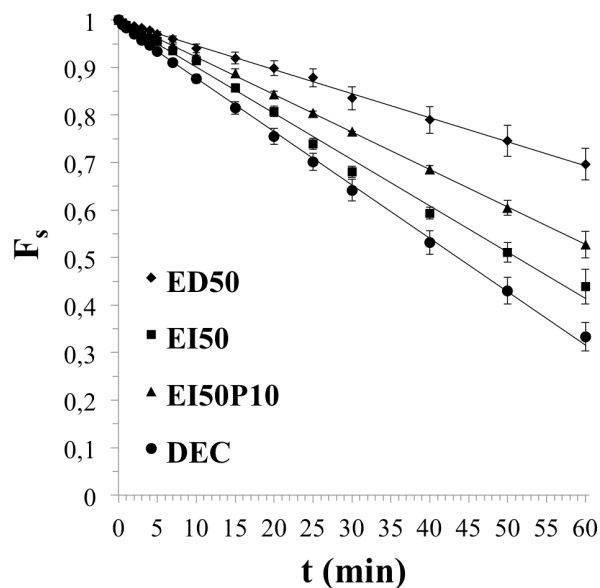


Figure 4 – Evaporation kinetics of DEC confined in the three gel formulations, compared to bulk solvent.  $F_s$  indicates the residual solvent fraction.

The ED50 gel, synthesized in DEC, shows the highest final  $F_s$  value (0,70) indicating that, after 1 hour, 70% of the initial DEC is still retained within the polymeric network. Interestingly, for the formulations prepared in a different reaction medium (i.e. EI50 and EI50P10, prepared in 2-propanol), a significant reduction of  $F_s$  is observed after 1 hour ( $F_s = 0.44$  and  $F_s = 0.53$ ), indicating faster solvent evaporation compared to ED50.

This behaviour is probably related to the different porogen effect of the two diluents (i.e. DEC and 2-propanol) on the polymeric network [17]. The solvating power towards the species that are present during the polymerization reaction (monomer and forming polymer) is one of the main parameters affecting the final structure of polymeric gels [18]: the lower solubility of the polymer, compared to the monomer, leads to a phase separation, which contributes to pores formation. Early phase separation may occur due to both polymer–solvent incompatibility and an increase in crosslinking density [18,19], leading to higher porosity percentage, higher specific surface, and lower apparent density [16,17], as well as higher pore volume with broader pore size distributions [16,17].

Because ED50 and EI50 formulations have the same cross-linker amount, we can hypothesize that the differences in their evaporation kinetics are due to the fact that, according to the Hansen solubility parameters, 2-propanol is a worst solvent for PEMA than DEC [20–22], thus leading to earlier phase separation in EI50.

On the other hand, the slight decrease in the evaporation rate for EI50P10 compared to EI50 can be explained considering that the EI50P10 formulation has lower monomer and cross-linker concentrations; therefore, a lower cross-linking density is expected to result in a phase separation occurring at a later stage of the polymerization process. Late phase separation could also be favoured by the presence of PEG, more soluble than PEMA in 2-propanol [21].

Their solvent uptake behaviour of the gels was investigated, as it provides insight about the diffusion mechanism of DEC from the bulk solution into the gel matrix. Figure 5-A shows the solvent uptake plots. The great affinity of PEMA networks for DEC is confirmed by the quick uptake kinetics: within 4-5 hours all the PEMA gels (initially dried) reach their  $ESC\%$  value. During the process all gels turn from a glassy polymer into a rubbery one; at the same time an increase in gels volume is observed. The diffusion of a penetrant into a polymeric structure can be treated as a flux of solvent molecules moving from a region at high concentration of solvent (i.e. the bulk solution) to a region of low concentration (i.e. the inner part of gels) [23]. If solvents penetrate

in a glassy polymer without swelling the chains, Fickian (concentration controlled) diffusion takes place; otherwise the interactions between the penetrant species and the polymeric network will cause anomalous effects due to the relaxation of polymers (relaxation-controlled transport); in one limiting case (Case-II transport) there is a sharp boundary which moves at constant rate, between the swollen gel and the glassy phase [24,25]. Peppas and Korsmeyer proposed a simple diffusion model for the treatment of experimental results:

$$F_s = kt^n \quad (4)$$

where  $F_s$  is the solvent fraction as described above,  $k$  is a constant depending on the gel network structure, and  $n$  is the diffusion exponential. For thin film samples,  $n = 0.5$  indicates a Fickian diffusion mechanism,  $n$  between 0.5 and 1 indicates anomalous transport, while  $n = 1$  implies a Case II transport [25]. It should be noted that this relation should be employed only for the first part of the uptake curve ( $F_s < 0.6$ ) [26].

Applying this model to our data, from the  $\ln F$  versus  $\ln t$  plot (see Figure 5-B)  $n$  was calculated as the slope of the linear fitting. Experimental results show that the swelling of all PEMA gels by DEC is relaxation-controlled: ED50 is characterized by a Case II (time independent) transport ( $n = 0.99$ ) whereas in EI50 and EI50P10 anomalous transport takes place ( $n = 0.72$  and  $n = 0.71$ , respectively). It has been shown that a change from Case II transport to Fickian diffusion can result from an increase in the gel's porosity, which increases the rate of diffusion [27]. This would lead to hypothesize a lower level of porosity for ED50 with respect to EI50 and EI50P10, in agreement with the considerations made above based on the evaporation kinetics data.

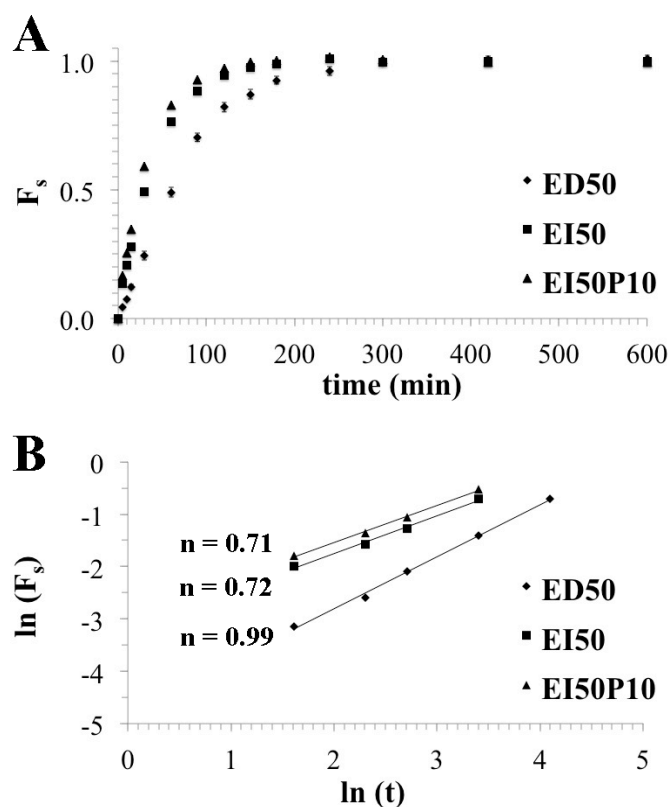


Fig. 5 – (A) Solvent uptake plots of  $F_s$  versus time for the three selected PEMA organogels; gel samples were completely dried previous to solvent uptake measurements; (B) Log-log uptake kinetic plots for  $F_s < 0.6$ , and linear fitting ( $R^2 > 0.99$  for all systems); for each gel formulation the obtained fitting parameter  $n$  is reported.

The mechanical dynamic response of the investigated gel formulations was studied by means of oscillatory shear measurements. Strain sweep tests were carried out at a fixed frequency (1 Hz) and increasing oscillation amplitude in order to determine the linear viscoelastic region and the critical oscillation strain  $\gamma_c$ . The linear viscoelastic region is characterized by a linear relationship between stress and strain and the rheological properties of the viscoelastic material are independent from the strain amplitude up to a critical level called critical oscillation strain,  $\gamma_c$ . Beyond this value the relationship between stress and strain becomes non-linear, resulting in a dependence of storage and loss moduli ( $G'$  and  $G''$ ) from the applied oscillation strain;  $\gamma_c$  indicates the strain at which the structure begins to break, which provides information on the nature of the internal structure of the material. Typically,  $G'$  is observed to deviate before  $G''$ , and  $\gamma_c$  is expected to decrease as the cross-linking density increases [28]. Table 3 shows  $\gamma_c$  for the three studied PEMA-DEC gels. Experimental data evidence that a change in the diluent used during polymerization leads to a considerable reduction of  $\gamma_c$  for the formulation prepared in 2-propanol (EI50,  $\gamma_c = 6\%$ ) with respect to that prepared in DEC (ED50,  $\gamma_c = 20\%$ ). This behaviour is probably correlated with the different

network structures resulting from polymerization in different media. As previously mentioned, phase separation, and consequently pores formation, occurs at earlier stages of the gelation process in EI50, due to the lower solubility of PEMA in 2-propanol compared to DEC. As a consequence, the resulting network presents polymer-rich zones with higher cross-linking density, which are responsible for the decrease of  $\gamma_c$ . Accordingly, a reduction in both the initial monomer (from 50% to 40% w/w) and cross-linker concentration in EI50P10, also polymerized in 2-propanol, leads to a complete recover of the original critical strain value ( $\gamma_c = 22\%$  for EI50P10).

Figure 6 shows the frequency dependence of the storage modulus  $G'$  and the loss modulus  $G''$  for the three organogels. As expected for chemically cross-linked gel systems, the behaviour is predominantly solid-like, being both moduli essentially frequency independent, and  $G' \gg G''$  over the entire range of investigated frequencies [29–32]. Moreover, the loss tangent values ( $\tan\delta = G''/G'$ ) are  $< 0.1$  (see Table 3), which is typical of strong gels systems [31,32]. From a practical point of view, this means that the permanent bonds within the network yield a gel with strong cohesion, which is able to maintain its shape. As a consequence, the gels are easily cut and manipulated, and removed in one piece without any additional mechanical action. A significant decrease in  $G'$  is observed for the EI50P10 system (Table 3), probably due to the lower monomer concentration and consequent lower cross-linking density. The presence of PEG probably contributes to lowering  $G'$ . In fact, this system is macroscopically less rigid, and softer than the other two formulations, which grants better adhesion to the treated surfaces. The enhanced flexibility of the gel represents an improvement, especially considering that the decrease in  $G'$  does not negatively affect the mechanical stability and the strong character of the gel network, as shown by the low loss tangent value for this formulation ( $\tan\delta = 0.03$ ).

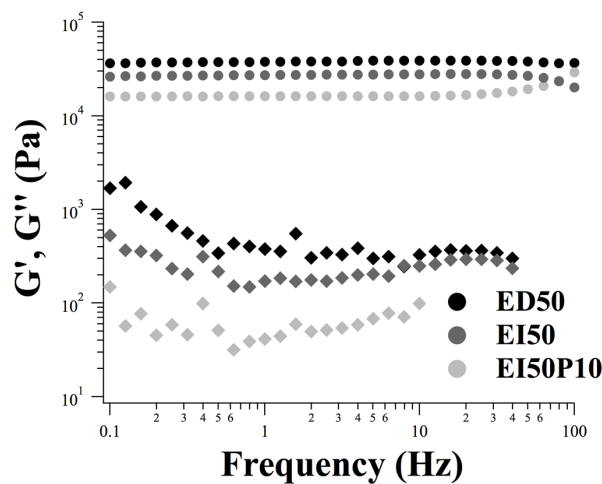


Fig. 6 – Frequency dependence of  $G'$  (circles) and  $G''$  (diamond) for the three investigated gel formulations.

	$G'$ (kPa)	$\tan\delta$	$\gamma_c$ (%)
<b>ED50</b>	37.7	0.010	20%
<b>EI50</b>	27.2	0.006	6%
<b>EI50P10</b>	16.7	0.003	22%

Table 3 – Storage modulus  $G'$  and  $\tan\delta$  values at 1 Hz; critical oscillation strain  $\gamma_c$ .

### Applicative tests on paper objects

Preliminary tests on representative paper mock-ups were performed using the ED50 gel, assessing the efficacy in PST removal and the absence of gel residues left after treatment.

Figure 7 shows the ATR-FTIR spectra of a Whatman® paper sample before and after application (15 minutes) and removal of the gel. For comparison, the spectrum of the ED50 gel is also displayed, the most intense band being at  $1724\text{ cm}^{-1}$  (C=O stretching of PEMA) [13]. After the application of the gel, no absorption ascribable to PEMA appears in the IR spectrum of the treated paper sample.

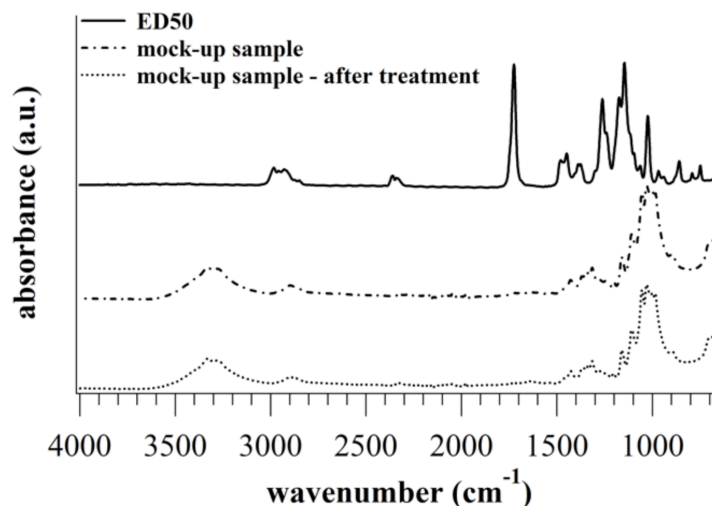


Fig. 7 - ATR-FTIR spectra of Whatman® paper sample before and after application and removal of an ED50 gel; for comparison, the spectrum of ED50 gel is also shown.

Figure 8 shows the 2D FTIR Imaging of the same Whatman® samples, where the intensity of the reflectance spectra in the  $1790\text{-}1700\text{ cm}^{-1}$  range was imaged, to double-check the presence of possible acrylate residues. In the maps of both samples (i.e. before and after application and removal of the ED50 gel), the large majority of the spectra show no significant absorbance in that spectral region (blue pixels in the maps, “low abs.” spectra in Figure 8). Some of the spectra in both maps show higher absorptions, with similar occurrence and intensity for both samples, between  $1720$  and  $1760\text{ cm}^{-1}$  (azure pixels, “high abs.” spectra in Figure 8), which were ascribed to the presence of original oxidized groups of cellulose [33]. No relevant difference was noticed between

the maps of the samples before and after the application and removal of the gel. It must be noticed that the sensitivity level of a FPA detector was shown to be significantly higher than that of a conventional MCT detector (e.g. decreasing detection limits of analytes from 0.35 wt% to 0.075 wt% [34]), owing to the possibility of detecting local (few  $\mu\text{m}^2$ ) concentrations of analytes over large areas ( $\text{mm}^2$ ).

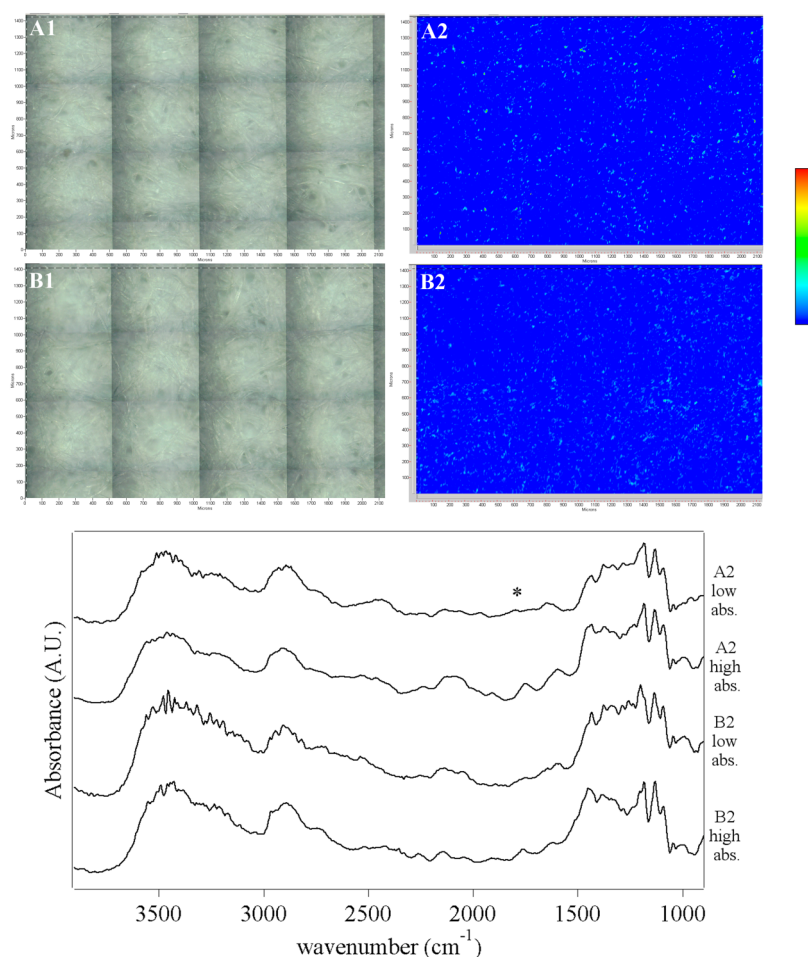


Fig. 8 – FTIR 2D imaging (using an FPA detector) of a Whatman® paper sample before (A1-2) and after (B1-2) application and removal of an ED50 gel. A1 and B1 are Vis light images. A2 and B2 show the 2D Imaging maps, where the intensity of the spectra in the 1790-1700  $\text{cm}^{-1}$  range was imaged. All maps have dimensions of 1400 x 2100  $\mu\text{m}^2$ . The FTIR Reflectance spectra shown below the maps correspond to higher intensity (azure) and lower intensity (blue) pixels from both A2 and B2 maps. The “\*” symbol highlights the spectral region that was imaged.

The gels efficacy in removing adhesive tapes was assessed on paper mock-ups featuring a highly solvent-sensitive ink (ball-point pen) covered by a polypropylene backing PST (PP-PST), representative of real case studies. Before application, the swollen organogels were shaped with a scalpel to match the dimension of the PST, and the excess of solvent was removed from the gels

surface with absorbent paper. Complete PST removal was achieved with two applications of 15 minutes. After the first application, the penetration of DEC from the gel matrix into the adhesive layer (as shown from LSCM measurements) causes the swelling of the adhesive and the detachment of the backing, which is removed by means of gentle mechanical action. Some adhesive residues are left after the first application of the gel, as shown by ATR-FTIR analysis of the treated surface (see Figure 9). The adhesive is then completely removed with a second gel application directly on the paper substrate (no bands of the PP-PST adhesive are observable in the spectra of the paper sample). After the intervention, no tidelines or alteration of the ink were observed, thanks to the controlled solvent release by the gel, and to the inertness of DEC towards most solvent-sensitive artistic media.

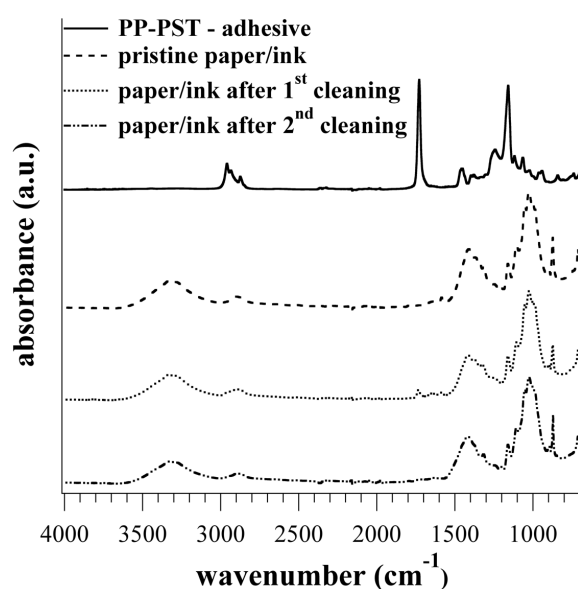


Figure 9 - ATR-FTIR spectra of (from top to bottom): the acrylic copolymer-based adhesive of the PP-PST; the pristine paper/ink mock-up sample (printing paper/blue ball point pen), i.e. before PST application; the paper/ink mock-up sample after the first gel application showing the removal of the PP-PST backing and a small adhesive residues (weak absorption band at 1730  $\text{cm}^{-1}$ ); paper/ink mock-up sample after the second gel application showing no bands of the adhesive.

Figures 10A and 11A show respectively the *recto* and *verso* sides of the drawing by Keith Haring (*Untitled*, Naples Series, 1983) which was selected for the present study. The *verso* presents six PSTs, which were applied to frame and mount the drawing to a board. The drawing, made using a black felt-tip pen, presents disfiguring stains due to the penetration of the aged and discoloured adhesive mass of the PST from the *verso* of the drawing, as can be seen in Figure 10B1.

Preliminary micro-solubility tests indicated that the original ink is sensitive towards the solvents commonly used for PSTs removal (i.e. ethyl alcohol, ethyl acetate, acetone, tetrahydrofuran, toluene, xylene, *N,N*-dimethylformamide) while showing substantial inertness towards DEC.

The removal of the PSTs from the drawing was carried out in two steps, i.e. the detachment of the PST backing, followed by the elimination of the adhesive. In the first application, ED50 organogels loaded with DEC were placed onto each of the six PSTs for a maximum of 30 minutes (in this case the gels were covered with a polyester film in order to further reduce solvent evaporation through longer applications); the detached backing was then simply removed with tweezers, with no damage or alteration of the inked artwork. The feasible and effective removal of the backing was deemed as a significant improvement on traditional applications.

The PST adhesive had penetrated deeply through the paper during the natural aging of the artwork; therefore, after the application of the gel and the removal of the backing, it was decided to combine gentle mechanical removal (using a crepe-rubber eraser, a common procedure for graphic arts) with the use of DEC, controlled by means of a vacuum suction table, in order to remove the deeply ingrained adhesive residues.

ATR-FTIR analysis (see Figure 12) performed on the adhesive tapes after their removal, revealed that the four brown PSTs (B-PST) on each corner and the two clear and transparent PSTs (T-PST) on the top edges were characterized by identical polypropylene backing [35,36] but different adhesives, i.e. respectively acrylic copolymer [35,37] and natural rubber [35,36].

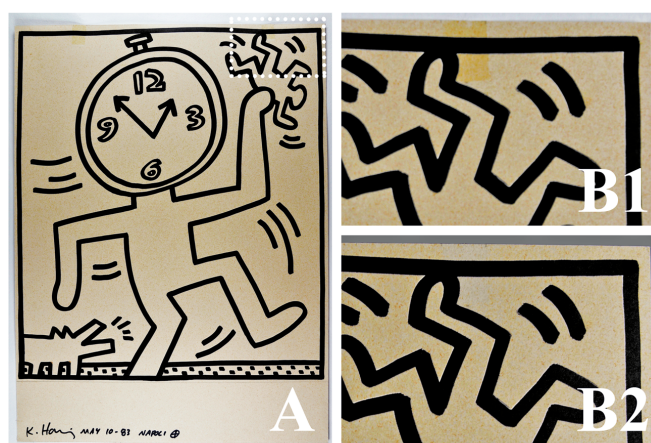


Figure 10 – (A) *Untitled*, K. Haring, 1983 - *recto* of the artwork, rectangle indicates the area with a greasy stain due the presence of the aged PST on the *verso*-side of the drawing; (B1) detail of the stain before and (B2) after cleaning.

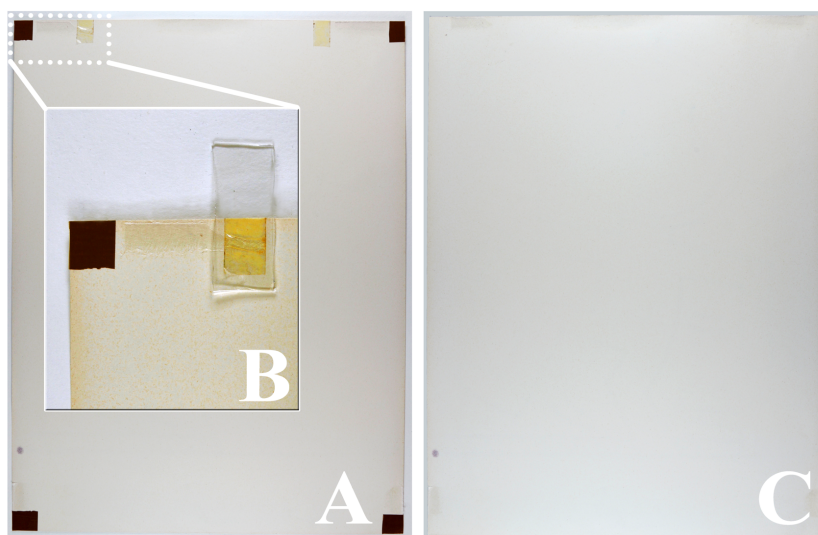


Figure 11 – (A) *verso*-side of the artwork by K. Haring before restoration showing the presence of the PSTs; (B) detail showing the application of a PEMA-DEC organogel; (C) *verso*-side of the artwork after removal of the PSTs.

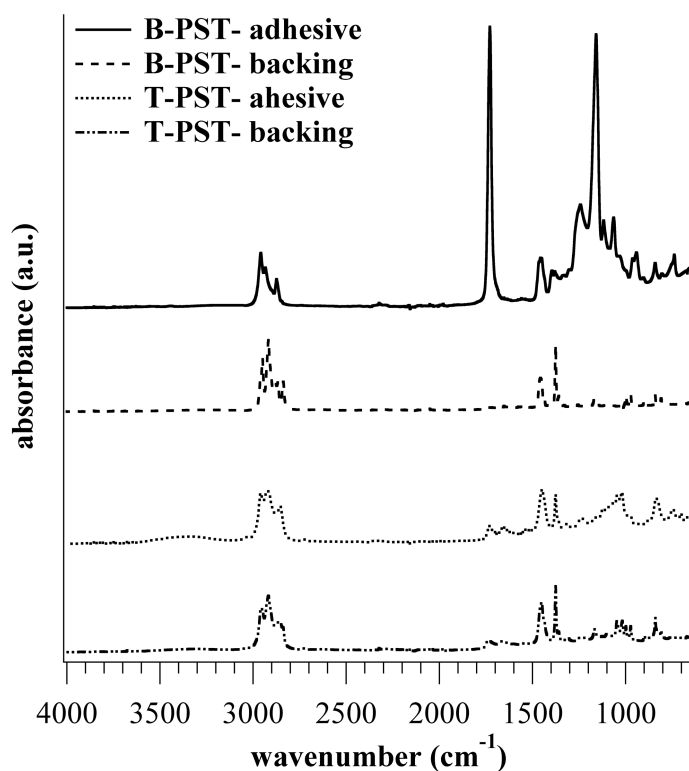


Figure 12 - ATR-FTIR spectra acquired on both the backing and the adhesive of the brown (B-PST) and transparent PST (T-PST), after their removal from the Keith Haring drawing.

## Conclusions

This paper presents an innovative methodology based on the use of polymeric organogels swollen in DEC, specifically tailored for the feasible and safe removal of aged pressure-sensitive tapes from paper artworks with solvent-sensitive artistic media. The gel network was obtained by radical polymerization of EMA using DEC as a diluent (formulation ED50). The resulting PEMA-DEC gel can be synthesized as transparent gel films of ca. 2 mm thickness, with suitable features for restoration interventions. The ED50 gels swell considerably in DEC, which indicates that they are good carriers for this solvent; moreover, as shown by evaporation kinetics, they are able to significantly slow down the evaporation of DEC, thus granting controlled and prolonged interaction of the solvent with PSTs. In fact, as shown by LSCM measurements, some minutes of contact between the DEC-loaded gel and the top surface of PSTs lead to the penetration of the solvent through the PST backing, and then the solvent interacts with the PST adhesive. It is expected that the interaction of the solvent with the PST depend on the type of PP backing, namely on the polymer microstructure, layer quality, and thickness, overall affecting the effectiveness of the treatment.

The typical strong gel behavior of the PEMA networks, evidenced by rheological studies, allows the easy manipulation and residue-free removal of the gels. In order to decrease processing costs, two other PEMA gel formulations, prepared using 2-propanol as diluent, were investigated. The different solubility of PEMA in 2-propanol than in DEC, leads to the formation of gel networks characterized by different pore architectures. This is shown by the faster evaporation rate of DEC from EI50 gel than from ED50. As shown by rheological characterization, EI50 shows a significant decrease in the critical oscillation strain, displaying a more rigid and fragile structure. The addition of PEG<sub>1000</sub> (formulation EI50P10) allows a general recover in the mechanical features, which are even improved as compared to the ED50 formulation; besides, a decrease in the evaporation rate of DEC is observed with respect to EI50.

All the formulations show high retentiveness, with similarly low solvent release rates; applicative tests on inked paper mock-ups showed that the controlled solvent release grants the feasible and effective removal of PSTs, avoiding the spreading of the solvent across the artworks' surfaces.

The absence of acrylate gel residues on the treated samples was verified both at the sensitivity of a standard ATR-FTIR (equipped with single-element MCT detector), and of a FPA detector (128 x 128 array) with spatial resolution of 5.5  $\mu\text{m}$ .

The ED50 gel was then successfully employed in the restoration intervention of a drawing by Keith Haring (*Untitled*, Naples Series, 1983): the use of PEMA-DEC organogels permitted the complete removal of the aged polypropylene backing tapes, avoiding the drawbacks usually correlated to dry and wet cleaning methodologies commonly used by restorers.

Overall, these results validate the use of PEMA-DEC organogels for the removal of PSTs from highly solvent-sensitive artworks, adding an innovative solution to the palette of tools currently available to conservators.

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### References

- [1] E. Noake, D. Lau, P. Nel, Identification of cellulose nitrate based adhesive repairs in archaeological pottery of the University of Melbourne's Middle Eastern archaeological pottery collection using portable FTIR-ATR spectroscopy and PCA, *Herit. Sci.* 5 (2017) 3. doi:10.1186/s40494-016-0116-z.
- [2] H.E. Ahmed, F.N. Kolisis, An investigation into the removal of starch paste adhesives from historical textiles by using the enzyme  $\alpha$ -amylase, *J. Cult. Herit.* 2 (2011) 169–179. doi:10.1016/j.culher.2010.08.001.
- [3] D. Chelazzi, A. Chevalier, G. Pizzorusso, R. Giorgi, M. Menu, P. Baglioni, Characterization and degradation of poly(vinyl acetate)-based adhesives for canvas paintings, *Polym. Degrad. Stab.* 107 (2014) 314–320. doi:10.1016/j.polymdegradstab.2013.12.028.
- [4] D. Satas, *Handbook of Pressure Sensitive Adhesive Technology*, Springer US, 1989. <http://www.springer.com/gp/book/9781475708684> (accessed January 30, 2018).
- [5] M.A. Smith, N.M.M. Jones, S.L. Page, M.P. Dirda, *Pressure-Sensitive Tape and techniques for its removal from paper*, (1984). <http://cool.conservation-us.org/coolaic/jaic/articles/jaic23-02-003.html> (accessed December 14, 2017).
- [6] PSTC-10, *Peel adhesion of pressure sensitive tape*, in: *Test Method Press. Sensitive Adhes. Tapes*, 15th ed., Pressure Sensitive Tape Council, Northbrook, IL, 2007.
- [7] F. Mizia, M. Notari, F. Rivetti, U. Romano, C. Zecchini, Carbonati alchilici: solventi della nuova generazione, *Chim. E Ind. -MILANO-*. 83 (2001) 47–54.
- [8] J.A.L. Domingues, N. Bonelli, R. Giorgi, E. Fratini, F. Gorel, P. Baglioni, Innovative Hydrogels Based on Semi-Interpenetrating p(HEMA)/PVP Networks for the Cleaning of Water-Sensitive Cultural Heritage Artifacts, *Langmuir.* 29 (2013) 2746–2755.

doi:10.1021/la3048664.

[9] M. Baglioni, A. Bartoletti, L. Bozec, D. Chelazzi, R. Giorgi, M. Odlyha, D. Pianorsi, G. Poggi, P. Baglioni, Nanomaterials for the cleaning and pH adjustment of vegetable-tanned leather, *Appl. Phys. A*. 122 (2016) 114. doi:10.1007/s00339-015-9553-x.

[10] M.D. Pianorsi, M. Raudino, N. Bonelli, D. Chelazzi, R. Giorgi, E. Fratini, P. Baglioni, Organogels for the cleaning of artifacts, *Pure Appl. Chem.* 89 (2017) 3–17. doi:10.1515/pac-2016-0908.

[11] P. Baglioni, N. Bonelli, D. Chelazzi, A. Chevalier, L. Dei, J. Domingues, E. Fratini, R. Giorgi, M. Martin, Organogel formulations for the cleaning of easel paintings, *Appl. Phys. A*. 121 (2015) 857–868. doi:10.1007/s00339-015-9364-0.

[12] L.J. Bellamy, *The infrared spectra of complex molecules*, 3rd ed., Chapman and Hall Ltd., London, 1975.  
<http://onlinelibrary.wiley.com/doi/10.1002/pol.1976.130140217/abstract> (accessed December 14, 2017).

[13] L.N. Sim, S.R. Majid, A.K. Arof, FTIR studies of PEMA/PVdF-HFP blend polymer electrolyte system incorporated with LiCF<sub>3</sub>SO<sub>3</sub> salt, *Vib. Spectrosc.* 58 (2012) 57–66. doi:10.1016/j.vibspec.2011.11.005.

[14] J.P. Baker, L.H. Hong, H.W. Blanch, J.M. Prausnitz, Effect of Initial Total Monomer Concentration on the Swelling Behavior of Cationic Acrylamide-Based Hydrogels, *Macromolecules*. 27 (1994) 1446–1454. doi:10.1021/ma00084a026.

[15] S.A. Kozlova, V.N. Emel'yanenko, M. Georgieva, S.P. Verevkin, Y. Chernyak, B. Schäffner, A. Börner, Vapour pressure and enthalpy of vaporization of aliphatic dialkyl carbonates, *J. Chem. Thermodyn.* 40 (2008) 1136–1140. doi:10.1016/j.jct.2008.02.012.

[16] A.S. Mujumdar, S. Devahastin, *Fundamental Principles of Drying*, in: Mujumdar's Pract. Guide Ind. Dry., Exergex Corporation, Montreal, 2000: pp. 1–22.  
<http://staff.sut.ac.ir/haghighi/download/documents/Drying.pdf>.

[17] E.V. Silletta, M.I. Velasco, C.G. Gómez, R.H. Acosta, M.C. Strumia, G.A. Monti, Evaporation Kinetics in Swollen Porous Polymeric Networks, *Langmuir*. 30 (2014) 4129–4136. doi:10.1021/la500031t.

[18] I. Küçük, A. Kuyulu, O. Okay, Effect of diluents on the porous structure of crosslinked poly(methyl methacrylate) beads, *Polym. Bull.* 35 (1995) 511–516. doi:10.1007/BF00297619.

[19] C.G. Gomez, C.I. Alvarez Igarzabal, M.C. Strumia, Effect of the crosslinking agent on porous networks formation of hema-based copolymers, *Polymer*. 45 (2004) 6189–6194. doi:10.1016/j.polymer.2004.06.053.

[20] C.M. Hansen, *Hansen Solubility Parameters: A User's Handbook*, Second Edition, CRC Press, 2007.

- [21] J. Brandrup, E.H. Immergut, E.A. Grulke, *Polymer Handbook*, 4th Edition, n.d. <https://www.wiley.com/en-us/Polymer+Handbook%2C+2+Volumes+Set%2C+4th+Edition-p-9780471479369> (accessed December 27, 2017).
- [22] J. Burke, *Solubility Parameters: Theory and Application*, Oakland Museum of California, 1984. <https://cool.conservation-us.org/coolaic/sg/bpg/annual/v03/bp03-04.html> (accessed December 27, 2017).
- [23] P.L. Ritger, N.A. Peppas, A simple equation for description of solute release II. Fickian and anomalous release from swellable devices, *J. Controlled Release*. 5 (1987) 37–42. doi:10.1016/0168-3659(87)90035-6.
- [24] N. A. Peppas, R. Korsmeyer, *Dynamically Swelling Hydrogel in Controlled Release Application*, 1986.
- [25] T. Alfrey, E.F. Gurnee, W.G. Lloyd, Diffusion in glassy polymers, *J. Polym. Sci. Part C Polym. Symp.* 12 (1966) 249–261. doi:10.1002/polc.5070120119.
- [26] J. Siepmann, N.A. Peppas, Modeling of drug release from delivery systems based on hydroxypropyl methylcellulose (HPMC), *Adv. Drug Deliv. Rev.* 48 (2001) 139–157. doi:10.1016/S0169-409X(01)00112-0.
- [27] R.A. Grinstead, L. Clark, J.L. Koenig, Study of cyclic sorption-desorption into poly(methyl methacrylate) rods using NMR imaging, *Macromolecules*. 25 (1992) 1235–1241. doi:10.1021/ma00030a006.
- [28] A.B. Rodd, D.E. Dunstan, S.B. Ross-Murphy, D.V. Boger, Dependence of linear viscoelastic critical strain and stress values on extent of gelation for a thermally activated gelling system, *Rheol. Acta*. 40 (2001) 23–29. doi:10.1007/s003970000131.
- [29] K. Almdal, J. Dyre, S. Hvidt, O. Kramer, Towards a phenomenological definition of the term ‘gel,’ *Polym. Gels Netw.* 1 (1993) 5–17. doi:10.1016/0966-7822(93)90020-I.
- [30] G.M. Kavanagh, S.B. Ross-Murphy, Rheological characterisation of polymer gels, *Prog. Polym. Sci.* 23 (1998) 533–562. doi:10.1016/S0079-6700(97)00047-6.
- [31] C. Mazzuca, L. Micheli, E. Cervelli, F. Basoli, C. Cencetti, T. Coviello, S. Iannuccelli, S. Sotgiu, A. Palleschi, Cleaning of Paper Artworks: Development of an Efficient Gel-Based Material Able to Remove Starch Paste, *ACS Appl. Mater. Interfaces*. 6 (2014) 16519–16528. doi:10.1021/am504295n.
- [32] S. Ikeda, K. Nishinari, “Weak Gel”-Type Rheological Properties of Aqueous Dispersions of Nonaggregated  $\kappa$ -Carrageenan Helices, *J. Agric. Food Chem.* 49 (2001) 4436–4441. doi:10.1021/jf0103065.
- [33] J. Łojewska, P. Miśkowiec, T. Łojewski, L.M. Proniewicz, Cellulose oxidative and hydrolytic degradation: In situ FTIR approach, *Polym. Degrad. Stab.* 3 (2005) 512–520. doi:10.1016/j.polymdegradstab.2004.12.012.

- [34] K.L.A. Chan, S.G. Kazarian, Detection of trace materials with Fourier transform infrared spectroscopy using a multi-channel detector, *The Analyst*. 131 (2006) 126–131. doi:10.1039/b511243e.
- [35] G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, 3rd Edition, JOHN WILEY & SONS, LTD, 2004. <http://www.wiley.com/WileyCDA/WileyTitle/productCd-0470093072.html> (accessed December 14, 2017).
- [36] S. Rolere, S. Liengprayoon, L. Vaysse, J. Sainte-Beuve, F. Bonfils, Investigating natural rubber composition with Fourier Transform Infrared (FT-IR) spectroscopy: A rapid and non-destructive method to determine both protein and lipid contents simultaneously, *Polym. Test.* 43 (2015) 83–93. doi:10.1016/j.polymertesting.2015.02.011.
- [37] E. Andreassen, *Infrared and Raman spectroscopy of polypropylene*, in: *Polypropyl. -Z Ref.*, J. Karger-Kocsis, Kluwer Publishers, Dordrecht, 1999. doi:10.1007/978-94-011-4421-6\_46.