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ORGANIC SOLVENTS CONFINED IN POLY (ETHYL METHACRYLATE) BASED ORGANOGELS FOR THE REMOVAL OF UNWANTED MATERIALS FROM WORKS OF ART

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ABSTRACT

Aged pressure sensitive tapes (PSTs) are widespread on paper artefacts due to their large use for mending, mounting, and framing operations. Their removal is mandatory due to associated degradation processes, but all common restoration techniques involve some drawbacks. In this work a new methodology is proposed: the embedment of proper solvents into gels that can be directly applied on PSTs surfaces. The tape detachment is achieved by solvents penetration in the backing and the later swelling of the underlying adhesive; in this way controlled solvent-artwork contact and decreased solvents evaporation are ensured. According to solubility parameters of PSTs compounds, we focused on diethyl carbonate (DEC) as cleaning fluid, a *green* solvent inert towards most common dyes. Its affinity to acrylic polymers addressed us to test DEC confinement in poly (ethyl methacrylate) networks: cross-linked chemical gels were synthesized since their mechanical strength prevents from residues left on substrates; blended systems, realized by embedding poly (ethylene glycol) chains, allowed significant improvements in gels flexibility. Physicochemical characterization on selected formulations was carried out by gravimetric measures, calorimetry, rheology, and IR spectroscopy. The ability of gels in retaining other solvents useful in the restoration practice was also tested. Gels applicative features were evidenced by testing representative samples: Confocal Microscopy, IR spectroscopy, pH measures, and thermogravimetry were performed. The developed gels were finally used in real *case study*: the interventions on drawings by Fellini, Haring, and Vedova, on a XIX century *Divina Commedia*, and on photographic and cinematographic films are here presented.

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General background and aims

The *cleaning* of cultural heritage is still nowadays a very debated topic in the field of restoration: within a conservative intervention *cleaning* is indeed an essential step since it allows to restore the original appearance of the object by removing degraded compounds; simultaneously it usually represents a precondition for all other interventions concerning the underlying layers; anyway cleaning is considered one of the most delicate and potentially harmful operations, mainly because of its intrinsic irreversibility.

Clearly cleaning procedures performed in each particular case-study are strictly related to the kind of artefact and to materials of which it consists: in order to minimize the invasiveness of treatments proper operations should be planned so as to exactly match each specific requirement.

Therefore, according to what above stated, a clearer contextualization of the purposes set for the project here discussed is essential, i.e. the removal of *Pressure Sensitive Tapes* (PSTs) and adhesive residues mainly from paper artworks.

Contrarily to popular opinion PSTs are widespread on artworks, and particularly on paper ones, since they were largely used to mend lacerated pages, to fix sheets separated from the book spine, to frame drawings or documents, etc. Nevertheless the test of time proved that PSTs may induce degradations on paper artefacts, such as the bleeding of graphic media, and penetration and oxidation of adhesives. Therefore their removal is currently considered essential but all the developed techniques, both dry and wet methods, have some associated drawbacks, e.g. skinning of paper, solubilization of inks, and use of toxic organic solvents.

Therefore the need of new strategies able to overcome such issues inspired this thesis, that was carried out in the framework of the *NANORESTART* project (Horizon 2020 research and innovation programme).

In this dissertation the development of an innovative tool for tape removal is presented: it is a solvent-confining system that, once cut so as to exactly match the PST shape and placed directly on its top surface, could release a fluid able to interact with tape components so as to penetrate the backing layer and then swell the underlying adhesive; the detachment of the tape might be achieved by means of a gentle mechanical action afterwards. Therefore the development of new gel systems specifically devised for this challenging task is the core aim of the present dissertation: high solvent content, proper degree of retentiveness, easy handling, adaptability to treated substrates, and absence of left residues are the required features for such tools.

In the past years, researches carried out at the CSGI (Center for Colloids and Surface Science) have largely contributed to the development of innovative and increasingly efficient gelled systems, able to be effective and versatile and, at the same time, to overcome some of the main drawbacks related to the traditional gels used in restoration. More in detail the present research arises from studies about chemically cross-linked poly (methyl methacrylate) (PMMA) organogels developed for the cleaning of artworks, e.g. easel paintings and paper. Anyway, in order to both improve mechanical features of organogels and decrease the health risks associated to the use of the methyl methacrylate (MMA) monomer, we decided to change the gelator by switching to ethyl methacrylate (EMA), less hazardous than the former one due to its smaller volatility. A further attempt to enhance the easily gels manipulation was the realization of semi-interpenetrating (semi-IPN) systems obtained through polymerization reaction of EMA in presence of poly (ethylene glycol) (PEG) linear chains.

Accordingly in this dissertation some of the systems tested and results obtained are discussed. The first part of the thesis is an overall introduction to the topic of *cleaning* in restoration and problems related to the presence of PSTs on artworks; advantages associated to the use of gels for *cleaning* are also debated. The following section is focused on fundamentals concerning mechanisms of polymers blending and related benefits, and processes leading to gelification; therefore gel definitions and classifications are proposed, and characteristic physico-chemical parameters of gels are introduced. The next experimental subdivision is committed to the description of synthesis methods, instrumental techniques used for characterization, and discussion of the experimental results. Finally, preliminary cleaning tests and gels application on real case-studies are presented.

PART I

INTRODUCTION

CHAPTER 1

Conservation issues

Cultural heritage conservation represents an actual challenging task due to the requested compromise between the preservation of the original artefacts appearance and properties, and the effectiveness and feasible reversibility of treatments. To this aim conservators are continuously demanding innovative materials and techniques: indeed conventional methods have lots of related drawbacks, e.g. uncontrolled action towards materials, and products toxicity. As a consequence new procedures allowing long-term protection and simultaneous minimal invasiveness and eco-toxicological impact are desired.

Among all the conservative interventions that can be performed on artworks, here we will focus on *cleaning*: the aim of this *Chapter* is therefore to give a general overview of cultural heritage *cleaning* and to introduce the specific topic of the occurrence of *Pressure Sensitive Tapes* on paper artefacts, the real core of the present dissertation.

1.1 Cultural heritage and cleaning: an introduction

The term *Cultural Heritage* encompasses several categories, comprising both tangible and intangible ones: the former class includes concrete objects (where the term *object* is used in its broadest sense), while oral traditions, performing arts, and rituals pertain to the latter group.

Tangible heritage consists of a wide variety worthy of preservation for the future: buildings, historic places, monuments, artefacts, etc., and all the things supposed significant to art, archaeology, architecture, science, and technology of a specific culture [1].

Works of art embrace both movable and immovable objects. The first category includes documentary and historical manuscripts, printed books, paper drawings, easel paintings on wood and canvas, and a large assortment of valuables such as statuettes, jewellery, and textiles. On the other hand immovable artefacts mainly consist of mural paintings, architectures, and statues.

Regardless of its nature, cultural heritage is irremediably exposed to several degradation agents: physical erosion, chemical degradation, temperature, relative humidity, light, and microorganisms, all accounting for the natural aging of art materials. Moreover in some cases conservation issues are due to past careless home-made restoration interventions or the use of products whose negative effects are known only nowadays. Depending on the kind of artistic substrate and occurring degradation, different tasks are necessary for conservation purposes: nevertheless a large fraction of restoration interventions may be grouped in *cleaning* from unwanted materials, *consolidation* of both surfaces and bulk layers, and *deacidification* [2,3].

Coming to the thesis topic, the term *cleaning* typically refers to the deletion of grime and soil from surfaces, but also to the partial or complete removal of degraded layers, such as aged and yellowed varnishes, adhesives, and other potentially harmful materials. Because of its irreversibility *cleaning* is one of the most delicate and controversial procedures during the restoration process of a cultural heritage artefact;

nevertheless it is also a fundamental step before performing other interventions. As stated by Bonsanti it represents [4]:

> *...the condition for the access to the surface of the artifact ... if there is no access to the artifact, also the conditions for other structural and conservative interventions are generally missing...*

Actually cleaning not only allows the removal of degraded compounds which may negatively interact with artistic substrates, but also grants the access to inner core of artworks permitting further interventions.

Anyway the cleaning degree at which operations should be stopped is not a simple task since it should be determined according to the concept of *patina*, its historical value, and its feasible protective role [5]. Nowadays its attenuation rather than its complete deletion is generally approved, thus requiring gradualness in cleaning interventions.

Over the centuries *cleaning* was performed using a great variety of materials, such as soaps, alimentary products (e.g. wine, vinegar, lemon juice) and even bio-fluids (e.g. saliva, urine, blood); in last decades, the traditional cleaning methods involved both dry and wet methods, the former including the use of tools like chisels and scalpels, the latter mainly aqueous and organic solvent treatments.

Anyhow such procedures are very often too aggressive towards materials mainly due to the lack in their control: therefore lacerations, undesired detachments, spreading of solvents, and solubilization of artistic media may occur. For this reason, as previously mentioned, nowadays much attention is addressed towards more innovative systems suitable to match specific conservative issues.

1.2 Pressure Sensitive Tapes (PSTs) on artworks

As we can conclude from the above general overview about *cleaning*, the removal of unwanted materials from works of art is actually a very broad theme: depending on the object to be restored, largely different procedures may be required. Nonetheless we anticipated in the *General background* that the precise topic of this dissertation is the removal of *Pressure Sensitive Tapes* (PSTs) and adhesive residues mainly from paper artworks.

Following their invention in 1845 (attributed to Dr. Horace Day) for medical purposes *Pressure Sensitive Tapes* - so-called because light pressure causes it to stick readily to most surfaces - were industrially developed in the 1920s, and then largely exploited in different applicative fields. Contrarily to popular opinion they are largely found on artworks, and particularly on paper objects: since they are inexpensive, universally available, and convenient to use, PSTs has been extensively used for framing, mounting, and mending operations on archival materials and art on paper [6,7].

Nevertheless time and experience have shown that they may provoke several drawbacks on artworks: beyond the aesthetic side, PSTs may indeed induce different kinds of degradations, e.g. penetration and yellowing of adhesives, and spreading of inks. So their removal is essential but it can be a challenging task particularly when they are applied over solvent-sensible artistic media. Such necessity promoted the development of several tape-removal methodologies, but they all pose risks to both artefacts and conservation professionals: both mechanical and wet methods have associated drawbacks, e.g. skinning of paper, lacerations, tidelines, media bleeding, and the use of toxic organic solvents. Therefore the development of new strategies to face this particular conservative issue is a considerable task [7,8].

1.2.1 Composition of Pressure Sensitive Tapes

PSTs are multi-layered materials made up of different compounds depending on their commercial end use: within their complex stratigraphy the adhesive and its carrier (i.e. the backing) are the most important layers; minor components include the release coat, ensuring an easy unrolling of the tape, and the primer, that enhances adhesive-backing adhesion. *Fig. 1.1* reports the typical stratigraphy of single-sided tapes.

The adhesive mass is usually composed of a synthetic or natural rubber, and more recently of acrylic co-polymers; it may contain also antioxidants, plasticizers, tackifiers, fillers, and curing agents so as to properly tune its features. The backing, which provides the support for the adhesive, is a thin flexible material: backing materials comprise crepe paper, fabric, cellophane, cellulose acetate, plasticized polyvinyl chloride, oriented polypropylene, and any of a number of other products which may be also reinforced with glass or other fibres [8–10].

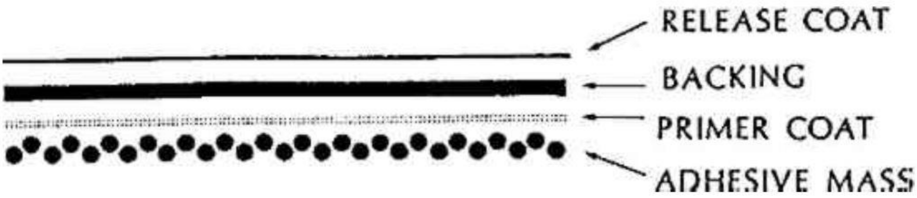

Figure 1.1 – Main components of a typical single-sided Pressure Sensitive Tape [8]

As mentioned in the previous *Paragraph*, PSTs were firstly developed in the middle of XIX century by Dr. Horace Day, a surgeon, who devised a method of applying a natural rubber adhesive to fabric, thus creating a kind of surgical tape. The next industrial development of the 1920s came from the automotive industry: two-toned automobiles were becoming increasingly popular, and manufacturers needed an efficient way to produce a clean edge where two colours met. *Minnesota Mining and Manufacturing Company* (3M) solved this problem in 1925 with the invention of the *masking tape*, a paper PST with a rubber adhesive. Since then the pressure-sensitive adhesive industry began to grow: new tapes were developed and new applications found. Gradually, the adhesive component was changed to synthetic rubbers, and a new transparent backing material was developed from regenerated cellulose, i.e. cellophane; in the 1950s cellulose acetate and synthetic polymers, mainly acrylics, combined with resins came into use respectively as backing and adhesive layers.

Over the years PSTs development proceeded and the clear advantages in their use to frame, mount, and mend almost anything that came to hand contributed to their wide diffusion. Several kinds of different PSTs were therefore produced for different commercial end use, being *ordinary tape*, b*rown tape*, m*agic tape*, *insulating tape* the most common. As a consequence of PSTs application on archival documents, manuscripts, printed books, drawings, etc., many questions arose about their stability, removability, and long-term behaviour of involved materials; in this context in the 1970s the so-called *archival* PSTs start to be produced, i.e. the well-known from paper conservators Filmoplast® [8].

1.2.2 Degradation of Pressure Sensitive Tapes

PSTs found by restorers on archival documents, books, and paper artworks may largely differs for nature of both tape and adhesive, even depending on the period of their production: indeed it is worth highlighting that PSTs composition was altered by manufacturers over time with no corresponding change in either trade name or packaging. At any rate mainly paper, cellophane, cellulose acetate, and polypropylene are mainly encountered as carriers, rubbers and acrylic co-polymers as adhesive layers [8,10,11].

Concerning rubber-based adhesives, their main degradation pathway is oxidation that occurs through distinct stages of deterioration. After an induction period, i.e. a phase in which little appreciable changes take place and removal is still relatively easy, as the oxidative process goes on a dramatic variation in adhesive consistency and colour arises; due to the breaking up of the rubber polymer, the adhesive mass starts to yellow, gradually becomes sticky and oily, and finally soaks the paper making it translucent. At this stage tape detachment is complex and the adhesive components may also affect graphic media, e.g. printing, typing, and ballpoint pen inks, causing them to bleed. Later over time the carrier may fall off, and the adhesive residues crosslink, thus hardening and brittling; since then the greasy stains due to adhesive residues are very difficult, sometimes impossible, to remove [8,12].

On the other hand acrylic adhesives are characterized by a different aging behaviour due to their chemical composition: since they are pre-crosslinked when coated onto the backing layer, they usually don’t appreciably oxidize, thus not yellowing. Nevertheless acrylic copolymers undergo cold flow so that penetration into paper and inks bleeding may occur [8].

1.2.3 Present techniques for PSTs removal

As a consequence of PSTs ageing, and degradation processes induced into artistic substrates, degraded tape need to be removed in order to preserve the integrity of artworks. Current strategies for PSTs removal include a large assortment of methods, the most common of which are below reported. Generally PSTs removal proceeds by firstly separating the carrier and only then by deleting adhesive residues; such separated stages may be performed by means of either dry or wet methods.

Among the former group, common methods involves microspatulas and scalpels used to gently work under the carrier; operations must proceed slowly, as aggressive movements may result in skinning of paper and lacerations. Other ordinary techniques for mechanical tape removal comprise the employment of dry ice, hand-held heat gun, and tacking iron. Concerning adhesive residues, if the paper surface is hard, the most efficient technique involves a crepe rubber dragged off the edge of the artwork onto a blotter, so that the sticky adhesive picks up the blotter fibres and the dirty mass can be easily cleaned off the crepe; in this way the redeposition of the adhesive on the artwork is avoided [8].

Wet tape-removal techniques differently involve the use of organic solvents able to swell the adhesive layer, so that the carrier is easily lifted away from the softened adhesive with a gentle action. Solvents may be applied by means of different methods, e.g. brush treatment, immersion, poultice, and suction table. In the first case the solvent is painted on the *verso* of the paper leaf in the area corresponding to the tape; following the swelling of the adhesive, the backing is removed with tweezers, while adding some more solvent along the peel line. As an alternative immersion treatments consist in submerging the entire object in a bath of solvent, which acts removing the carrier (if not previously detached), the surface adhesive, and any resins possibly migrated into the paper; clearly the proper choice of solvent is essential in order to selectively remove the undesirable layers without altering the artwork. Solvents may be applied even by means of a poultice, i.e. an absorbent material, such as clays, siliceous or cellulosic materials able to prevent from a too fast solvent evaporation while keeping it close to the adhesive up to its swelling or solubilization. Suction table is instead used only for the removal of adhesive residues: it is a flat porous surface, sealed on top of a plenum chamber that is connected to a vacuum pump: the reduced pressure below the surface allows liquids used in the restoration intervention to pass through the artwork (placed on top), also carrying the solubilized stain [8].

Unfortunately, each of the above mentioned wet methods have associated risks, such as formation of tidelines, media bleeding, and undesired solubilisations. Obviously prior to use a specific solvent throughout the tape-removal operations, solubility tests of artistic media must be performed; anyway inks that were stable during testing may start to move during prolonged treatments. Furthermore, immersion treatments may be too aggressive for the paper cellulose matrix due to physical, chemical, and mechanical stresses that may lead to its weakening. Another disadvantages ascribable to poultices is the leaving of residues that may also penetrate into the porous matrix of paper: they are particularly evident on dark paper and pigments and have to be removed by mechanical action, thus causing additional stress. Moreover wet methods often involve the use of volatile and toxic organic solvents, such as cyclohexane, tetrahydrofuran, toluene, xylene, acetone, and N,N-dimethylformamide, considerably hazardous for conservation professionals [7,8].

CHAPTER 2

Cleaning with gels

The topic of gels for the cleaning of works of art has been receiving increasing interest in last decades from professionals operating in all the different fields of art restoration: since their employment allows to overcome issues related to the use of free solvents, gels became attractive in the conservation of painted surfaces, metals, wood, paper, etc. [13–17].

The aim of this *Chapter* is therefore to introduce to the main concerns on the use of bulk solvents and to advantages achieved by their confinement within gelled systems. Moreover, an overview about conventional gels already used in the restoration practice and on the most recent advances in this field is provided.

2.1 Traditional cleaning methods: the use of free solvents

As outlined in the previous *Chapter* (see *Par. 1.1*), cleaning is a procedure that aims to bring the surface back to a state closer to its original appearance, in compliance with the concept of *patina*.

Traditional methods used by restorers for the cleaning of works of art were mainly based on the application of solvents directly on the surface with a brush or soaked in a cotton swab. In the past, the most common used solvent was water either pure or in solution with some compounds such as wine, ammonia, potassium carbonate, potassium and sodium hydroxides, urine, and saliva [3,18,19]. Organic solvents were used for the first time at the beginning of the XIX century, thus giving to restorers a wider spectrum of ways for the selective removal of unwanted materials [19].

Cleaning with solvents is usually achieved according to the principle of *like dissolves like*, choosing a solvent with proper solubility parameters to remove, by solubilizing or swelling, undesired materials without affecting the underlying layers [20,21]. Such selectivity is very often an unlikely matter and requires the performing of solubility tests for both substances to remove and artistic substrates to preserve [22,23]. Nevertheless the final evaluation of selectivity performed by operators with a simple visual analysis is unable to detect possible undesired consequences on a microscopic or molecular level: specific diagnostic analysis should always be carried out so as to avoid both short- and long-term negative side-effects.

Solubilization of artistic media, uncontrolled diffusion and penetration of solvents are the main risks associated to the use of free solvents. Depending on the nature of the artwork free cleaning fluid may also diffuse into the porosity of the underneath layers causing phenomena like swelling and leaching that may cause the embrittlement of top surfaces with loss of mechanical strength; furthermore solubilised materials may migrate through the substrate remaining on treated artworks after the complete evaporation of the solvent [24–26].

Besides all the drawbacks related to the preservation of artefacts, eco-toxicological impact of cleaning fluids used in the restoration practice should also be taken into account: several organic solvents used in cleaning procedures (e.g. cyclohexane, tetrahydrofuran, toluene, xylene, etc.) pose risks to operators health and generate wastes which may cause environmental damages if not disposed correctly [7,24].

At the beginning of XXI century, aqueous methods were introduced as an alternative to toxic organic substances: surfactants, chelating agents, and enzymes proved a satisfactory cleaning action but they cannot be used indiscriminately over all kind of surfaces. Indeed, water may be aggressive towards artistic media such as protein-based materials, polysaccharides, and inorganic pigments [24,27].

Therefore the constant research in new tools able to overcome the above explained cleaning issues and the increased awareness on safety of the working environment, resulted in a demanding looking for alternative products.

2.2 Confining solvents: gels for the restoration practice

Nowadays gels are becoming more and more attractive for restoration professionals, that over time have adopted several gel and gel-like formulations (e.g. thickening agents); more in detail the advantages entailed by the confinement of cleaning fluids within gels or highly viscous matrices can be summarized as follows [13]:

- increasing solvents viscosity drastically lowers both degree and rate of penetration into the porous substrate, thus the cleaning action is selectively limited at the interface between the gel-artefact
- the reduced solvents mobility inside gels due to high viscosity of such systems induces a smaller solubilization rate of unwanted materials as

compared to the use of free fluid phases; as a consequence lower solubilization kinetics allow higher control on the cleaning action

- solvent-gels interaction results in a drastic decrease of evaporation rate, with a strong reduction of toxicity issues
- gel systems are very versatile; depending on their chemical composition they can be used as carriers for both organic solvents and aqueous fluids
- according to their mechanical features and release capability gels can be used on a great variety of supports

Depending on their field of application, a large assortment of different gels and gel-like systems were developed over the years: a general overview of gels currently used in restoration and the most recent advances in these field is provided below.

2.2.1 Conventional gels for cleaning

Gelators traditionally used by restorers for the cleaning of artistic substrates comprises thickeners and gelled systems. Conservation professionals commonly refer to the overall typologies of confining systems with the term *gel* due to their applicative features: even if some of the systems do not correspond to the strict definition of gels, for simplicity we will adopt the terminology in use among restorers.

Apart from wax emulsion and resin soaps, the most common highly viscous systems used in cultural heritage conservation for the cleaning of painted surfaces usually contain water soluble macromolecules (i.e. the gelators), both natural products derivatives (i.e. cellulose ethers) and synthetic polymers (i.e. polyacrylic acid, Carbopols®) [13].

Cellulose ethers, e.g. Klucel® and Tylose®, represent one important and widespread class of materials commonly employed in the restoration practice: these hydrophilic polymers are used to thicken water and, in some cases, polar solvents like alcohols. The preparation procedure is quite simple and consists in dispersing the polymer into the liquid phase by stirring at room temperature or under heating, then the mixture is let to equilibrate for at least one day. The obtained jam-like system can be applied on the surface to be cleaned, as showed in *Fig. 2.1,* displaying an excellent adaptability also to rough surfaces. However, lots of gel residues are left on treated substrates owing to the prevalence of adhesive forces over cohesive ones; the complete residues removal is essential due to the possibility of microbial proliferation, but often it implies the use of invasive methods, thus cancelling all advantages of the employment of confining system [28,29].

Figure 2.1 - Application and removal of a Klucel® gel

Another class of gel commonly used as cleaning system is based on the gelation of synthetic polymers derived from polyacrylic acid (e.g. Carbopol®, Pemulens®). The use of polyacrylic acid was introduced along with the development of *solvent gels*, a class of materials proposed in the late 1980s by Richard Wolbers [18]. *Solvent gels* are prepared by dispersing the polyacrylic acid gellant (≈ 1% w/w) into the solvent, or solvent mixture, and then adding a non-ionic surfactant like Ethomeen C12 or C15 (10-15 % w/w) under stirring. Gelation occurs to the partial neutralization of the acid carboxylic groups of polyacrylic acid thanks to the weak basic properties of the used surfactant: the formation of negatively charged carboxylate groups that repel each other due to electrostatic interactions induces the significant extension of polymer chains, otherwise in folded conformation, thus forming the gelled network. However, as for cellulose ethers, leaving residues after treatment is the main limitation to a safe use of *solvent gels*: indeed degradation phenomena induced by the presence of residues of the non-volatile components (i.e. both polymers and surfactants) are unpredictable [30,31].

Recently, polysaccharide materials such as agar and gellan gum have been proposed as residual-free and biodegradable substances for surface cleaning purposes [17,22,32,33]. The former, i.e. agar, is extracted from cell walls of red seaweed and is composed on agaropectin and agarose; the latter, i.e. gellen gum, also branded as Phytagel® and Kelcogel®, is produced by the bacterium *Pseudomonas Elodea*, and its repeating unit is a tetrasaccharide consisting of (1-4)-β-D-glucose, (1-4)-β-D-glucuronic acid, (1- 4)-β-D-glucose, and (1-4)-α-L-rhamnose [17].

Polysaccharide gellants can be used either as a highly viscous solution or as so-called *rigid gels* (like the one shown in *Fig. 2.2*), the latter allowing to perform cleaning treatments leaving almost no residues [16,34]. Their preparation procedure, very similar for the two polymeric gels, starts with the addiction of the gellant to water (1 - 4% w/w), then the mixture is heated up to 80°C; as a result random coil conformation of gellant macromolecules occurs and their rearrangement upon cooling results in formation of a thermo-reversible highly porous gel structure.

Both agar and gellan gum gels allow gentle surface cleaning or controlled humidification also on water-sensitive artefacts such as paper; nevertheless in some cases their water retention features are not sufficient, as for instance where leaching or loss of components (water-soluble colours or inks) might take place due to excessive wetting [27].

More recently the use of gellan hydrogel carrying α-amylase enzymes were successfully experimented as innovative tools for the removal of starch paste residues from paper supports [17].

Figure 2.2 - Application of a rigid agar gel to a tempera-painted wooden cross to remove a degraded proteinaceous coating [22]

2.2.2 Advances in gels technology for art

As clearly arisen from the above discussion, the main intrinsic limits of highly viscous solutions used as cleaning tools is the leaving of residues on treated substrates and the scarce retention properties; conversely, rigid systems are less prone to gel residues but higher retentiveness and adaptability to rough surfaces may be important features in some applications.

Therefore recent experimentation of new gel formulations has been directed to the overcoming of such drawbacks by developing materials with enhanced properties. To this aim on-going research has been mainly focused to the improvement of gels retentiveness, of gradual release of fluids for highly controlled cleaning procedures, and of gels mechanical properties so as to promote completely residue-free treatments, ease of handling, and adaptability even to irregular surfaces. Thereon a large number of different systems has been developed trying to fit such requests.

The adopted strategies for the easy and complete removal of gels after cleaning treatments comprise the development of stimuli-responsive gels, i.e. gels able to be easily and rapidly removed owing to their responsiveness to either a chemical, physical, or mechanical switch.

As an example, rheoreversible polyamine based gels, i.e. polyallilamine (PAA) and polyethylenime (PEI), are able to change from a solution into gel by simply bubbling CO_2: the formation of polyallylammonium carbamate ($PAACO_2$) leads to a gel characterized by strong inter-chain interactions that can be applied directly onto a painted surface; after the cleaning action, the responsive stimulus is applied by adding in situ a small amount of a weak acetic acid aqueous solution: decarboxylation reverts the gel back to a liquid which can be soaked up with a cotton swab (*Fig. 2.3*) [35,36].

Stimuli-responsive gels was further investigated by realizing systems able to react to an external magnetic field: acrylamide-based gels containing functionalized magnetic nanoparticles were experimented as confining tools for water or aqueous solutions (e.g. microemulsions); thanks to magnetic properties acquired by the gel, its removal can be carried out by means of a permanent magnet, as depicted in *Fig. 2.4*, completely avoiding any direct handling of gels; such feature is particularly suited when the artistic substrate is extremely sensitive to mechanical stress [37].

The attempt to realize tools more and more fitting to the tasks advanced by restorers led to the development of *gel-like* poly (vinyl alcohol) based systems (PVA, or partially hydrolysed poly (vinyl acetate), PVAc). These *Highly Viscous Polymeric Dispersions* (HVPD) cannot be strictly defined as gels because of their rheological behaviour. Their gel network is obtained by adding borax to a PVA aqueous solution and the subsequent formation of cross-links between borax and PVA hydroxyl groups. As compared to conventional cellulose- or polyacrylic acid-based gels, the major innovation of these systems is the possibility of their removal by means of a simple residue-free peeling action: due to their visco-elastic properties, that are also tuneable depending on the borax content, PVA- and PVAc-borax HVPDs react in a more elastic way allowing a safe removal action (*Fig. 2.5*). Moreover, these gel-like systems are also able to load different solvents, e.g. ethanol, 1- and 2-propanol, 2-butanol, 1-pentanol, acetone, cyclohexanone, N-methyl-pyrrolidinone, and propylene carbonate [38,39].

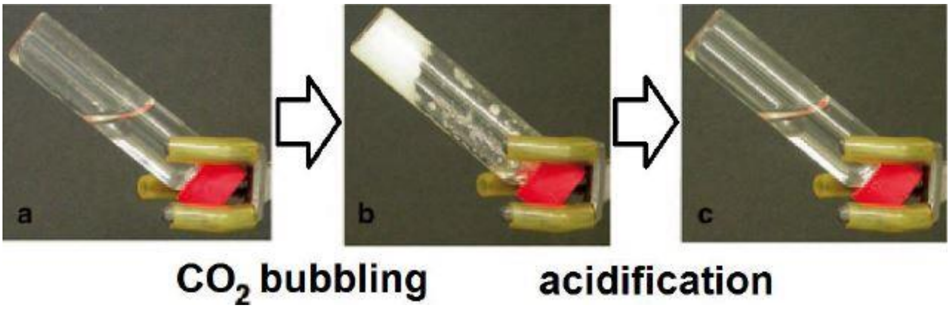

Figure 2.3 - Rheoreversible PAA-based gel: the switching from solution to gel through chemical action, and then again to the liquid form is reported [36]

Figure 2.4 - Removal of a microemulsion-loaded nanomagnetic gel using a permanent magnet [37]

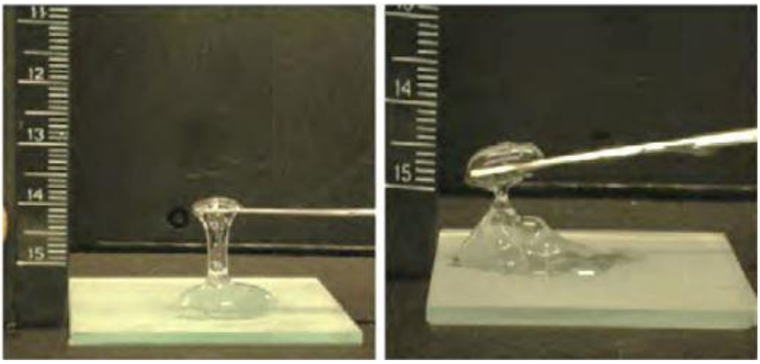

Figure 2.5 - Removal of PVA-borax HVPDs characterized by different borax contents [38]

More recently a PVA-based film forming system specifically devised for the controlled and selective cleaning of copper-based artefacts was realized. Such tool is able to combine advantages of chemical and mechanical treatments thanks to the confinement of a complexing agent, EDTA, within a fluid polymeric matrix that is able to form a solid thin film upon drying; in this way after the treatment the polymeric film can be completely removed through a gentle peeling action [15].

In order to ensure complete absence of gel residues on substrates and greater retentiveness, even gels leading covalent bonds between polymeric chains (i.e. chemical gels, see *Par. 4.1.2.2*) were experimented.

Chemical hydrogels were realized so as to allow safe and effective cleaning even on highly water-sensitive artefacts. In particular *semi-interpenetrating networks* (semi-IPN) were obtained by embedding poly (vinylpyrrolidone) (PVP) within a poly (2-hydroxyethylmethacrylate) (p(HEMA)) network. Blending p(HEMA) and PVP permits to take advantage of the best features of both polymers, i.e. the good mechanical strength provided by p(HEMA) and the high PVP hydrophilicity. Moreover tuneable water retention properties are obtained by varying compositional ratios. Such transparent hydrogels can be easily manipulated and removed from surface after cleaning without leaving residues (see *Fig. 2.6*); they can be loaded with water or water-based nanostructured fluids (i.e. microemulsions) for the removal of both, hydrophilic surface grime or hydrophobic materials [27,40].

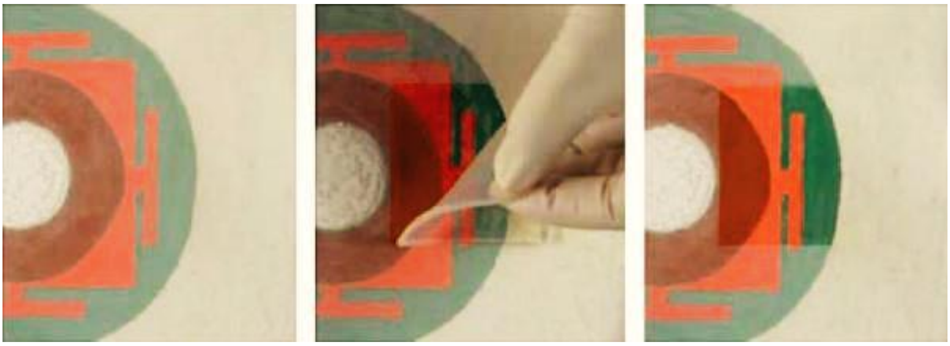

Figure 2.6 - Removal of hydrophilic grime using a p(HEMA)/PVP semi-IPN water-loaded hydrogel [27]

As a counterpart also chemical organogels, i.e. containing organic solvents rather than aqueous systems (see *Ch. 4* for major details), were developed as cleaning tools complementary to hydrogels, maintaining good retentiveness and mechanical properties. Poly (methyl methacrylate) (PMMA) chemical organogels have been prepared using different solvents and applied to the removal of unwanted adhesives and varnishes from canvas painting samples and the deletion of wax residues from paper (*Fig. 2.7*) [16,34]. The PMMA gels retentiveness was proved to be adjusted by tuning the monomer and cross-linker concentration in the pre-gel solution; gelification occurs by thermal-induced solution polymerization.

The attention to the development of green methods which foresee the use of renewable and biodegradable materials led recently to the

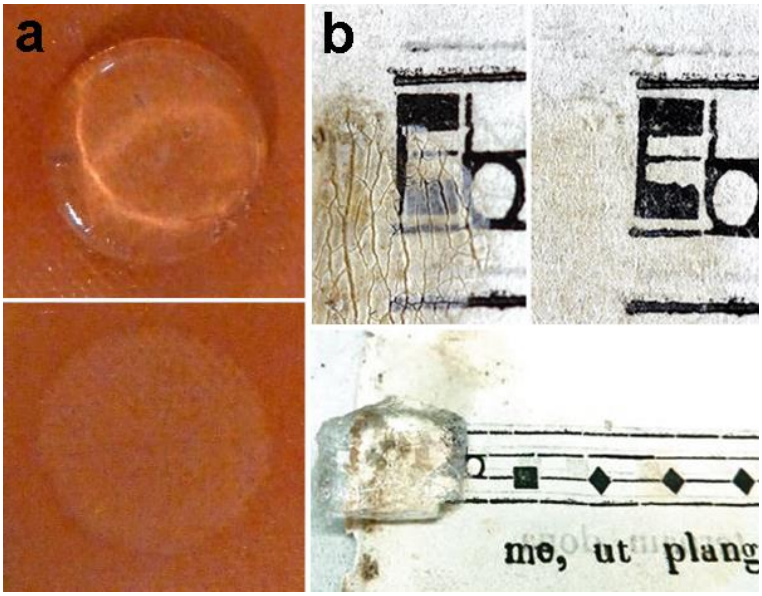

Figure 2.7 - PMMA organogels for the removal of hydrophobic unwanted materials from different substrates: a) elimination of a Paraloid B72 film from a canvas painting models using an ethyl acetate-loaded gel [34]; b) deletion of wax residues from a XIX century missals by applying a methyl ethyl ketone-PMMA system [16]

realization of bio-based organogels for the cleaning of water sensitive surfaces. Polyhydroxybutyrate/γ-valerolactone (PHB-GVL) gels were prepared by cooling the solution at room temperature; even the addition of a plasticizer, triethyl citrate (TEC) was tested. The stiffness of these thermoreversible gels makes them not prone to stick to the surface and so to leave debris. Their applicability to the cleaning of painted surfaces from degraded varnishes was successfully tested [24].

Figure 2.8 – Detail of the cleaning treatment of «The Majesty of Santa Maria dei Servi» attributed to Cimabue (XIII century) performed with a 5 minutes application of the PHB-GVL gel [24]

PART II

FUNDAMENTALS

CHAPTER 3

Polymer solutions and gelation

In this *Chapter* the thermodynamic fundamentals about polymer solution, blends, and gels are introduced. Interactions occurring in polymer solutions and blends, feasible advantages achieved through the blending process, and different kinds of multi-polymer materials are discussed. The two most common theories dealing with gel formation (i.e. the *Flory-Stockmeyer theory* and the *percolation model*) are also presented.

3.1 Blending polymers

In the last decades the research in the field of polymer blend technology has been largely improved since it often represents a low-cost alternative to the development of new monomers and polymers, and to block and graft copolymerization: it permits similar results with reduced research and development expense [41,42]. Matching the requested properties by blending different macromolecules is related to the combination of polymer properties according to concepts of *additivity* and *synergism* [43] (see *Fig. 3.1*). *Additivity* of polymer properties means that in the resulting blend specific polymer features occur in a weighted way as compared to that of the pure components; as a consequence this allows to obtain a specific requirement by properly tuning polymers amount. Less frequently *synergism* takes place: in this case the maximum value of a certain property is larger than for the single components. On the other hand, if a minimum in the specific feature is exhibited, blended polymers are called *incompatible* (*Fig. 3.1*): such a circumstance is mainly due to limited interfacial adhesion between the components and often results in poor mechanical properties. Polymer *incompatibility* has not to be confused with *immiscibility*: if a blend system is able to form miscible amorphous phases, that is a single-phase system, the components are able to mix at the molecular level; on the contrary, when immiscible polymers are mixed together, the blend components tend to separate into phases containing mainly their own kind.

Therefore *incompatibility* and *immiscibility* are the most important limitation for the development of new materials through polymer blending; however many strategies have been devised to address these issues so that nowadays the vast majority of commercial polymer blends

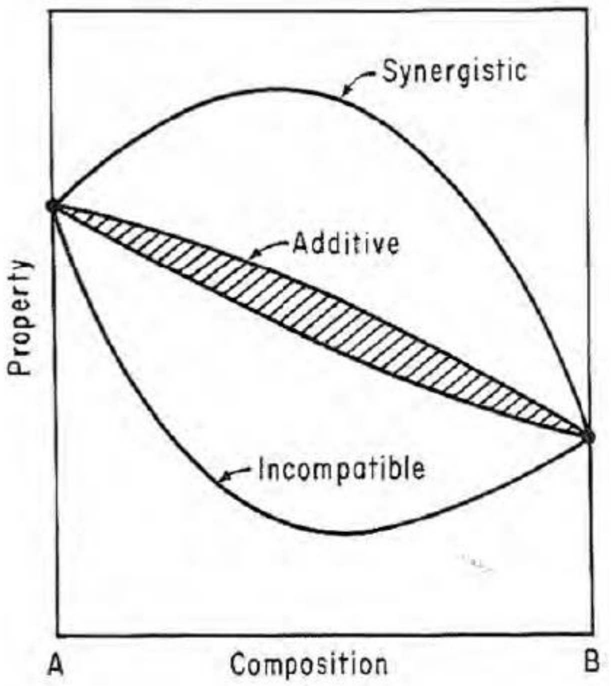

Figure 3.1 - Possible effects on polymers properties in relation to the blending concentration of polymers A and B [43]

is made up by immiscible polymers. Compatibilization methods are mainly based on a proper control on phase behaviour during processing, on functionalization of the polymer chains, and on modification of the interface between the immiscible and incompatible components [44–47]. Such compatibilized blends are often labelled as polymer alloys, due to some similarity to heterogeneous systems obtained in metal mixtures.

3.1.1 Polymers in solution

The basic thermodynamic concepts regarding the interaction that may occur in a blended polymer system will be here briefly discussed, concerning both polymer solubility and polymer-polymer miscibility.

3.1.1.1 Polymer-solvent systems

The theoretical basis to understand polymer behaviour in solution was developed independently by Flory and Huggins around the mid-twentieth century [48,49]. The *Flory-Huggins theory* is based on a simplified model but it is still very useful for the theoretical prediction of experimental data; it leads to a modification of the classical expression of the free energy of mixing, ΔG_{mix}, by taking into account for both the entropic and the enthalpic terms the specific properties of polymer solutions owing to the very large size of polymer solute molecules as compared to solvent ones. It also introduces the *Flory-Huggins parameter* χ, which permits a quantitative description of the interactions between solvent and polymer segments and thus predicts the affinity of a solvent for a given polymer.

The entropic term is approached statistically by describing the polymer solution as a three-dimensional lattice (*Fig. 3.2a*) in which all the sites are randomly occupied by either solvent molecules or polymer segments, being the latter assumed to have the same size as a solvent molecule. Considering the case of monodisperse layers, by means of statistical computations about the feasible polymer-solvent arrangements (i.e. much smaller than for small molecule solutions) the expression of the entropy of mixing becomes:

$$\Delta S_{mix} = -R\left(n_s \ln \phi_s + n_p \ln \phi_p\right) \qquad \text{(Eq. 3.1)}$$

where R is the gas constant, n_s and n_p are the number of moles of each component, and ϕ_s and ϕ_p are the volume fractions of solvent and polymer, respectively. Such expression is similar to the classical one for small molecules systems; the innovation here introduced by the *Flory-Huggins theory* is that volume fractions rather than molar ones are considered. Since for small molecule solutes the mole fractions are essentially the same than the volume fractions, *Eq. 3.1* is indeed a more general expression for the entropy of mixing.

The enthalpic term was then derived by introducing the χ parameter that gives a measure of the energetic change that occurs when a mole of solvent molecules is removed from pure solvent and immersed in a finite amount of polymer. This dimension-less parameters was defined as:

$$\chi = \frac{Z\Delta w}{RT} \qquad \text{(Eq. 3.2)}$$

where Z is the coordination number (i.e. the number of possible adjacent sites to a position in the lattice), Δw is the energy change related to dissolution, and T the temperature. By introducing χ the enthalpy of mixing for polymer solutions becomes:

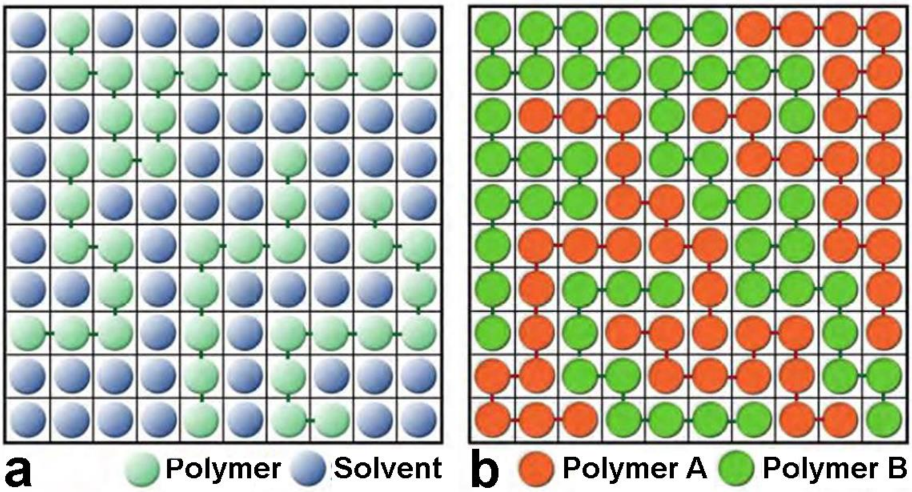

Figure 3.2 - a) Schematic representation of the lattice model for a binary polymer-solvent system in the Flory-Huggins theory; b) Lattice model for a binary polymer-polymer system

$$\Delta H_{mix} = RT\chi n_s \phi_p \qquad (Eq.\ 3.3)$$

Since χ is generally positive, the dissolution of a polymer in a solvent takes place through an endothermic process.

As a consequence of the relations obtained for ΔS_{mix} and ΔH_{mix} the free energy of mixing ΔG_{mix}, for a polymer-solvent system is:

$$\Delta G_{mix} = -RT\left(\chi n_s \phi_p + n_s \ln \phi_s + n_p \ln \phi_p\right) \qquad (Eq.\ 3.4)$$

From this expression is clear that the dissolution of a polymer occurs depending on both polymer and solvent concentration, and sign and magnitude of χ: since χ is inversely related to temperature, increasing T thermodynamically favours dissolution; in general, the smaller the value of χ the greater the decrease in free energy during dissolution. Accordingly to what above said, χ is related to both polymer-solvent and polymer-polymer interactions so that its assumed value can predict if a solvent is good or poor for a given polymer:

- $\chi > 0$: the selected solvent is a poor one and polymer will not dissolve

- $\chi = 0$: the so-called *theta* condition; polymer chains, acting as ideal ones, are not affected by wide range polymer-polymer interactions because of the effect of the solvent
- $\chi < 0$: negative values may indicate strong polar polymer-solvent attractions
- $\chi < 0.5$: selected solvent acts as a good solvent for the given polymer

3.1.1.2 Polymer-polymer systems

The *Flory-Huggins theory* for polymer-solvent miscibility can be applied also to polymer-polymer systems, but, due to high molecular dimensions of both components, some additional limitation must be taken into account. After such pioneering work, several authors discussed this topic.

By applying the lattice model to a polymer-polymer system (see *Fig. 3.2b*), it easy to compute that the possible arrangements strongly decrease if only long-chain molecules are considered: the lower the possible configurations, the lower the favourable contribution to the ΔG_{mix} given by the combinatorial entropy; in the limit of infinitely high molecular weight polymers, this contribution goes to zero. Concerning the enthalpic term, since it is related to energy changes associated to nearest neighbour contacts, it can be approximately supposed independent from molecular lengths; nevertheless significantly different results are obtained for non-polar components and highly polar or hydrogen bonding liquids.

In non-polar systems, polymers interact only via dispersive or van der Waals bondings; in such case the enthalpy of mixing may be estimated through the use of the *Hildebrand solubility parameters*, thus predicting always $\Delta H_{mix} > 0$, and possibly 0 when the polymers solubility parameters are the same. Therefore, considering the insignificant contribute due to the combinatorial entropy in polymer-polymer systems, structural similarity between components is needed and complete miscibility is expected to be a highly unlikely event [50].

On the other hand the solubility parameter approach is less suitable for highly polar or hydrogen bonding liquids: actually such polymers may mix exothermically. Thus, to achieve miscibility, a negative heat of mixing must be obtained: this condition is fulfilled when strong intermolecular interactions exist between the components of the blend ($\chi < 0$); conversely moderate interactions results in limited miscibility, depending mainly on temperature and composition [43,51].

3.1.2 Phase separation in polymer solutions

Phase separation processes within miscible polymer-polymer or polymer-solvent systems may occur if they undergo temperature variation or solvent removal (evaporation or non-solvent addition).

Concerning changes in temperature, typically small molecule mixtures undergo phase separation upon cooling, displaying an *Upper Critical Solution Temperature* (*UCST*); differently many long-chain molecules mixtures interestingly show a *cloud point* upon heating, i.e. a *Lower Critical Solution Temperature* (LCST) exists. Examples of phase diagrams displaying UCST and LCST are shown in *Fig. 3.3*. The LCST behaviour falls outside the *Flory-Huggins theory* which does not take into account volume changes during mixing: actually LCST is related to finite volume variations that occur upon heating and to the not purely enthalpic nature of χ; therefore pressure dependence of the mixing process and additional entropic contribution are introduced, the latter resulting in an increased entropy at high temperatures in the separated phases rather than in the mixed state [52]. Modifications to the original model by Flory-Huggins allow to theoretical predictions [53,54].

Two distinct phenomena, i.e. solid-liquid and liquid-liquid demixing, may occur in phase separation processes. Solid-liquid phase transitions

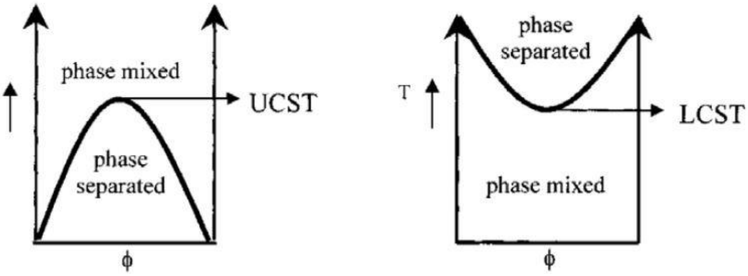

Figure 3.3- Typical Upper Critical Solution Temperature (UCST) and Lower Critical Solution Temperature (LCST) phase diagrams [55]

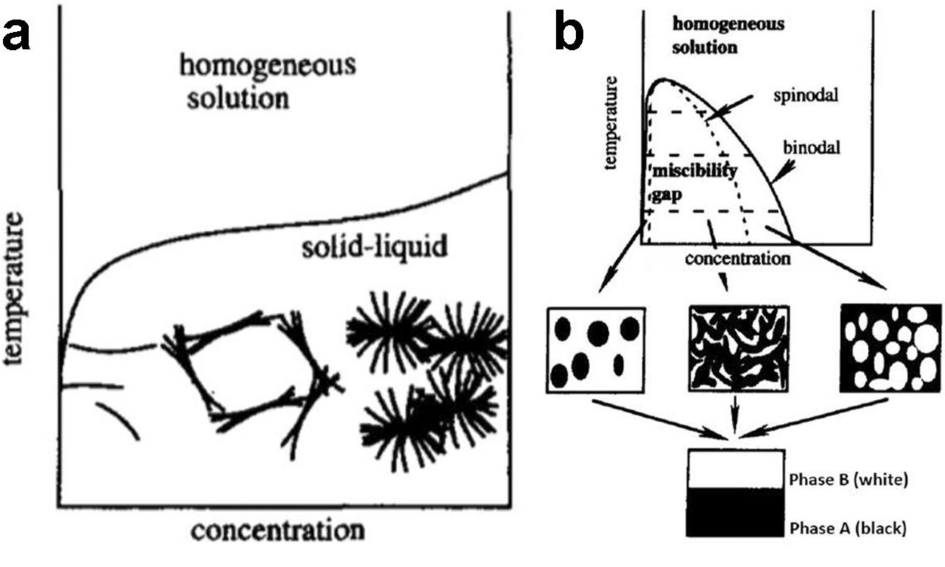

Figure 3.4 - a) Equilibrium phase diagram for a solid-liquid transition: different morphologies are obtained depending on polymer concentration (e.g. single crystals, lamellar stacks, spherulites;) b) Phase diagram for a binary system showing a liquid-liquid demixing gap: according to temperature and concentration, nucleation and growth of phase A (black), bicontinuous morphology due to spinodal decomposition, or nucleation and growth of phase B (white) take place; coarsening may produce two fully separated layers [56]

takes place through vitrification or crystallization of at least one of the equilibrium liquid phases (see *Fig. 3.4a*): it usually follows the classic mechanism of nucleation and growth [55]. On the contrary the liquid-liquid phase transition is related to the thermodynamic stability of the system: depending on where the phase boundaries are crossed, nucleation and growth or spinodal decomposition are observed (see *Fig. 3.4b*); the boundary of the liquid-liquid demixing gap is named binodal or cloud point curve [56].

3.2 Multi-polymer combinations

The combination of two or more polymers may give rise to complex networks that are classified according to how polymers are interconnected in the overall structure. Multicomponent polymer materials, depicted in *Fig. 3.5*, are classifiable as [57]:

- *polymer blends*, given by simple polymer mixing (*Fig. 3.5a*)
- *graft copolymers*, due to bonding between the end of one polymer with some portion of the backbone of another polymer (*Fig. 3.5b*)
- *block copolymers* obtained by chains bondings end to end (*Fig.3.5c*)
- *cross-linked copolymers*, that are two polymers constituting the network (*Fig. 3.5d*)
- *interpenetrating networks* (IPNs), based on the synthesis of one or both polymers in juxtaposition, thus composing two or more networks from different polymers (IPNs, *Fig. 3.5e*) or one network in the presence of another linear or branched polymer (semi-IPNs, *Fig. 3.5f*), without any covalent bond between them

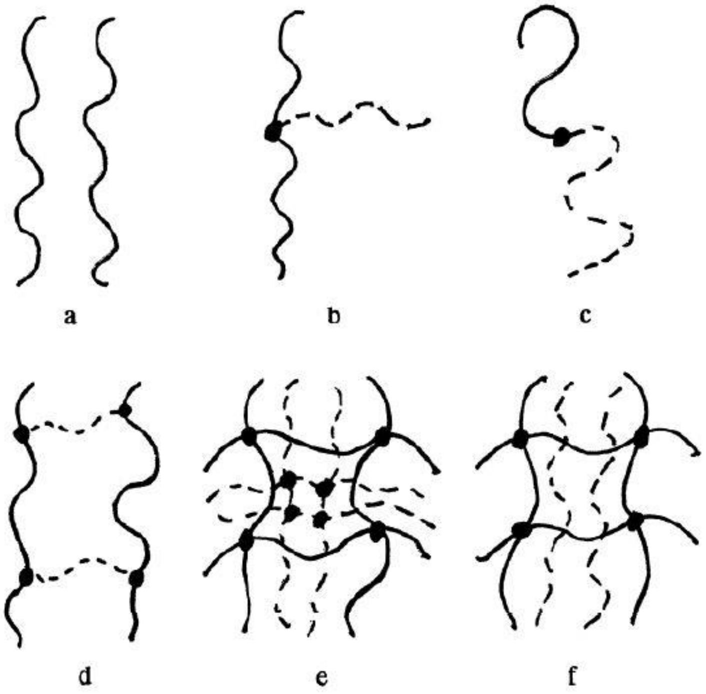

Figure 3.5 - Possible structures resulting from the combination of two or more polymers: a) polymer blend; b) graft copolymer; c) block copolymer; d) cross-linked polymer; e) interpenetrating polymer network; f) semi-interpenetrating polymer network [57]

According to the thesis topic, a more extensive description of IPN systems is proposed below.

3.2.1 Interpenetrating Polymer Networks (IPNs)

Due to the several pathways through which IPN systems can be produced, a wide assortment of them exists; therefore largely different multicomponent polymer materials, characterized by various network structures, arise [57,58]:

- sequential IPNs: firstly polymerization of polymer A is carried out, then polymer B is polymerized in the presence of the previous formed network
- simultaneous IPNs: monomers or pre-polymers are mixed together, then the polymerization reactions are carried out simultaneously, with the condition that they do not interfere between them
- latex IPNs: IPNs beads form an emulsion film; alternatively two different beads form the IPN film
- gradient IPNs: the overall composition or cross-link density of the material varies from point to point on the macroscopic level
- thermoplastic IPNs: IPN systems containing physical rather than chemical crosslinks
- semi-IPNs: polymeric compositions in which one or more polymers are cross-linked and one or more polymers are linear or branched
- homo-IPNs: Comprise two networks prepared from the same cross-linked polymer

3.3 Gelation in polymer solution

The gelation process consists in the evolution of the polymer cluster growth until the gel point that is the moment of the sol-gel transition of the cross-linked polymer. Before the gel point, the substance is called *sol* and is composed by a distribution of finite clusters, which makes it soluble in good solvents; after the gel point, the new compound named *gel* is made up of an infinitely large macromolecule, which can only swell in a good solvent [59].

Several theoretical approaches have been used for the prediction of the gel point and the modelling of the gel formation process; the two most important milestones were set by the development of statistical approaches: they are the *classical statistical theory* postulated by Flory [60] and Stockmayer [61], and the *percolation model* introduced by de Gennes [62] and Stauffer [63], as briefly discussed below. Both theories predict the sol-gel transition occurring at a critical point when an infinite cluster is formed.

3.3.1 Flory-Stockmayer theory

In its essential features, the *Flory-Stockmeyer theory* is based on multifunctional molecules between which covalent bonds are formed to yield a network structure: actually only molecules with functionality $z > 2$ will be able to form 3-D networks [60]. In this statistical approach all the functional groups of the forming chains are assumed to have the same reactivity, and no intramolecular reactions are supposed to take place [60,61]; the possible formation of covalent bonds between monomers is considered a random event, characterized by the probability p. When p is small, the system consists only in finite molecules (e.g. monomers, dimers, trimers, oligomers, etc.) and exists as a *sol* phase (see *Fig. 3.6a*); on the other hand when p exceeds a critical threshold value, named p_c, also a single molecule, infinite in spatial extend, occurs, giving rise to the gel phase (*Fig. 3.6b*): therefore the weight fraction of monomers belonging to the gel molecule is zero for $p \leq p_c$ and non-zero for $p > p_c$. By means of a combinatorial approach, the *Flory-Stockmeyer theory* derives the molecular weight distribution and the critical threshold value p_c at which the molecular weight goes to infinity.

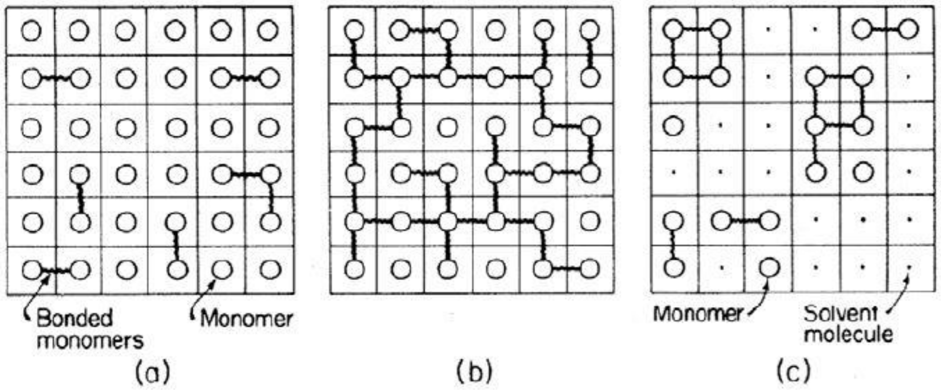

Figure 3.6 – a, b) Representation of the Flory-Stockmeyer model, where open circles represent monomers and wavy lines covalent bonds: all sites are occupied by monomers, below (a) and over (b) the critical threshold where $p > p_c$ and the infinite network is formed; c) percolation model depiction: each site can be occupied by either a monomer or solvent molecule (dot) [64]

3.3.2. Percolation model

Differently from the *Flory-Stockmeyer theory*, the percolation approach takes into account both the presence of solvent and of correlations between the molecules of the system (see *Fig. 3.6c*); moreover it does not imply unlimited mobility and accessibility of all groups. In this model four types of nearest-neighbour interactions are considered:

- solvent-solvent interactions;
- solvent-polymer interactions
- monomer-monomer van der Waals interactions
- bonding energy between monomers

According to this description, the gel phase is defined as the phase where a non-zero finite fraction of monomers is chemically bonded together to form a macroscopic molecule [62–64]. Also in this model the probability p of random bonding is defined, and the critical value p_c as well: beyond such percolation threshold the formation of an infinite cluster occurs [59].

CHAPTER 4

Gels

Notwithstanding the wide variety of gels types and their large employment in different fields, their definition and classification is a hard matter on which lots of authors has been working. In this *Chapter* a brief synopsis about this topic is presented, and the main gels physico-chemical properties are introduced.

4.1 Definition and classification of gels

Lyophilic materials are defined in colloid science as a class of compounds characterized by a strong affinity between the dispersion medium and the surface molecules of the dispersed phase. When the interactions acting between them are able to entrap the continuous phase, they might behave as good fluids carriers. Different kinds of such systems, known as gels, might be identified depending on the characteristics of the entrapped liquid phase, the gelator, and the gelation process.

4.1.1 How gels has been defined over time

Despite the work of several authors, still nowadays a general, clear, and universally accepted definition of the term *gel* has not yet been formulated: its in-between-state, being neither only solid nor liquid, makes gels difficult to categorize. That this is a complicated matter was already recognized by D. Jordan Lloyd in 1926 in the paper *The problem of gel structure* [65]:

> *The colloidal condition, the 'gel', is one which it is easier to recognize than to define, and even recognition is confused by the fact that the limits between gel and sol, on the one hand, and gel and what may be termed curd, on the other, are not precise, but consist of a gradual change. For this reason some workers classify as 'gel' systems which others exclude.*

And still in 1996, 70 years later, Heinz Heinisch in *Crystal grow in gels* wrote [66]:

> *[...] it is useful to note that no clearcut demarcation lines between gels, sols, colloidal suspensions and pastes have ever been established. [...] a gel, for instance, has been defined as "a two-component system of a semi-solid nature, rich in liquid"[67], and no one is likely to entertain illusions about the rigor of such a definition.*

In the past decades lots of definitions have been formulated, taking into accounts different points of view, like macroscopic behaviour, microscopic structure, and rheological features. Again Lloyd in the same paper tried to offer a first general definition of gel [65]:

> *Only one rule seems to hold for all gels, and that is that they must be built up from two components, one of which is a liquid at the temperature under consideration, and the other of which, the gelling substance proper, often spoken of as the gelator, is a solid. The gel itself has the mechanical properties of a solid, i.e., it can maintain its form under the stress of its own weight, and under any mechanical stress it shows the phenomenon of strain.*

Several attempts were made to include structural characteristics in the definitions of gels, such as infinite network, three-dimensional structure, coherence, etc. The definition gave by Hermans is a good example of it [68]:

> *i. [Gels] are coherent colloid disperse systems of at least two components.*
> *ii. They exhibit mechanical properties characteristic of the solid state.*
> *iii. Both the dispersed component and the dispersion medium extend themselves continuously throughout the whole system.*

All these definitions clearly exclude one-component systems such as fully cross-linked linear polymers, thus apparently conflicting with the

Flory-Stockmayer gelation theory (see *Par. 3.3.1*) [61,69,70]; however we have to notice that Hermans in his introduction included inside the gels family even substances capable of swelling in the presence of a second component. Being the definition of gels based on structural criteria clearly a formidable task, many authors tried an identification of phenomenological characteristics common to all gels. With the statement that a gel

> *is a substantially diluted system which exhibits no steady-state flow*

Ferry [71] excluded viscoelastic liquids irrespective of the magnitude of the longest relaxation time. Nevertheless there are lots of systems which behave as typical gels and that are not true solids: so Burchard and Ross-Murphy admitted some of these systems as gels [72]:

> *they all possess at least one property which can stand as the operational definition of a gel; they possess a plateau in the real part of the complex modulus extending over an appreciable window of frequencies - i.e, they are, or can be coaxed under appropriate conditions to be, viscoelastic solids*

Starting from this definition the work of Almdal et al. [73] gave a rheological definition of gels:

> *As a result of the preceding arguments, the following phenomenological characteristics can be specified:*
>
> *a) A gel consists of two or more components, one of which is a liquid, present in substantial quantity.*
>
> *b) A gel is a soft, solid or solid-like material.*
>
> *For gels which are only solid-like, we propose that the characteristics should be defined in terms of the dynamic mechanical properties, e.g. a storage modulus, G'(to), which exhibits a pronounced plateau extending to times at least of the order of seconds, and a loss modulus, G"(to), which is considerably smaller than the storage modulus in the plateau region.*
>
> *It should be noted that materials that are heterogeneous to the naked eye or at low magnification in a microscope cannot be accepted as gels.*

This is the first definition in which some measurable parameters are given for the classification of gels; for *G’* and *G’’* definitions see *Par. 4.2.2*.

Keeping in mind all the reported definitions, for our purpose gels can be described as semi-solid systems, including solids dispersed in large amounts of liquids that still show solid-like behaviour, e.g. keeping their shape under the stress of their own weight.

4.1.2 Classes of gels

As well as for gels definition, gels classification strictly depends on the discriminating characteristics taken into account, i.e. nature of the gelator, physical structure, mechanical and thermal properties, field of application, etc. Here, only classifications useful for a better understanding of the systems developed in this work will be examined. Depending on the nature of the gelator molecule, gels can be divided into biological, inorganic, and organic ones. Actually the latter is the widest and most studied class of gels and it is also the one to which the gels developed throughout this project belong. *Fig. 4.1* schematically represents the further classification of organic gels: indeed they can be categorised according to the liquid component, that can be both water

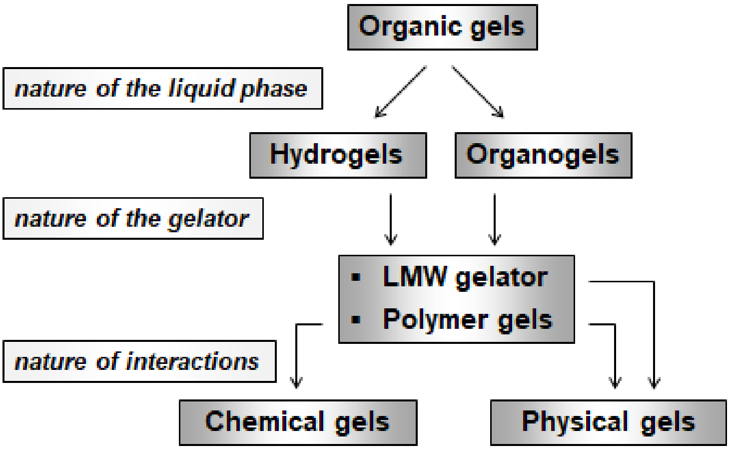

Figure 4.1 - Classification of organic gels: categorisation may be done according to the nature of the liquid phase, the kind of gelator, and the existing network interactions

(i.e. hydrogels) and an organic solvent (i.e. organogels), to the dimension of the gelator, a polymer (i.e. polymer gels) or a small molecule (i.e. low molecular weight gelator), and to the kind of interactions occurring between gelators molecules, thus being divided into physical and chemical gels [74–76].

4.1.2.1 Gels from low molecular weight gelators and polymers

Taking into account gels preparation methods we can recognize three types of gels, as illustrated in *Fig. 4.2.* Gels belonging to *Type 1* are characterised by a network constituted by the self-association of low molecular weight gelator molecules in a one dimensional fibrous form (i.e. they are named *Low Molecular-weight Gelator* gels, LMG gels);

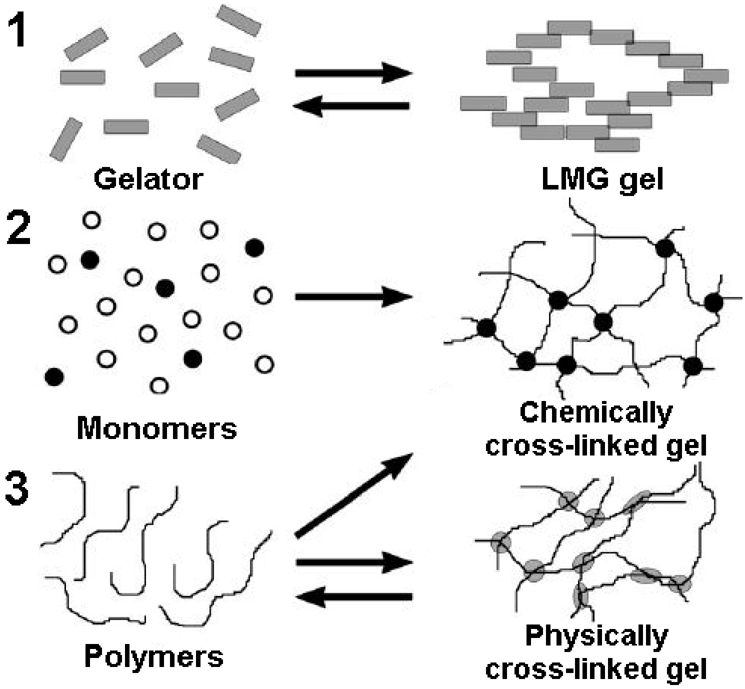

Figure 4.2 - Three types of gels can be identified depending on the gelator nature: the Type 1 gels are made by self-aggregation of low molecular weight compounds; Type 2 are synthesized by polymerization of a mixture of monomer (open circles) and cross-linker (solid circles); Type 3 gels are obtained by physically or chemically cross-linking polymer chains in solution

both organo- and hydro-gelators may belong to this class [74,75,77,78]. *Type 2* gels are instead synthesized from a proper solution of monomers, by polymerization reactions performed in the presence of cross-linkers so as to obtain a swollen three-dimensional network [74]. Conversely *Type 3* gels are made by physically or chemically cross-linking polymer solutions: in the former case aggregation due to hydrogen or ionic bonding, van der Waals forces, etc., takes place, while in the latter one gels are prepared by creating covalent bonds between chains [74,76]. The features of chemical and physical gels are further described in the next *Paragraph*.

4.1.2.2 Physical and chemical gels

All existing polymer gels are classified into two types: chemical and physical ones. Thereon the fundamental characteristic that differentiates them is the nature of the bonds between the polymer chains building the gel structure: in chemical gels the so called *strong bonds* (such as covalent bond) occur, while the typical interactions in physical gels are *weak bonds* (like dipole-dipole interactions, the London dispersion forces and hydrogen bonding). Their different nature clearly affect the macroscopic behaviour of the two types of gels.

The main features of physical gels are thermoreversibility, changeable shape, and dissolution if further liquid is added after the achievement of their equilibrium liquid content; moreover they don’t present an equilibrium modulus of elasticity and their storage modulus is sensibly lower than that one of chemical gels. All these characteristics derive from the capability of *weak bonds* to recreate themselves once external conditions allow this again [74]. On the other hand, the covalent bonds of chemical gels cannot be recreated once broken. Therefore, they are thermally irreversible, their shape is unchangeable, and when they achieve their maximum liquid content a further addition of liquid don’t make them to dissolve; furthermore they always have an equilibrium modulus of elasticity [74].

In the context of the topic of the present dissertation, importance will be addressed to this second class since all the systems developed throughout this work belong to it.

4.2 Characteristic chemical gels parameters

As the favourable properties of chemical gels results from the affinity of the network to the liquid phase, i.e. the ability of embedding and retaining considerably large amounts of solvent, it is of paramount importance to describe and understand them from a physico-chemical standpoint. To this aim some characteristic parameters related to both structural and mechanical properties will be introduced.

4.2.1 Structural properties

According to Lowman and Peppas the three main parameters that define the structure and properties of swollen gels are [79]:

- the polymer volume fraction in the swollen state
- the molecular weight of the polymer chain between two neighbouring crosslinking points
- the characteristic mesh size

Some observations about them will be made in next sections.

4.2.1.1 Polymer volume fraction and related features

The polymer volume fraction (F_v) in the swollen state refers to amount of the liquid fraction absorbed and retained by the gel. A direct way for its measure is from the volume of the dry polymer, V_d, and the one of the swollen gel, V_g, as follows [80]:

$$F_v = \frac{V_d}{V_g} = \frac{1}{Q} \qquad \text{(Eq. 4.1)}$$

where Q is the volumetric swelling ratio: since the higher the Q value, the greater the polymer affinity to the solvent, F_v decreases when strong polymer-solvent interactions occur. Knowing F_v, or the reciprocal Q, it is possible to tune the gel's affinity to a specific solvent by adding different monomers or polymers to the formulation.

A further easily measurable parameter that is related to this property is the Equilibrium Solvent Content, *ESC%* [45,80]:

$$ESC\% = \frac{W_s}{W_g} \cdot 100 \qquad \text{(Eq. 4.2)}$$

where W_s and W_g are respectively the mass of the retained solvent and of the fully swollen gel. This value is also related to gels porosity: actually an increased pore to polymer volume ratio can lead to the loading of high amounts of solvent. Since the addition of a liquid medium during the gel synthesis is able to create polymer voids, this is the reason why liquid polymerization is usually preferred to bulk one. It is worth noting that a decrease of *ESC%* over time or after de-solvation/re-solvation cycles, can be associated to pores collapse.

Therefore the examination of gels porosity can offer relevant information on the retention/release capacity of the gel system. As previous mentioned the gel porosity, ε, is defined as the fraction of the pore volume, V_p, to the apparent gel volume, V [81,82]:

$$\varepsilon = \frac{V_p}{V} \tag{Eq. 4.3}$$

Obviously ε is strongly affected by the methods used to determine both the apparent volume V, which has to exclude interparticles voids (e.g. geometrical determination, fluid displacement), and the pores volume V_p, (e.g. adsorption and capillary condensation, ultrasounds, etc.). On the basis of the pores size, materials are usually classified as micro-, meso-, and macro-porous: since such terms have been defined in many different ways, here the IUPAC classification is adopted, even if it accounts only for the porosity in the nanometer scale [82]:

- *micropores*: pore widths of up to 2 nm
- *mesopores*: the width lies between 2 and 50 nm
- *macropores*: pore widths greater than 50 nm

4.2.1.2 Average molecular weight

Polymers molecular weight distribution depends on the method of synthesis and fractionation procedure. The average molecular weight between two consecutive cross-links, M_c, can be assessed by means of the *number average molecular weight*, M_n, and the *weight average molecular weight*, M_w. The former, M_n, can be calculated as follows [83]:

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \tag{Eq. 4.4}$$

where N_i is the number of molecules with mass M_i. On the other hand M_w is defined by [83]:

$$M_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i} \qquad \textit{(Eq. 4.5)}$$

where w is the weighting factor for each molecular weight species.

As compared to M_n, M_w is more sensitive to high molecular weight species and therefore larger than M_n; since for a monodisperse polymer $M_w \approx M_n$, the ratio M_w/M_n is a measure of the degree of polydispersity of the systems [83]. The degree of cross-linking of the polymer network, X, can be therefore defined as follows [80]:

$$X = \frac{M_0}{2M_c} \qquad \textit{(Eq. 4.6)}$$

where M_0 is the molecular weight of the repeating units in the polymer chains. We have to highlight that the M_c value in chemical gels don't vary with the swelling degrees as contrarily occurs for the mesh size ξ, as described in the next *Paragraph*.

4.2.1.3 Mesh size and inhomogeneities

The mesh size ξ of the network is defined by the distance between two consecutive cross-linking points: therefore it is strongly affected by the swelling degree of the polymeric system (see *Fig. 4.3*). Due to the random nature of the gelation process a polydispersity in the value of ξ is always observed. The distribution in ξ is related to the presence of inhomogeneities in the polymer network; that can be categorized in three types, according to Ikkai [84] (see *Fig. 4.4*): *spatial inhomogeneities* represent non-uniform spatial distributions of cross-links; *topological*

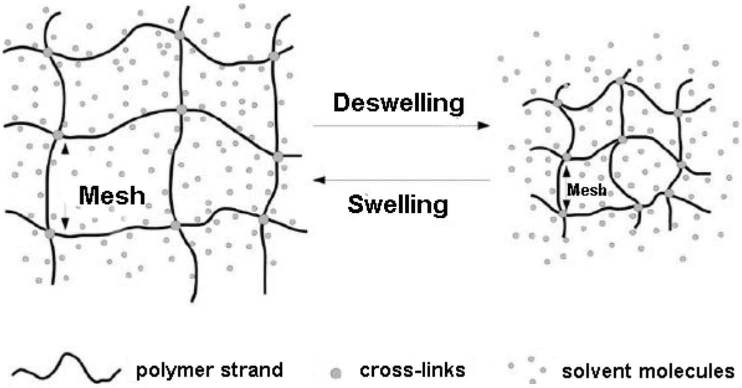

Figure 4.3 - Schematic representation of gels swelling-deswelling behaviour and the corresponding change in mesh size

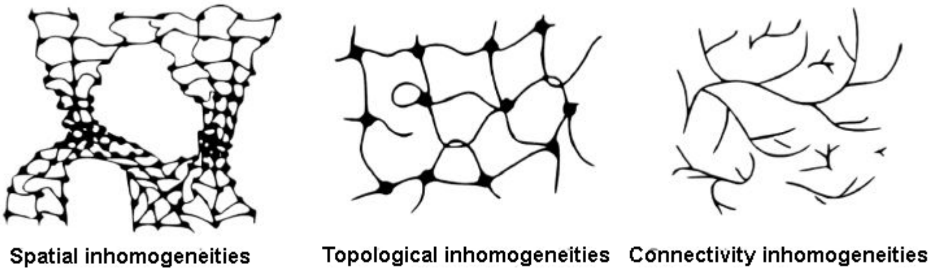

Figure 4.4 - Different kinds of inhomogeneities in gels [84]

inhomogeneities denote defects in the topology of the polymer network (e.g. loops, trapped entanglements, dangling chains); *connectivity inhomogeneities* are in relationship with the distributions of clusters.

4.2.2 Mechanical properties

From a mechanical point of view gels are viscoelastic systems, thus simultaneously showing mechanical behaviours typical of both liquids and solids. When a material undergoes a constant force and sinusoidal oscillating stress or strain, its mechanical response gives important information for its characterisation. The applied sinusoidal oscillating strain can be expressed as [85–87]:

$$\gamma(t) = \gamma_0 \sin \omega t \quad \text{(Eq. 4.7)}$$

where γ is the strain at time t, γ_0 is the strain amplitude, and ω is the oscillating or angular frequency. The applied strain generates two stress moduli represented by an elastic component, also named *in-phase stress* and by a viscous component, also called *out-of-phase stress*, the latter being characterised by a phase lag $\delta = \pi/2$ (see *Fig. 4.5*); their sum generates the total stress σ [85]:

$$\sigma(t) = G'\gamma_0 \sin(\omega t) + G''\gamma_0 \cos(\omega t) \quad \text{(Eq. 4.8)}$$

Therefore in viscoelastic materials, the induced stress shows a phase lag of δ radians as compared to the applied strain; thus for a peak stress σ_0 we observe a viscoelastic stress response $\sigma(t)$ displaced by the phase difference δ [85]:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \quad \text{(Eq. 4.9)}$$

By combining the previous equations it is possible to obtain relations for *G'* and *G"*, respectively the *storage* and the *loss moduli* (already mentioned in previous *Paragraphs*) [85]:

$$G' = \frac{\sigma_0}{\gamma_0} \cos \delta \quad \text{(Eq. 4.10)}$$

$$G'' = \frac{\sigma_0}{\gamma_0} \sin \delta \quad \text{(Eq. 4.11)}$$

where *G'* (Pa) is associated with the elastic response of the material, and *G"* (Pa) to the energy loss in internal motion. Therefore, for an ideal elastic (Hookean) solid *G"* is zero, while for an ideal (Newtonian) liquid *G'* is zero since no elastic component is observed: as a consequence if *G' >> G"* the material behaves more like a solid since deformations are essentially elastic or recoverable; on the other hand if *G" >> G'* then the energy used to deform the material is dissipated by the viscosity of the system in a more liquid-like way.

Rearranging *Eq. 4.10* and *4.11*, we can define the tangent of the phase angle δ as [87,88]:

$$\tan\delta = \frac{G''}{G'} \qquad \text{(Eq. 4.12)}$$

where *tan* δ, also named *damping factor* or *loss tangent*, is the ratio of the

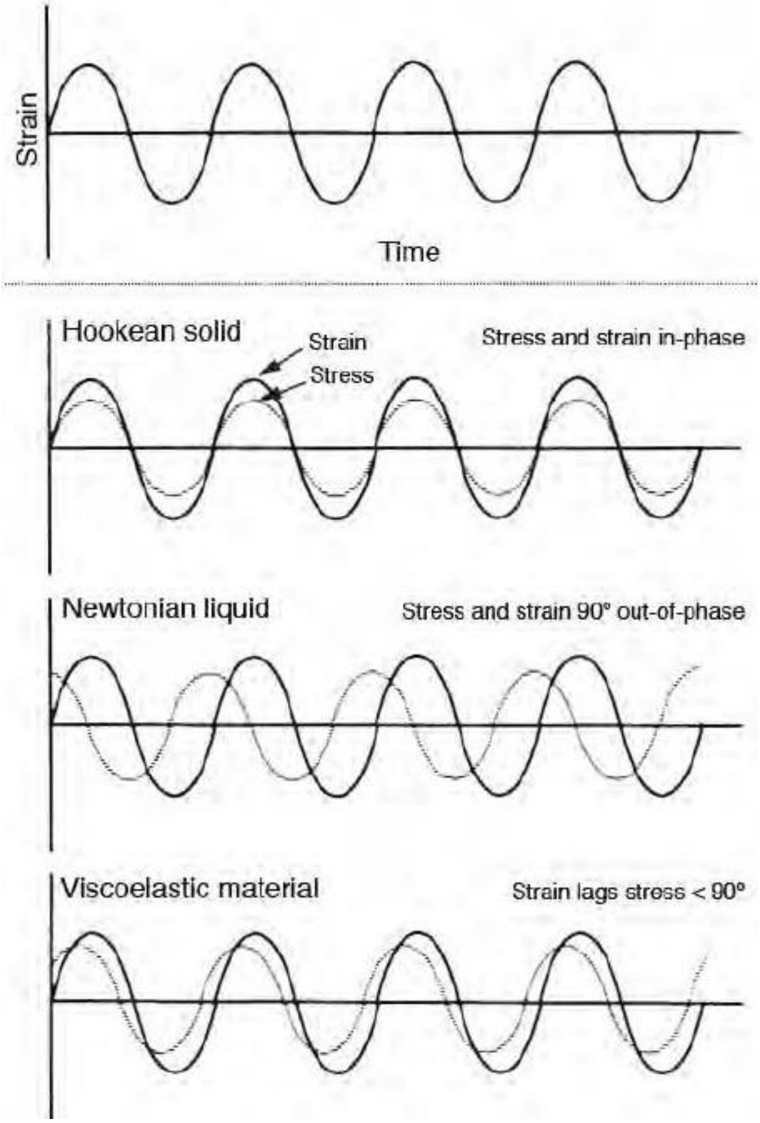

Figure 4.5 - Stress and strain responses of an ideal solid, an ideal liquid, and a viscoelastic material [88]

energy dissipated to the one stored per cycle of deformation; therefore it defines how efficiently the material loses energy to molecular rearrangements and internal friction.

Concerning the mechanical properties of gels, as previous mentioned in *Par. 4.1.1*, Almdal gave the first definition of gels based on rheological measurable parameters [73]: the authors divided gels into two main classes, i.e. soft solid material and soft solid-like material. Their discriminating feature is the existence of the equilibrium modulus, always present for solids [89], and the occurrence of *G' >> G"* in the plateau region of *G'* over a wide range of frequencies, as shown in *Fig. 4.6*. This last statement implies that gels on a time scale of seconds should exhibit no flow, thus differentiating them from colloidal solution. As upper *G'* limits for solid gels, Almdal asserted

> *Materials with moduli of the order of* 10^8 *Pa are in our opinion far too rigid to be included in the family of gels*

thus meaning that aerogels, xerogels, and highly cross-linked polymers with a low swollen degree cannot be defined as gels.

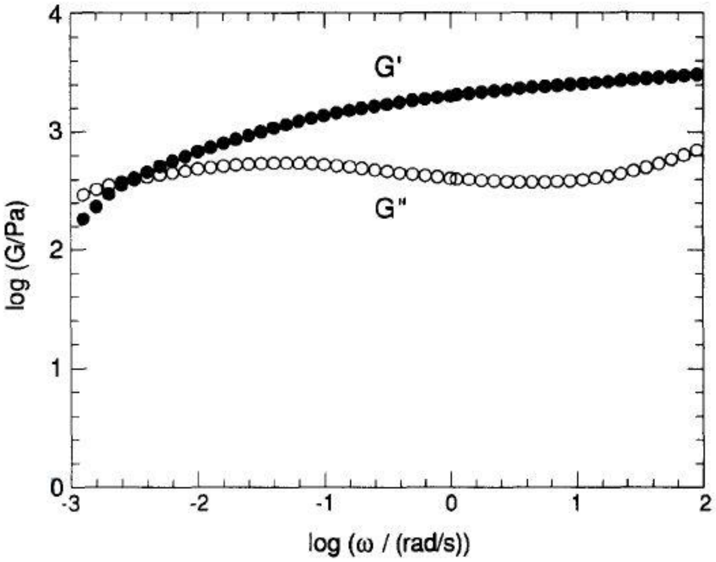

Figure 4.6 - Log-log plot of storage and loss modulus against angular frequency for a 13.9% (w/w) solution of polystyrene in di(2-ethylhexyl) phthalate [73]

CHAPTER 5

Gels as PSTs removal tools

The fundamental idea behind this PhD project, that is the realization of gels specifically tailored for the removal of PSTs and adhesive residues from paper artworks, is extensively explained in the present *Chapter*. Research guidelines, desired features for such tools, choice of proper solvents, selection of gelators suitable to confine them, and characteristics of such materials, are also fully reported.

5.1 The core aim of the present dissertation: organogels for the removal of PSTs

As broadly discussed in *Ch. 1* the removal of PSTs from paper artworks is still nowadays a challenging task for restorers: aged PSTs are indeed largely found on such artefacts due to their use for mending, mounting, and framing operations; nevertheless, they may provoke several drawbacks, e.g. media bleeding, adhesive mass migration, formation of greasy stains. So their removal is essential, but all current techniques have some associated negative side effect, like skinning of paper, lacerations, tidelines, graphic media solubilization; moreover wet methods often involve the use of volatile and toxic organic solvents, such as tetrahydrofuran, toluene, xylene, acetone, and N,N-dimethylformamide, all of them considerably hazardous for conservation professionals.

Therefore the present project arose from the intention to provide a new tape-removal tool able to overcome the above mentioned drawbacks by combining minimal invasiveness towards artworks and operators’ health.

The fundamental concept was hence to create a solvent-confining system, i.e. a gel, that could be placed directly on the top surfaces of PSTs applied on artworks. We conceived these tools to be able to maintain their shape, to be possibly easy to cut so as to exactly match shape and dimension of PSTs, and to release fluids able to interact with PSTs components: penetration through PSTs backing, achievement of the underlying adhesive and its ensuing swelling, detachment of the tape by means of a gentle mechanical action are the supposed steps for these innovative tools. In order to achieve such a result, the main features we hypothesized for these gels and that addressed our efforts can be summarized as follows:

- high solvent content, so as to grant an effective interaction with PSTs components and so tape removal
- high retentiveness, namely the gels capability in retaining the solvent so as to reduce its evaporation rate and release it gradually on a wettable substrate; moreover a quick solvent uptake is also a desirable feature since we aimed to reusable systems
- absence of residues in the exchange solvent (i.e. the solvent released from gels) that directly interact with artistic substrates; indeed it has to be free from any kinds of debris that can be possibly hazardous towards artefacts even in the long-term period

- good gels handling, in order to easily manipulate them, ensure their adhesion even to non-planar and irregular surfaces, and avoid the leaving of gels residues on treated substrates

5.2 Choice of solvents and gelators

The starting point of the research was then the selection of proper cleaning fluids, and consequently of gelled systems able to confine them. In particular we focused on *chemical organogels* due to their good mechanical properties that should grant the absence of gels remains and practicality in their use. Moreover the attainment of a low eco-toxicological impact guided us in the selection of materials for the realization of these novel tape-removal systems, concerning both solvents and gelators.

5.1.1 The selected solvent: diethyl carbonate

As stated in *Par. 1.2.3* several solvents are currently used in tape removal intervention, e.g. acetone, cyclohexane, and toluene. Nevertheless we were interested in more eco-friendly cleaning fluids; the other guideline that directed our choice was obviously the feasible PSTs components-solvent interaction. Therefore, among solvents classified as *green* ones, on the basis of *Hansen solubility parameters* our attention was caught by alkyl carbonates, and particularly by diethyl carbonate (DEC), since its solubility parameters point out the capability in interacting with oils, and both natural and synthetic resins, as displayed in the *Teas plot* reported in *Fig. 5.1*; moreover several solubility tests revealed diethyl carbonate to be also inert towards most common inks and dyes, as better discussed in *Ch. 8*, unlike other commonly used cleaning fluids, e.g. other organic solvents and microemulsions. It is also worth noting that its lower evaporation rate as compared to other solvents commonly used in paper restoration (e.g. acetone, methyl ethyl ketone, ethyl acetate) could allow a more prolonged interaction with PSTs components (see *Tab. 5.1* for DEC physico-chemical properties).

5.1.1.1 Diethyl carbonate features and applications

Alkyl carbonates are a family of organic compounds characterized by an increasing employment, both as reaction intermediates and solvents, owing to the growing sensitivity towards toxicological and environmental issues throughout last decades [90]. Following the introduction of laws that more and more strictly has been regulating both quantity and quality of *volatile organic compounds* (VOCs), the market for oxygenated solvents was the only one to grow. However, even in this class several problems arose related to their employment, e.g. esters have been gradually replacing ketones. Besides the general lower toxicity of alkyl carbonates as compared to other oxygenated solvents, even the green production technology promotes their use: actually alkyl carbonates are easily obtained by the transesterification of dimethyl carbonate, in turn synthesized by the oxidative carbonylation of methanol, a *green* reaction without any hazardous intermediates and by-products [90,91]. As a consequence, alkyl carbonates are widely used in a large assortment of fields, e.g. electrochemistry, fuels, pharmaceuticals, and medical application [92–94].

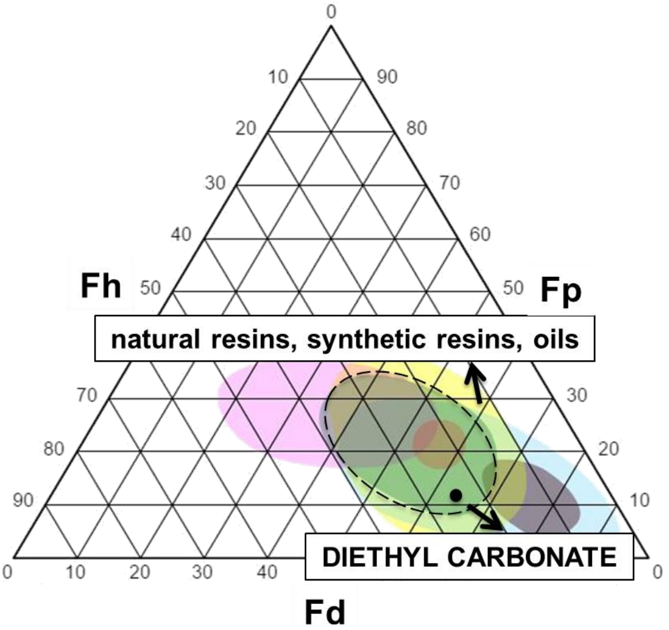

Figure 5.1 - Teas plot of the major PSTs components and diethyl carbonate; DEC reduced solubility parameters here reported are recalculated from values listed in Tab. 5.1: Fd = 64.34, Fp = 12.02, Fh = 23.64; the Teas plot is a readjustment from http://www.icr.beniculturali.it/flash/progetti/TriSolv/TriSolv.html)

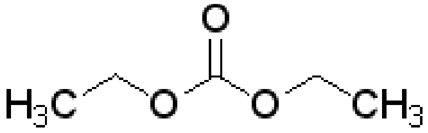

Figure 5.2 - Diethyl carbonate structural formula

Melting point (°C)	*-74.3*	[95]
Boiling point (°C)	126	[92]
Density (g/cm^3)	0.975	[92]
Viscosity (cP)	0.753 (at 100°C)	[96]
Enthalpy of fusion (kJ/mol)	9.24	[95,97]
Enthalpy of vaporization (kJ/mol)	39.7	[98]
Heat capacity (J/K)	1.0916	[95]
Vapour pressure (Pa)	$1.5356 \cdot 10^3$ (at 25°C)	[99]
Solubility parameter (MPa)	$\delta_{tot} = 18.0$ $\delta_d = 16.6$ $\delta_p = 3.1$ $\delta_h = 6.1$	[100]

Table 5.1 – Main physico-chemical properties of diethyl carbonate

Concerning specifically diethyl carbonate, the applications of this *green* solvent are a large number [101], due to its low eco-toxicological impact and physic-chemical properties, some of them listed in *Tab. 5.1*, such as its quite low volatility (as compared to other common oxygenated solvents, i.e. acetone), its thermal and hydrolytic stability, its solvent capability and immiscibility in water. Actually it is considered to be the best option to fit the oxygenated specifications and to minimize pollution in fuels [102]; it is also largely used to prepare electrolytes in capacitors and lithium batteries, and employed even as ethylating and carbonylating reagent in organic synthesis [103,104]; further applications of DEC are in the textile printing and dyeing industry as solvents of nitro-cotton, cellulose ether, synthetic and natural resin; it is also fundamental in the pharmaceutical industry [94].

5.1.2 The selected gel system: poly (ethyl methacrylate)

The criterions that guided the choice of the gelator were essentially two, i.e. the gel capability in interacting with diethyl carbonate, and so to confine it, and the perspective to create a chemically bonded 3-D network, thus leading to a solid-like system.

As mentioned in *Par. 2.2.2*, in our research group poly (methyl methacrylate) (PMMA) organogels had been already developed as confining tools for solvents like methyl ethyl ketone, ethyl acetate, butyl acetate, and cyclohexanone, successfully applied to the cleaning of easel paintings and paper [16,34]. 3-D polymeric matrices characterized by good mechanical features had been synthesized by solution polymerization of the methyl methacrylate (MMA) monomer; the obtained gels, both as small cylinders and flat sheets, can be applied and easily removed on artworks without any leaving of residues. Despite this, they are quite fragile during manipulation and undergo significant shrinkages and wreckages over drying, thus making them no reusable if not re-immersed quickly into the solvent; moreover due to their high stiffness, they are useless on non-planar and rough surfaces, like the spine of a book or an irregular painted layer.

From an applicative standpoint these features assume an essential role, consequently we decided to change the gelator in order to overcome such issues. Anyhow the ability of PMMA networks in confining even DEC, indeed with a very high retentiveness degree, persuaded us in proceeding with acrylic polymers.

In order to increase the system flexibility we looked at glass transition temperature (T_g) of acrylic and methacrylic polymers, some of them being displayed in *Tab. 5.2*. T_g results to be strongly affected by both the presence of the methacrylic group and the length of the alkyl side chain: as a consequence methacrylic polymers are characterized by higher T_g values, that gradually lowers passing from methyl to butyl side chains, due to an increased polymer flexibility and smaller chains interactions [105]; however even the presence of the solvent in the polymeric matrices to prepare may induce a reduction in T_g due to solvent-polymer interactions [106]. Therefore, since too low T_g values may result in rubbery polymers prone to the leaving of residues, we selected poly (ethyl methacrylate) (PEMA) as polymeric network for DEC confinement. Furthermore we excluded acrylates also because of their higher monomer eco-toxicological impact as compared to the homologous methacrylates [107–109].

	Acronym	***T_g (°C)*** [100,110]
Poly (methyl acrylate)	**PMA**	10
Poly (ethyl acrylate)	**PEA**	-24
Poly (propyl acrylate)	**PPA**	-57
Poly (butyl acrylate)	**PBA**	-54
Poly (methyl methacrylate)	**PMMA**	105
Poly (ethyl methacrylate)	**PEMA**	74
Poly (propyl methacrylate)	**PPMA**	35
Poly (butyl methacrylate)	**PBMA**	24

Table 5.2 - Glass transition temperature of several acrylic and methacrylic polymers

	Solubility parameter (MPa) [20,100,111]			
	δ_{tot}	**δ_d**	**δ_p**	**δ_h**
PMMA	22.7	18.6	10.5	7.5
PEMA	20.5	17.6	9.7	4.0
DEC	17.9	16.6	3.1	6.1

Table 5.3 – Hansen solubility parameters of poly (methyl methacrylate) (PMMA) and poly (ethyl methacrylate) (PEMA) as compared to diethyl carbonate (DEC)

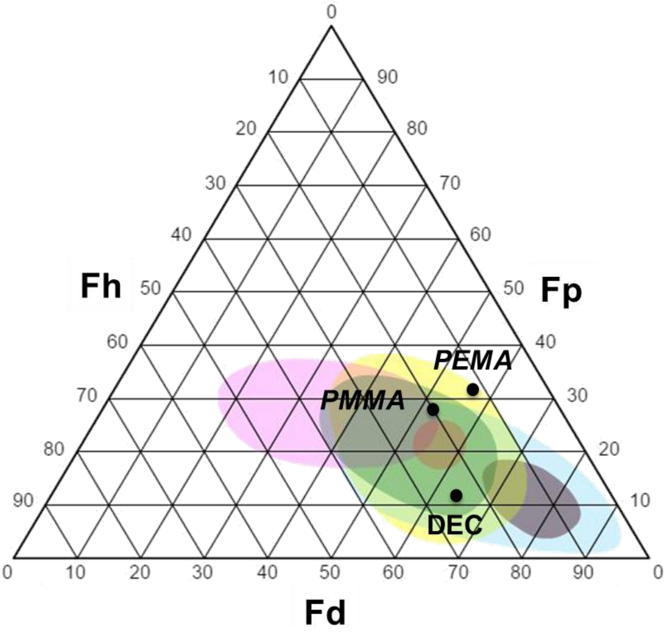

Figure 5.3 - Teas plot: reduced solubility parameters for PMMA and PEMA; data recalculated from values reported in Tab.5.3

In addition, according to *Hansen solubility parameters* shown in *Tab. 5.3* and depicted in the *Teas plot* of *Fig. 5.3*, a smaller affinity between the PEMA network and DEC should take place as compared to the PMMA matrix, thus possibly leading to reduced damages during drying, and increased capability in tuning solvent release (e.g. by varying polymer/solvent ratio and the amount of crosslinker in pre-gel formulations).

5.1.2.1 Applications and eco-toxicological impact of methacrylates

Polymethacrylates are an important class of materials used in a wide variety of commercial applications comprising engineering plastics, energy storage materials, functional coatings, food technology, quality control systems, and cosmetics (e.g. artificial fingernails); their biocompatibility allowed also their employment in biomedical devices e.g. dental composites, contact lenses materials, drug delivery, biosensor membranes, and bone cement [112–118].

The first reported methacrylate polymer was poly (methacrylic acid) in 1880; after that poly (methyl methacrylate) was marketed in 1933, becoming nowadays the world’s most widely produced methacrylate polymer. Since then several different kinds of polymers, both homo-, co-, and ter-polymers, were developed displaying varied features according to the pendent functional ester groups that can be incorporated into the methacrylic molecule [113]. Anyway the chemical structure of a polymer repeat unit is only one of the many parameters affecting its properties; actually the fabrication method is equally important. Free radical polymerization is currently the most widely used synthetic pathways, being cost effective, easy to implement, and conductible by means of different methods, e.g. bulk, solution, suspension, and emulsion. It involves the formation of free radicals from an initiator, the following reaction of the free radicals with monomers to form radical monomer species, the subsequent propagation to high polymers by repeated addition of monomers to the growing radical chains, and eventually the termination by radical-radical reaction through coupling or disproportionation. In the last decades new living radical polymerization techniques arose, their distinctive feature being the suppression of irreversible chain termination by adding compounds able to react with propagating radicals by reversible deactivation or reversible chain transfer; as a result, the most of the propagating chains are in a dormant form, and the rapid equilibration between active and dormant species ensures the chains growth at an equal rate, thus allowing a great control over the polymer composition, molecular weight, and architecture as compared to standard free radical polymerization [113,119].

Since alkyl methacrylates are high production volume chemicals due to their wide industrial and commercial employment, their potential for human exposure had been assessed through several studies. They were commonly considered responsible of skin and respiratory irritation and sensitization, and also possible carcinogenic compounds [107,120]. Despite this recent studies performed mostly on methyl methacrylate (MMA), provided evidence of respiratory irritation but neither airway sensitization nor occupational asthma; moreover it is worth noting that all the diagnosed respiratory and skin irritation was about workers employed in the secondary industries, such as dental, surgical, and cosmetic products, maybe due to lack of proper exposure controls that are instead present in the primary industry (i.e. raw materials production). Additionally we have to highlight that MMA is also the most volatile among methacrylates, with human occupational exposure occurring primarily by inhalation; contrarily, methacrylates with longer C-chain esters (i.e. ethyl methacrylate) may not be sufficiently volatile to produce high inhalation exposures [107,120]. Concerning skin sensitization ethyl methacrylate was found to be only a weak sensitizer in case of repeated skin contacts occurred in fingernails treatments [112]. The carcinogenicity of alkyl methacrylates had been also assessed by means of both *in vitro* and *in vivo* studies: lower alkyl methacrylates (i.e. alkyl methacrylates characterized by a short side-chain, such as methyl-, ethyl-, butyl-methacrylate, etc.) were found to be genotoxic *in vitro* where they are able to induce DNA damages, nevertheless recent studies verified that such events had been observed following applications of toxic doses of the tested agent. Furthermore, despite this *in vitro* capacity, alkyl methacrylates were proved to be non-carcinogenic in either animals or humans; the dichotomy between the *in vitro* and *in vivo* effects may be explained by considering the genotoxic agents responsible for the *in vitro* behaviour, all of them derived from the detoxification metabolism [107,121].

Further studies on the environmental impact of methacrylates, even proved they don’t undergo bioaccumulation and that methyl- and ethyl-methacrylate are characterized by a low aquatic toxicity [108,109].

PART III

EXPERIMENTAL

CHAPTER 6

Organogels: synthesis and characterization

The present *Chapter* describes the materials used for the synthesis of organogels, the preparation procedures, and the experimental techniques performed for their physico-chemical characterization.

6.1 Synthesis of organogels

Chemically cross-linked organogels were prepared by solution polymerization starting from the monomer solubilized in an organic solvent together with initiator and cross-linker. The presence of the liquid medium should grant the formation of polymer voids, thus increasing the porosity of the network and the amount of solvent loaded inside it.

Different gel formulations were prepared to understand the role of the different components in final properties: in particular several diluents were tested to verify their porogen action, and also to decrease processing costs. Poly (ethyl methacrylate) (PEMA) gels were obtained starting from ethyl methacrylate (EMA) organic solutions. Also blended systems were prepared by adding linear poly (ethylene glycol) (PEG) with different average molecular weight to the monomer solution, in the attempt to realize semi-interpenetrating (semi-IPN) systems: its

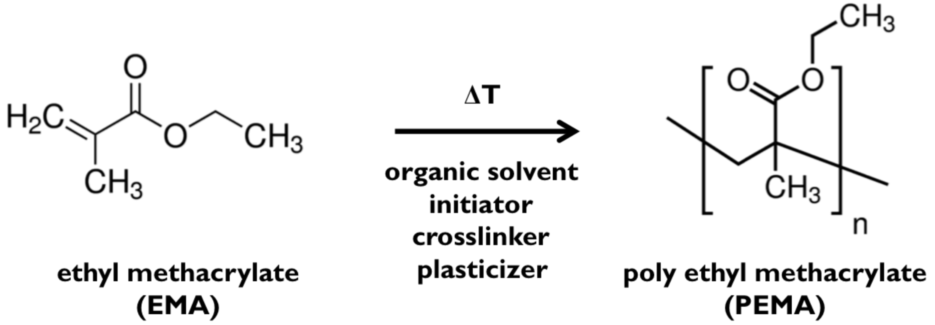

Figure 6.1 - Scheme of the reaction for gels synthesis

influence on gels mechanical properties (e.g. softness and adhesion) and on tuning network the affinity to organic solvents, was investigated.

6.1.1 Materials

Tab. 6.1 shows the chemicals used for the preparation of PEMA based organogels and their function in the synthesis. All products were used as received.

Chemicals		**Company**	**Purity**	**Function**
ethyl methacrylate	EMA	Sigma-Aldrich	≥ 98.5%	monomer
poly (ethylene glycol)	PEG	Fluka	-	plasticizer
2-(2-methyl-acryloyloxy)ethyl 2-methylacrylate	EGDMA	Sigma-Aldrich	≥ 98%	cross-linker
poly (2-(2-methyl-acryloyloxy) ethyl 2-methylacrylate)	poly (EGDMA)	Sigma-Aldrich	-	cross-linker
2, 2’-azobis(isobutyronitrile)	AIBN	Fluka	>98%	initiator
diethyl carbonate	DEC	Sigma-Aldrich	≥ 98.5%	diluent
ethyl acetate	EA	Sigma-Aldrich	≥ 99%	diluent
2-butanone	MEK	Sigma-Aldrich	≥ 99%	diluent
2-propanol	IP	CTS	≥ 96%	diluent

Table 6.1 - Chemicals used for organogels preparation

Several trials were needed to develop gels with the desired characteristics for cleaning purpose, i.e. mechanical strength, adhesiveness, suitable and tuneable solvent release.

In order to achieve satisfying systems both chemicals and reaction parameters were changed, as shown in *Table 6.2*.

MONOMER/SOLVENT RATIO (w/w)	1 ÷ 0.25	
INITIATOR % **(w/w respect to EMA)**	0.5 ÷ 5	
CROSSLINKER % **(w/w respect to EMA)**	0.5 ÷ 5	
SOLVENT	DEC, EA, MEK, IP	
PLASTICIZER	PEG	*molecular weight*: > 400 kDa
		PEG/EMA ratio (w/w): 0.1 ÷ 0.3
TEMPERATURE (˚C)	45 ÷ 70	
TIME OF REACTION (h)	4 ÷ 8	

Table 6.2 - Chemicals and reaction parameters changed to improve gel systems

6.1.2 Methods

Pre-gel formulations were poured into 13 x18 cm^2 glass moulds (*Fig. 6.1*) so as to obtain gel sheets of 1–2 mm thickness. The polymerization reaction was carried out at constant temperature (55 ÷ 65°C) for 6 hours, in a similar way as described in previous works [16,34,7]. After the gelation process, gel films were cut in pieces of about 2 x 5 cm^2 (about 5 g each) and then put in DEC (about 100 mL for 10 pieces) for 24 h, to extract possible unreacted monomer and not embedded polymer chains. After the first extraction, the solvent was refreshed. Before characterization, organogels were let to equilibrate with DEC.

Figure 6.2 - Representation of the mould for casting organogel films: (1) glass plates; (2) rubber thickener

Figure 6.3 - After the synthesis gels were put in DEC both for the removal of undesired monomer residues and the loading of the solvent

6.2 List of prepared materials and general observations

Tab. 6.3 displays a list of selected systems among all the ones prepared: they were considered the most promising for cleaning applications and, therefore their physico-chemical characterization will be shown. Indeed not all the prepared pre-gel formulations led to interesting results: some systems did not gelate and in some cases the obtained gels were not suitable for applications to the restoration of artefacts due to their poor mechanical properties, e.g. when a large amount of solvent (≥ 70%) was used.

	PRE-GEL FORMULATION			
SAMPLE	**EMA % (w/w)**	**DILUENT % (w/w)**		**PEG % (w/w)**
ED50	50	diethyl carbonate	50	-
P10	40	2-propanol	50	10
P10-E2	40	2-propanol	50	10
P5	45	2-propanol	50	5

Table 6.3 – Major components in the selected pre-gel formulations; the initiator concentration (w/w respect to EMA) was the same in each pre-gel formulation; the cross-link concentration (w/w respect to EMA) was the same for ed50, P10, and P5; P10-E2 gel was instead prepared with a double crosslinker concentration

As we can notice from *Tab. 6.3*, the selected formulations were synthesized using either diethyl carbonate or 2-propanol as diluent; in the last case PEG was added.

As a matter of fact the use of different liquids instead of diethyl carbonate during gelification (i.e. ethyl acetate, 2-butanone, 2-propanol) did not improve the mechanical properties of gels, quite the opposite worsening them; anyway the possibility of reducing processing costs thanks to the use of 2-propanol guided us towards the addition of plasticizers. Poly (ethylene glycol) with different average molecular weight were therefore tested: in a previous work we noticed that PEG with an average molecular weight of 1000 kDa affected positively the mechanical properties of gels [7], but actually the most satisfying results reported in *Tab. 6.3* were achieved by further increasing the polymer chains length (av. MW ≈ 35000 kDa). This is probably due to a better embedment of PEG linear chains within the PEMA network when the average molecular weight increases; actually we experimented that higher molecular weight PEG linear chains give rise to weak gels in diethyl carbonate at room temperature (see *Fig. 6.4*).

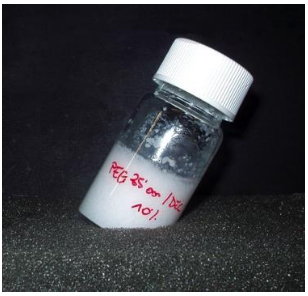

Figure 6.4 - PEG$_{35000}$ *in DEC gives rise to weak gels at room temperature*

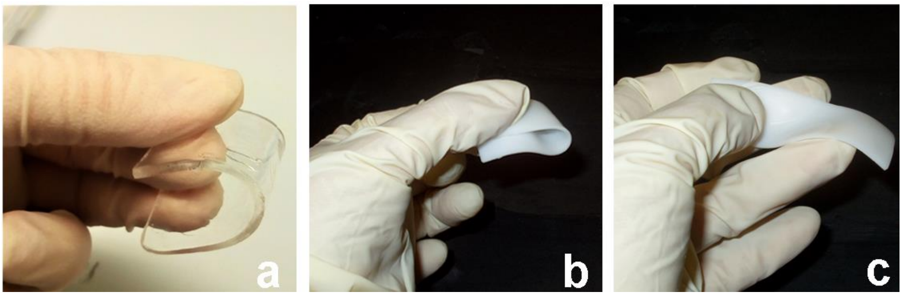

Figure 6.5 - Turning from PEMA (6.5a) to PEMA/PEG (P10) gels (6.5b, c) we can notice a loss in transparency and an improve in flexibility

From a macroscopic point of view PEMA and PEMA/PEG formulations are similar concerning their swelling in diethyl carbonate when put in the solvent after their synthesis. Anyway the addiction of PEG with increasing chains length led to some different features, i.e. greater flexibility and adaptability to non-planar surfaces, and optical opacity: actually gels turn from transparent to opalescent/white ones at increasing PEG concentrations; such behaviour may be related to network inhomogeneities (i.e. causing light scattering) due to the presence of PEG [122,123].

6.3 Physico-chemical characterization of gels

The prepared organogels underwent a deep physico-chemical investigation to assess the characteristics of the polymeric networks and the solvent-related features. Here equations and instrumental conditions used are presented; analysis were always performed on gels previously equilibrated with diethyl carbonate by immersion in it (as previously said the solvent was added and then refreshed just one time after the synthesis).

6.3.1 Reaction yield and monomer residues

The reaction yield quantifies the amount of product obtained after the extraction of the soluble components by one week immersion in DEC. The reaction yield was determined gravimetrically 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 was considered:

$$Yield\ (\%) = \frac{W_d}{W_0} \cdot 100 \qquad \text{(Eq. 6.1)}$$

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

The presence of both monomer and polymers in the refreshed solvent was checked with Fourier Transform Infrared Spectroscopy (FTIR): a BioRad FTS-40 spectrometer recorded spectra from 4000 to 400 cm^{-1}, at 4 cm^{-1} 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, FTIR grade ≥ 99%, trace metal basis).

6.3.2 Composition of gels

Organogels composition was checked by means of Attenuated Total Reflectance FTIR spectroscopy (ATR-FTIR). In particular PEMA/PEG systems were examined in order to verify the efficiency of the blending process. On account of this, the presence of PEG in organogels was investigated by examination of variations in their characteristic absorptions before and after one month immersion in DEC. 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^2), averaging 128 scans in the 4000 – 650 cm^{-1} range, with a spectral resolution of 4 cm^{-1}.

6.3.3 Solvent content in gels: gravimetric and thermal analysis

The assessment of the content of both the total and the free solvent loaded within the polymeric networks is of great importance to evaluate if organogels are suitable for being used as PSTs-removal tools.

6.3.3.1 Equilibrium Solvent Content

In order to have information about the affinity of organogels to the liquid phase the Equilibrium Solvent Content (*ESC%*) was determined both gravimetrically (*ESCg%*) and through calorimetric analysis (*ESCc%*). As already stated in *Ch. 4*, *ESC%* was calculated as follows [45,80]:

$$ESC\% = \frac{W_s}{W_g} \cdot 100 \qquad \text{(Eq. 6.2)}$$

were W_s is the amount of solvent loaded in the sample, as evaluated by gravimetric measures or thermal analysis, and W_g is the mass of the fully swollen gel.

Concerning the gravimetric method W_s was determined as

$$W_s = W_g - W_d \qquad \text{(Eq. 6.3)}$$

where W_d is the mass of the dried gel obtained as described in *Par. 6.3.1*. Two different values were measured for W_g, at two different times: 1) before the drying process, W_g1; 2) after the drying process, W_g2 , i.e. by putting the dried gels into the solvent up to complete re-swelling. In this way *ESCg1%* and *ESCg2%* were assessed: by comparing such values we can verify if possible alterations of the porous structure (e.g. pore collapse), that would affect the Equilibrium Solvent Content, occur during the drying procedure.

Thermal analysis were performed by means of Derivative Thermogravimetry (DTG) using a SDT Q600 (TA Instruments) apparatus. Fully swollen gel samples of 2–3 mg were placed in aluminum pans and subjected to a temperature scan from 20 to 250°C (10°C/min) in a nitrogen atmosphere (100 mL/min).

6.3.3.2 Free Solvent Index

Differential Scanning Calorimetry (DSC) was used for the assessment of the Free Solvent Index, i.e. the amount of solvent within organogels acting as bulk solvent and therefore available for the cleaning process. The general formula for the calculation of *FSI* is [124]:

$$FSI = \frac{\Delta H_{exp}}{\Delta H_{bulk} \cdot ESC\%} \cdot 100 \qquad \textit{(Eq. 6.4)}$$

where ΔH_{exp} (J/g) is the enthalpy of fusion of solvents in gels, as determined by DSC measures, ΔH_{bulk} (J/g) is the value for the enthalpy of fusion of the bulk solvents, and *ESC%* is the Equilibrium Solvent Content as previously defined.

For the determination of *FSI*, DSC analysis were performed on 3 - 5 mg of equilibrium-swollen organogels, while the ΔH_{bulk} values were acquired on 10 - 20 mg of pure solvent; both gels and solvents samples were put in Tzero™ aluminum hermetic pans. For analysis a Q2000 Calorimeter (TA Instruments), equipped with an autosampler and a cooling device (Refrigerated Cooling System, RCS90 - TA Instruments) was used. Measurements were carried out at a constant nitrogen flow rate of 50 ml/min. Temperature range scan was from -90 to 25°C with 0.5°C/min rate.

FSI values calculated as above, represent an index of the free solvent over the total amount of solvent loaded within gels; to a better comprehension of results, we also report the value of the percentage free solvent (*FSC%*), bound solvent (*BSC%*), and polymer content (*PC%*) as compared to the total mass of the gel; such values were calculated as follow:

$$FSC\% = ESC\% \cdot FSI \qquad \textit{(Eq. 6.5)}$$

$$BSC\% = ESC\% - FSC\% \qquad \textit{(Eq. 6.6)}$$

$$PC\% = 100\% - ESC\% \qquad \textit{(Eq. 6.7)}$$

6.3.4 Solvent-related properties: release, evaporation, and uptake

From an applicative point of view the retentiveness of gels is a very important characteristic: in general terms gels tailored for the restoration of works of art should release a proper amount of solvent: neither too high, so as to avoid uncontrolled spreading, nor too low, so as to be effective. Moreover the decrease in the evaporation of the confined solvent as compared to the free one limits the eco-toxicological impact on operators, and costs related to treatments. Even a rapid solvent uptake is a desirable feature that simplify restoration operations.

6.3.4.1 Solvent release

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 (Ø = 55 mm, grade 1) for 15 minutes, a representative time of real applications in cleaning interventions. During tests, gels were covered with plastic foils to prevent solvent evaporation. The amount of released solvent was measured gravimetrically and normalized by unit area.

6.3.4.2 Solvent evaporation

The evaporation rate of both confined and bulk solvents was assessed gravimetrically by exposing both the swollen gels and the free solvents to room conditions (T = 25°C, RH = 65%) and normal air circulation (no ventilation/aspiration) within 60 minutes; 0.30 g of solvent were compared to a mass of swollen gels containing approximately a similar amount of liquid, as calculated from ESC%. The residual solvent fraction at time t, F_s, is defined as follows:

$$F_s = \frac{M_t}{M_\infty} \qquad \textit{(Eq. 6.8)}$$

where M_t is the mass of residual solvent at the given time, and M_∞ is the total amount of solvent in the fully swollen gel, as derived by calorimetric analysis.

6.3.4.3 Solvent uptake

Solvent uptake kinetics were evaluated by immersing the completely dried gels (following the previously described procedure, see *Par. 6.3.1*) in the organic solvent; the initial weight of swollen gels samples was about 0.30 g. After immersion gels were weighted at given time intervals, up to complete swelling. F_s values, as defined in *Eq. 6.4*, were reported.

By measuring gels volume before and after the solvent uptake (i.e. the volume of both dried and fully swollen gels, V_d and V_s respectively) we calculated the *Percentage Volume Swelling* (*S%*):

$$S\% = \frac{V_s}{V_d} \cdot 100\% \qquad \textit{(Eq. 6.9)}$$

6.3.5 Viscoelastic behaviour of gels: rheological analysis

The mechanical dynamic properties of fully swollen organogels were assessed by means of rheological studies. Such analysis gave important information about the polymeric networks structure and their response to external stress. Rheological measurements were performed on a TA

Instrument Hybrid Rheometer Discovery HR-3, using a plate-to-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 confined solvents. Oscillatory shear measurements (shear strain between 10^{-3} and 80%, oscillation frequency 1 Hz) were carried out in order to determine the linear viscoelastic region and the critical oscillation strain (γ_c). Frequency sweep tests for the determination of the frequency dependence of the storage and loss moduli, respectively *G'* and *G'',* were carried out within the linear viscoelastic range (shear strain 0.1%) over the frequency range 0.01 – 100 Hz. Even the loss tangent values, *tan δ*, are reported, thus being an important index to discriminate between weak and strong gels [17,125]. Creep tests were then performed so as to obtain information about the permanent deformation after compression, i.e. the viscous reformation v_{ref}; for analysis a constant stress of 30 Pa was applied for a compression time of 1 minute on gels samples, then data concerning the relaxation of samples (i.e. their *strain vs time*) were acquired up to 3 minutes.

CHAPTER 7

Results and discussion

The results of the physico-chemical investigation performed on the selected gels mentioned in the previous *Chapter* (see *Tab. 6.3*) are discussed here. By comparing this different systems we will notice how their features are affected by the presence of PEG, its percentage in the pre-gel mixture, and the amount of used crosslinker.

7.1 Reaction yield and monomer residues

Organogel synthesis through solution polymerization of both PEMA networks and PEMA/PEG systems leads to the formation of polymeric matrices insoluble in DEC at room temperature. The evaluation of the yield provides information about the process efficiency, i.e. polymerization reaction, the cross-links between PEMA chains, and embedment of PEG linear chains within the PEMA 3-D network.

As reported in *Tab. 7.1*, the yield for PEMA/PEG systems (i.e. P10, P10-E2, and P5 gels) is significantly higher than the one of pure PEMA network (i.e. ED50 gel): actually an increase of about 20% was observed. A reaction yield below 100% in ED50 gel is mainly ascribed to the volatility of the EMA monomer, which may provoke its evaporation in the early stages of the polymerization reaction; possibly in PEMA/PEG systems the decrease in the amount of EMA in the pre-gel mixture, the feasible interaction between EMA and PEG, and the efficient embedment of PEG into the PEMA network may lead to the yield increase.

	Yield (%)
ED50	73 ± 3
P10	94 ± 3
P10-E2	86 ± 5
P5	92 ± 2

Table 7.1 – Reaction yield (%) for different organogel formulations after one week extraction in diethyl carbonate; the solvent was renewed after 24 h from the synthesis, and then equilibrated with gels

Owing to the incomplete polymerization reaction, the assessment of possible residues of both monomers and polymers in the exchange solvent was of paramount importance before applying DEC loaded gels on artworks, due the possible negative drawbacks of such impurities on treated substrates. *Fig. 7.1* compares the FT-IR spectra of pure DEC, EMA monomer, PEMA, and PEG (all reported in *Fig. 7.1a*), with the ones acquired on the exchange solvent for each gel system (see *Fig. 7.1b*), that is DEC equilibrated with gels for one week after the synthesis (as previously said the solvent was changed only once after 24 h from the synthesis); only the spectral range between 1000 and 1400 cm^{-1} is reported since both monomer and polymers have their strongest IR absorptions in this region allowing their identification in the solvent at concentration up to 0.5 mg/ml (at different wavenumbers no significant differences with the spectrum of pure DEC arise even at concentration of 10 mg/ml). In all the spectra of *Fig. 7.1b* no detectable bands were found in the region between 1220 - 1060 cm^{-1} ascribable either to EMA, PEMA, or PEG (stretching of C–O–C in ester groups [126–129]).

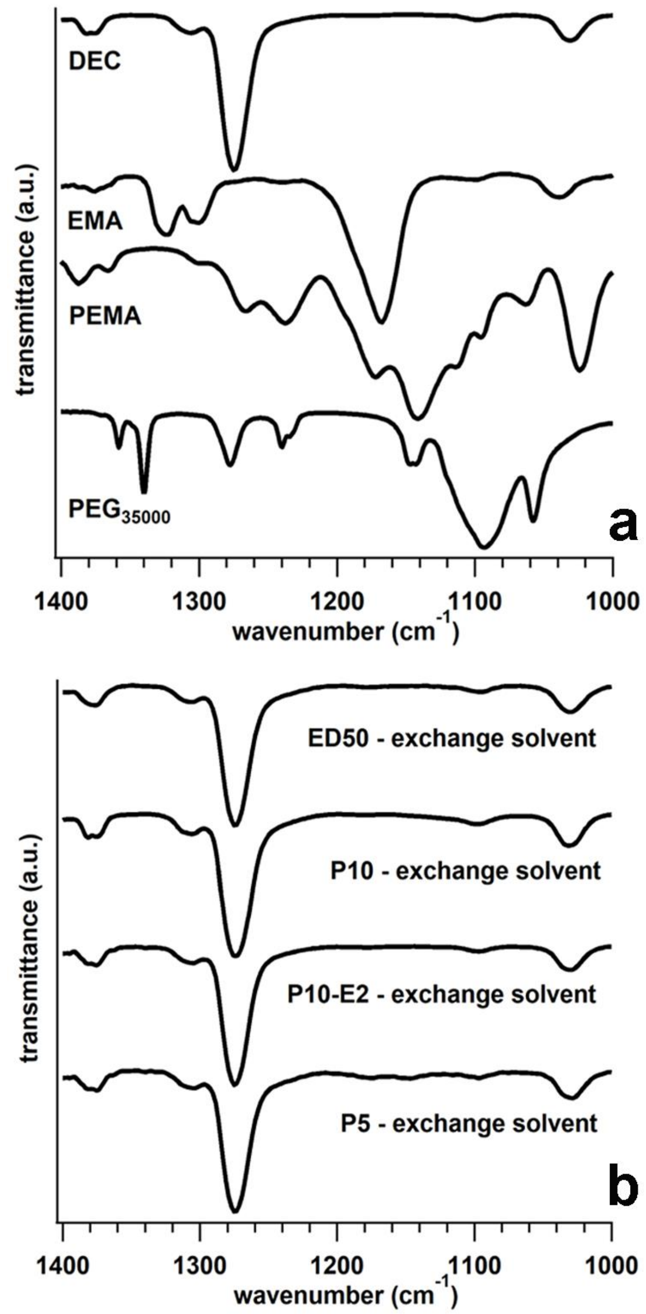

Figure 7.1 – a) FT-IR spectra (1400 – 1000 cm^{-1}) of diethyl carbonate (DEC), pure ethyl methacrylate (EMA) monomer, poly (ethyl methacrylate) (PEMA) and poly (ethylene glycol) (PEG$_{35000}$, average molecular weight = 35000 kDa); b) FT-IR spectra of DEC used as exchange solvent for one week, after preparation of gels and a first 24 h extraction in DEC: the spectra of DEC equilibrated with ED50, P10, P10-E2, and P5 are all displayed

7.2 Composition of gels

The investigation on organogels composition was performed through ATR-FTIR analysis mainly in order to verify in PEMA/PEG systems the efficiency of the embedment of PEG linear chains within the PEMA 3-D network. For this purpose, infrared spectra of previously dried gels were collected before and after one month extraction in DEC.

Fig. 7.2 compares the spectrum of ED50 with the ones of PEMA/PEG gels, all acquired after DEC extraction. In each spectrum we can recognize absorptions distinctive of PEMA, whose most intense peaks are at 1722 and 1143 cm^{-1}, respectively the C=O stretching vibration and the C-O-C stretching mode of the ester group [127,129]. Moreover in PEMA/PEG gels some signals diagnostic for the presence of PEG arise: in *Fig. 7.2* peaks highlighted by the "*" symbol and located at 2891,

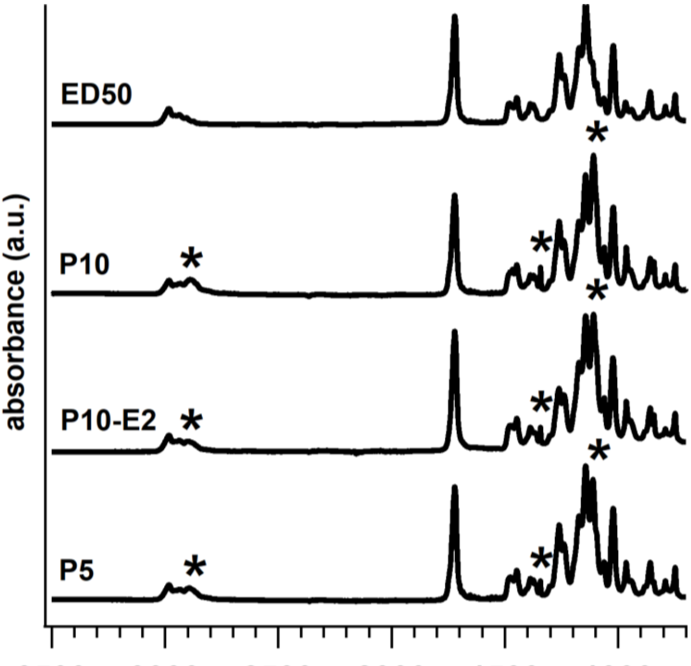

Figure 7.2 - ATR-FTIR spectra of PEMA (ED50) and PEMA/PEG gels (P10, P10-E2, P5); the "" symbol highlights the absorptions distinctive for PEG*

1343, and 1109 cm^{-1} are ascribable respectively to the CH_2 stretching mode of methylene groups, to the CH_2 wagging, and to the C-O-C stretching of the ether linkage [128,129]. By comparing the spectra of P10 and P5 we can also notice that the relative intensity of peaks assigned to PEG decrease with the increasing of the EMA/PEG ratio in the pre-gel mixtures (i.e. 40/10 w/w in P10 and 45/5 w/w in P5).

Spectra acquired on gels before and after one month extraction in DEC

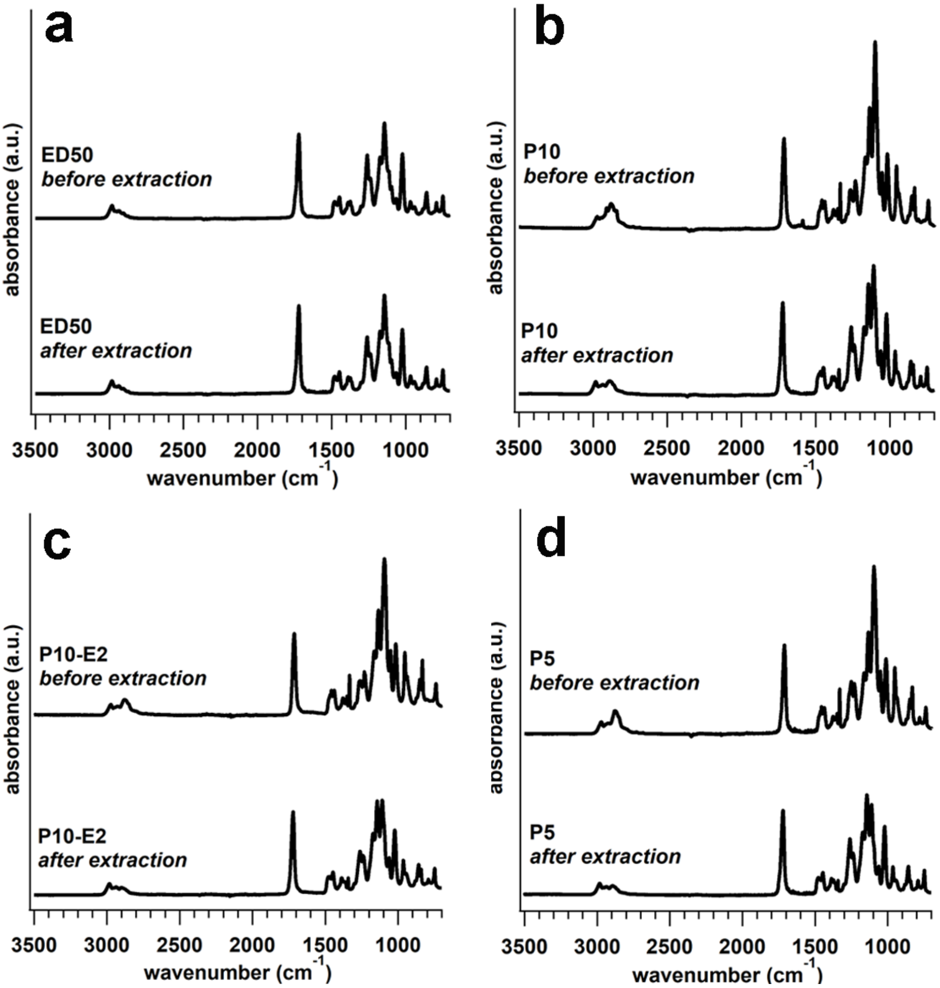

Figure 7.3 - ATR-FTIR spectra of each gel before and after extraction in DEC: a) ED50, b) P10, c) P10-E2, d) P5; the spectra of PEMA/PEG gels are all characterized by a decrease in the relative intensity of bands ascribable to PEG after DEC extraction

are displayed in *Fig. 7.3*: in P10, P10-E2, and P5 spectra we can notice after the extraction process an inversion in the intensity of peaks at 1143 and 1109 cm^{-1} (respectively PEMA and PEG IR absorptions), thus pointing out a release of PEG throughout this period (i.e. one month). Nevertheless a constant monitoring of gels was carried out by acquiring IR spectra once a week both on them and on exchange solvents: no significant changes were observed after the first week of extraction, thus pointing out the effectiveness of PEG embedment into the PEMA 3-D network.

7.3 Solvent content in gels

The amount of solvent retained within gels is a measure of the capacity of these networks to swell in a specific solvent. The kind of interactions occurring between the solvent and the polymeric matrix strongly affects gels retentiveness, that is both the amount of released solvent over time and the ability in avoiding the spreading of solvent beyond their edges. The total amount of DEC loaded in the presented polymeric gels and its fraction as free solvent were assessed by gravimetric and calorimetric methods.

7.3.1 Gravimetric analysis

Tab. 7.2 lists experimental results about the solvent content assessed gravimetrically for each gel at its equilibrium. As explained in *Par. 6.3.3.1* the two values here displayed are acquired at different times: *ESCg1%* is the solvent content of organogels equilibrated with DEC just after the synthesis; *ESCg2%* is the solvent content for gels dried after the first equilibration with DEC, and then re-loaded with the solvent. The comparison between this two values is important in order to understand if the adopted drying process leads to the polymeric network breakage: actually even a partial collapse of the porous structure may induce different values in *ESCg2%* [34].

As we can notice from *Tab. 7.2* all the presented formulations are characterized by an Equilibrium Solvent Content between 70% and 80%, much higher than the percentage of solvent used during the synthesis (i.e. 50% w/w for all gels): such a behaviour is clearly related to the high affinity of DEC for PEMA based polymeric networks. All gels are characterized by very similar content of loaded solvent regardless the presence of PEG; a slightly lower content is observed for the P10-E2 formulation: according to literature, the increased chain interpenetration, due to the higher cross-linker concentration in the pre-gel reaction mixture, may result in a reduced swelling ability [130]. No relevant differences are observed among *ESCg1%* and *ESCg2%*, thus pointing out that no significant wreckages in the polymeric structure take place throughout the drying process.

	ESCg1%	***ESCg2%***
ED50	78 ± 1	78 ± 1
P10	78 ± 1	78 ± 1
P10-E2	72 ± 1	70 ± 1
P5	79 ± 1	79 ± 1

Table 7.2 – Equilibrium Solvent Content assessed by gravimetric analysis: ESCg1% is the amount of solvent retained in gels before the drying process, ESCg2% is the same parameter measured after the drying of gels and their re-swelling

7.3.2 Thermal analysis

ESC% values obtained through Derivative Thermogravimetry (DTG) measures are presented in *Tab. 7.3*: they are in good agreement with the values assessed gravimetrically for all the presented gels, except for the P10-E2 formulation which is characterized by a higher calorimetric value (i.e. *ESCg1%* = 72%, *ESCc%* = 77%); this is possibly related to an incomplete gel drying in gravimetric analysis.

	ESCc%	***FSI***	***ΔH_{exp} (J/g)***
ED50	76 ± 3	0.08 ± 0.01	4.7 ± 0.6
P10	79 ± 2	0.79 ± 0.03	48 ± 2
P10-E2	77 ± 1	0.54 ± 0.02	33 ± 1
P5	80 ± 2	0.16 ± 0.02	10 ± 1

Table 7.3 – Experimental thermal parameters for DEC loaded organogels: Equilibrium Solvent Content (ESC%) was assessed by Derivative Thermogravimetry (DTG); Free Solvent Index (FSI) and enthalpy of melting of the free solvent in gels (ΔH_{exp}) were obtained by Differential Scanning Calorimetry

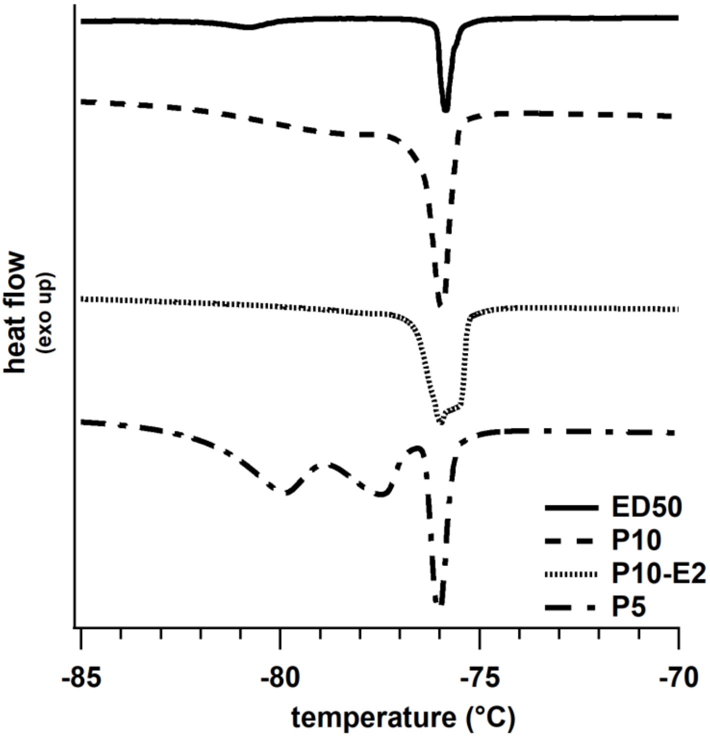

Figure 7.4 – DSC measures on PEMA based organogels loaded with DEC: the main peak in each thermogram corresponds to the melting of the free solvent fraction; other bands at lower temperature are ascribable to the melting of the freezable solvent fraction

As previously said in *Par. 6.3.3.2*, before performing Differential Scanning Calorimetry (DSC) on gels, a preliminary assessment of the temperature of melting (T_m) and the enthalpy of fusion (ΔH_{bulk}) of DEC was carried out, due to the conflicting data available in literature for this solvent: DSC analysis on pure DEC gave T_m = -75°C and ΔH_{bulk} = 77 J/g, in agreement with *Ding et al.* (2001 and 2004) and *Pokorný et al.* (2017) [95,97,131].

DSC was then performed on fully swollen gels to determine the relative contents of the different solvent states in organogels (i.e. free and bound solvent): *Tab. 7.3* reports the Free Solvent Index and the enthalpy of fusion for each gel, as calculated by the thermograms of *Fig. 7.4*. In this chart the main endothermic peak in each plot is observed near the T_m of pure DEC, thus representing the melting of the free solvent or of solvent very close to a free state [132]. The broadening of the melting peak of free DEC from PEMA to PEMA/PEG networks may be ascribed to the heterogeneity in the confinement distribution of the solvent: actually the lowering of T_m of the liquid phase is reported to be related to the radius of pores of the gel network mesh in which the solvent crystallizes [133–135]. From experimental data we can also notice that both *FSI* and ΔH_{exp} strongly increase with the embedment of PEG within the PEMA network: on the contrary the greater affinity of DEC to PEG rather than to PEMA, according to Hansen solubility parameters [20,111], should address the solvent towards a bound state [136]; anyway, as proved by ATR-FTIR analysis (see *Par. 7.2*) the partial solubilization of the embedded PEG carried out by DEC, leads to a less dense structure, so that decreasing the monomer concentration (i.e. ED50 > P5 > P10) and the network scaffolding (P10-E2 > P10) results in an increased amount of free solvent, in agreement with the literature [132–135].

Concerning the bound solvent, from the DSC chart of *Fig. 7.4* different behaviours arise: in ED50 and P5 bands related to the freezable solvent appear, i.e. at T_m = -81°C in ED50, and T_m = -79°C and -77°C in P5; the higher T_m for the freezable solvent in P5 suggests weaker interaction between DEC and the PEMA/PEG network and differences in the cluster size [132,135,136]. This trend is confirmed in P10 and P10-E2 by both the disappearance of the freezable solvent and the increased *FSI*. In none gels we can exclude the presence of a portion of non-freezable bound solvent.

From experimental data listed in *Tab. 7.3*, we also extracted the gels composition in term of *Polymer Content* (*PC%*), *Bound Solvent Content* (*BSC%*), and *Free Solvent Content* (*FSC%*), as defined in *Par. 6.3.3.2*. Differently from *FSI*, *FSC%* is referred to the overall mass of gels: in this way the histograms reported in *Fig. 7.5* clearly show the real solvent content available for cleaning interventions for each gel formulation.

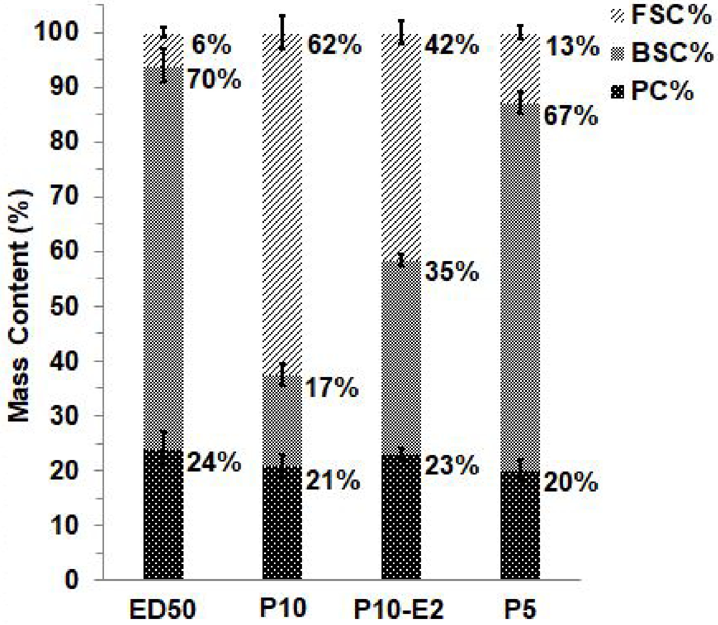

Figure 7.5 - Percentage composition of gels: Polymer Content (PC%), Bound Solvent Content (BSC%), and Free Solvent Content (FSC%) are displayed for each system in histograms

7.4 Solvent-related properties: release, evaporation, and uptake

The evaluation of the solvent content in the presented polymeric matrices is of great important but not sufficient to grant their suitability for restoration interventions: even DEC release, evaporation, and uptake have to take place properly. Obviously, even such parameters are affected by polymer-solvent interactions: indeed different formulations lead to tuneable gels solvent-related features. All these properties were assessed gravimetrically.

7.4.1 Solvent release

Solvent release tests provide useful information on gels retention properties: although the amount of solvent released on a specific substrate depends on its particular characteristics, the assessment of the amount of solvent released on a highly wettable support (e.g. filter paper) allows a more conscious choice on the proper formulation. For instance, if the materials constituting the artefact are highly solvent-sensitive, enhanced retention features are required and a system characterized by a low solvent release will be the most suitable. On the other hand, if the layer to be removed is very tough and hardened or difficult to solubilize, the gel must be able to exchange higher quantities of liquid phase with the surface; thus, a formulation with greater solvent release ability might better match this requirement.

Tab. 7.4 lists the mass of DEC (normalized per unit area) released from each gel formulation in 15 minutes of application on Whatman® paper samples. As mentioned in the previous paragraph, the solvent available for release is the one in a free state (or very close to it): actually a trend similar to the one observed for the Free Solvent Content takes place for the release of solvent from gel matrices [27]. Conforming to previous works [16,27,40] a tuneable release is achieved by varying chemicals concentrations in pre-gel formulations: a greater chain interpenetration in organogels (i.e. due to both a lower amount of PEG and a higher cross-linker quantity) leads to more retentive systems.

	Solvent Release (mg/cm^2)
ED50	1.7 ± 0.4
P10	5.0 ± 0.1
P10-E2	4.1 ± 0.5
P5	1.5 ± 0.1

Table 7.4 - Solvent release on Whatman® filter paper for the different gel formulations after 15 min contact

7.4.2 Solvent evaporation

The reduction in the evaporation rate of DEC confined in the polymeric matrices was another aim that we had set: actually the volatility of DEC (vapour pressure of free DEC is $1.5356 \cdot 10^3$ Pa at 298.2°K [99]) is quite enough to cause its evaporation before any interactions with the treated substrates takes place; moreover a high solvent retention is significant also to preserve the health of operators and to reduce costs.

Fig. 7.6 shows the solvent loss of PEMA based gels and bulk DEC up to 1 hour at room conditions (T = 25°C, RH = 65%): all the evaporation processes occur according to a zero-order kinetic, evidencing a drying rate constant with time. Since the evaporation of solvents from a polymer network can be compared to a drying process, if we could assume a constant drying area, the constant evaporation rate would reveal a process fully governed by the rates of external heat and mass transfer; in such a case a film of free solvent would be always available at the evaporating surface after 1 hour [137].

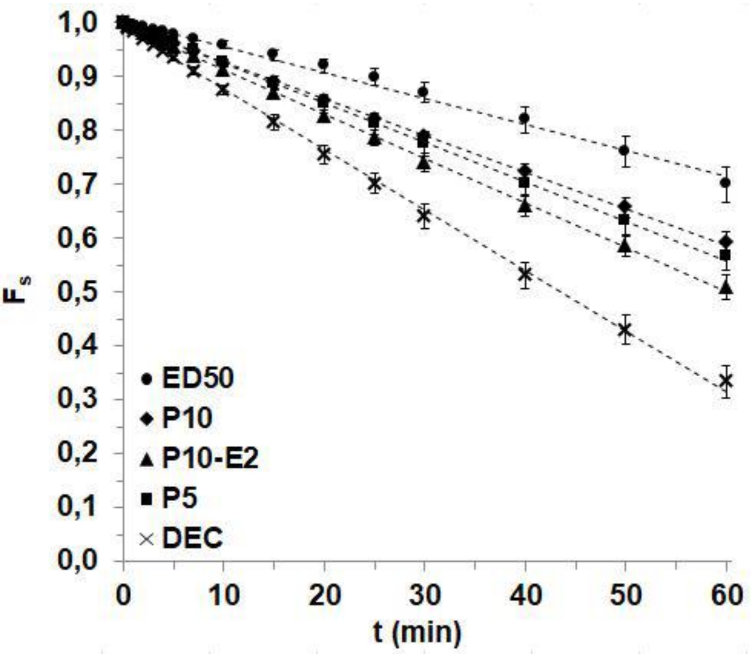

Figure 7.6 - Evaporation kinetics of DEC confined in organogel formulations, compared to bulk solvent; F_s is the residual solvent fraction plotted versus time

	F_s (60 min)
DEC	0.33 ± 0.03
ED50	0.70 ± 0.03
P10	0.59 ± 0.02
P10-E2	0.51 ± 0.02
P5	0.57 ± 0.02

Table 7.5 – Residual solvent fraction (F_s) after one hour evaporation at room conditions for the selected organogels loaded with DEC and the bulk solvent

The residual solvent fraction (F_s, as defined in *Eq. 6.8*) after 1 hour for both the bulk solvent and gels are reported in *Tab. 7.5*: F_s is higher for all the gel formulations as compared to DEC (0.33 ± 0.03), proving their ability in retaining the solvent. Interestingly, the ED50 gel, the only one synthesized in DEC, shows the highest final F_s value (0.70 ± 0.03) pointing out that 70% of the initial DEC is still retained within the polymeric network after 1 hour evaporation. On the other hand, PEMA/PEG gels, all prepared in a different reaction medium (i.e. 2-propanol) are characterized by a significant reduction of the residual solvent fraction ($F_s = 0.59$, 0.51, and 0.57 respectively for P10, P10-E2, and P5 formulations), thus indicating a faster solvent evaporation as compared to ED50. In a previous work [7] we observed that the increase in the evaporation rate may be related to the different diluent used during gels synthesis: indeed we highlighted that a DEC loaded PEMA gel (EI50), characterized by the same formulation of ED50 but synthesized in 2-propanol, was affected by a significantly faster evaporation of DEC ($F_s = 0.44 \pm 0.04$); in agreement with literature, we hypothesized that this behaviour was related to the different porogen effect of the two diluents (i.e. DEC and 2-propanol) on the polymeric network [138]. Actually the solvating power towards the species that are present during the polymerization reaction (i.e. monomer and forming polymer) is one of the main parameters affecting the final structure of polymeric gels [139]: their formation takes place by a phase separation induced by the lower solubility of the polymer in the diluent medium as compared to the monomer solubility; clearly the reaction conditions strongly affect the network architecture and then pores formation. Early phase separation may occur due to both polymer–solvent incompatibility and increase in cross-linking density [139,140], leading to higher porosity percentage, higher specific surface, lower apparent density, and higher pore volume with broader pore size distributions [137,138]. Therefore, since 2-propanol is a worst solvent for PEMA than DEC, according to the Hansen solubility parameters [20,111,141], this may lead to earlier phase separation in EI50, and so to a more porous network that could promote a faster evaporation kinetic.

Comparing such results with the one obtained on P10, P10-E2, and P5 formulations, we can notice a decrease in their evaporation rate as compared to EI50: in according to what above said, this behaviour can be explained considering the lower monomer concentrations of such formulations, that is expected to result in a phase separation occurring at a later stage due to the lower cross-linking density. Moreover late phase separation could also be favoured by the presence of PEG, highly soluble in 2-propanol at synthesis temperature (T = 55°C): the precipitation of the most of PEG linear chains could occur only with the lowering of temperature at the end of the synthesis, so a greater amount of PEG may lead to reduce gels porosity and so to higher residual solvent fraction after one hour evaporation (F_s acquired for P10 > P5). On the contrary a higher cross-linker concentration may cause more porous systems and so faster evaporation rate (F_s for P10 > P10-E2).

7.4.3 Solvent uptake

Solvent uptake curves are a measure of the velocity at which the solvent is loaded into gels starting from the dried matrices: since we aimed to reusable systems, a desirable applicative feature is a fast uptake of solvents. Moreover the investigation of the solvent uptake behaviour is able to provide further insights about the polymeric networks and the polymer-solvent interactions, since these factors significantly affect the diffusion mechanism of DEC from the bulk phase into the gel matrix.

Fig. 7.7a shows the solvent uptake plots. The great affinity of PEMA based networks for DEC is confirmed by the quick uptake kinetics: within 4–5 hours all the PEMA gels (initially dried) reached their *ESC%* value, but the uptake is much faster for gels characterized by a larger amount of embedded PEG (i.e. P10 and P10-E2). As we can see from *Tab. 7.6*, in all cases the solvent uptake occurs with a significant increase in gels volume; at the same time all gels turned from a glassy polymer into a rubbery one.

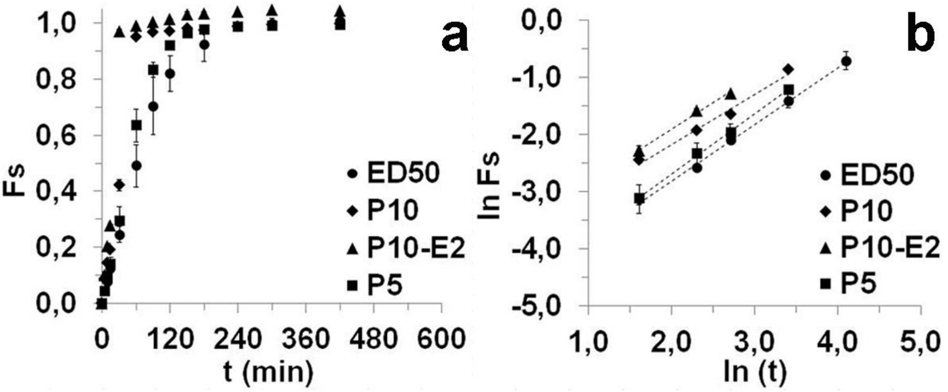

Figure 7.7 - a) Solvent uptake plots of the Solvent Fraction F_s versus time for the DEC loaded organogels; gel samples were completely dried previous to solvent uptake measurements; b) Log-log uptake kinetic plots for $F_s < 0.6$, and linear fitting ($R^2 > 0.99$ for all systems)

	$t_{95\%}$ *(h)*	*n*	*S%*
ED50	4	0.99 ± 0.06	380 ± 30
P10	1	0.87 ± 0.01	390 ± 10
P10-E2	0.5	0.93 ± 0.07	280 ± 40
P5	2.5	1.05 ± 0.09	470 ± 30

Table 7.6 – Experimental data extrapolated from DEC uptake measures into gel matrices: time required to reach 95% of ESC% value for completely dried gel sample ($t_{95\%}$), and the diffusion exponential (n), distinctive for the kind of occurring solvent-transport mechanism, and the percentage volume swelling (S%)

The diffusion of a penetrant into a polymeric network can be treated as a flux of solvent molecules moving from a region at high concentration of solvent (i.e. the bulk phase) to a low concentration zone (i.e. the inner part of gels) [142]. If solvents penetrate in a glassy polymer without swelling its 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 [143,144]. Peppas and Korsmeyer proposed a simple diffusion model for the treatment of experimental results:

$$F_s = kt^n \qquad \text{(Eq. 7.1)}$$

where F_s is the solvent fraction as described in *Par. 6.3.4.2*, k is a constant depending on the gel network, and n is the diffusion exponential. For thin film samples, $n = 0.5$ points out a Fickian diffusion mechanism, $0.5 < n < 1$ an anomalous transport, $n = 1$ a Case II transport [144]; it must be noted that this relation should be employed only for the first part of the uptake curve ($F_s < 0.6$) [145]. Applying this model to our data, n was calculated as the slope of the linear fitting of the $\ln F_s$ versus $\ln t$ plot (see *Fig. 7.7b*). Experimental results show that the swelling of all PEMA based gels by DEC is relaxation-controlled: in the limits of experimental error, we can recognize a diffusion behaviour closer to Case-II transport for ED50, P10-E2, and P5 gels, while in the P10 system an anomalous diffusion occurs. These results might be explained by taking into account the effect of PEG on the polymeric network: the embedded PEG, acting as a plasticizer, could enhance the total mobility of the network, thus decreasing the value of *n*. Actually Fickian transport takes place even in rubbery polymers where the solvent transport is not affected by polymer interactions since the rate of relaxation is much higher than the rate of diffusion [143,146]; therefore an increase in chain mobility could lead to increase the Fickian component in the transport mechanism, changing from a Case II to an anomalous transport.

7.5 Viscoelastic behaviour of gels: rheological analysis

The mechanical dynamic response of the PEMA based organogels loaded with DEC was studied by means of oscillatory shear measurements; experimental rheological data for the presented formulations are summarized in *Tab. 7.7*.

	G_p *(kPa)*	*tan* δ	γ_c *(%)*	v_{ref} *(%)*
ED50	37.7	0.010	20	0.10
P10	23.0	0.013	2	-0.02
P10-E2	50.0	0.015	2	0.00
P5	23.0	0.019	1	0.00

Table 7.7 - Rheological quantities for the DEC loaded PEMA based organogels: the plateau modulus G_p *and the loss tangent tan* δ *were extrapolated at 1 Hz from frequency sweep measurements; the critical oscillation strain* γ_c *was acquired from amplitude sweep analysis, the viscous reformation* v_{ref} *was obtained from creep tests*

As described in *Par. 6.3.5,* strain sweep tests were carried out at a fixed frequency and increasing oscillation amplitude in order to determine the linear viscoelastic region, i.e. the LVE range; here a linear relationship occurs between stress and strain, so that the rheological properties of viscoelastic materials are independent from the strain amplitude. The upper limit of the LVE range is the critical oscillation strain, γ_c, beyond which the applied stress is no more linearly proportional to strain: this results in a dependence of the storage and loss moduli (*G'* and *G"*) from the applied shear perturbation.

The behaviour of *G'* and *G"* at increasing frequency was then assessed in the LVE region, at a fixed strain [88]: the plateau modulus G_p, identified where *G'* is nearly constant, and the loss tangent *tan δ* (defined in Par. 3.2.2 as *G"/G'*), are reported in *Tab. 7.7*. *Fig. 7.8* shows the frequency sweep plots: as expected for chemically cross-linked gels, the behaviour is predominantly solid-like, being both moduli essentially frequency independent for several decades (in the timescale of the order of seconds), and *G' >> G"* over the entire investigated range [17,73,147]. Moreover *tan δ* is << 0.1 for each formulation (see *Tab. 7.7*), which is

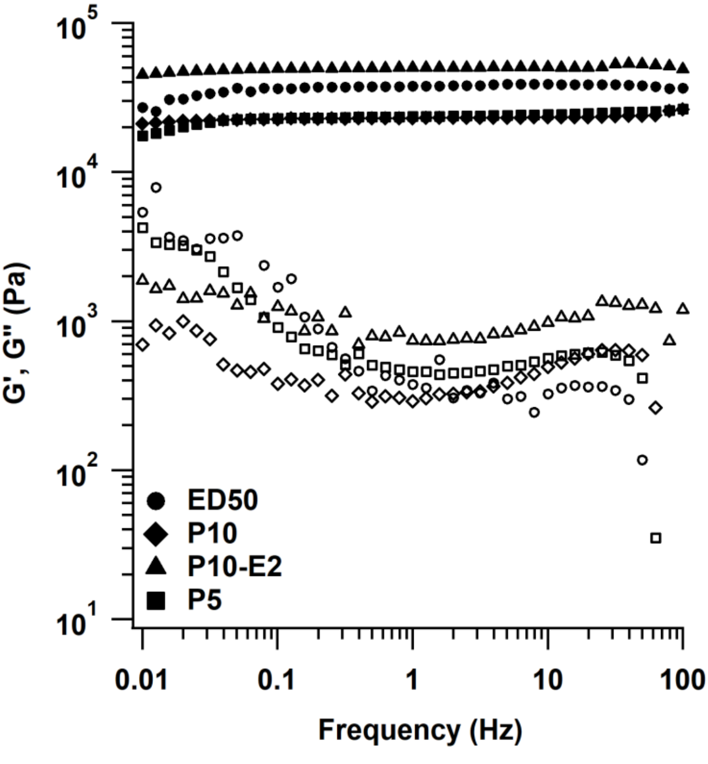

Figure 7.8 - Frequency dependence of the storage modulus, G' (filled markers), and the Loss Modulus, G" (empty markers), for the selected gel formulations

distinctive of strong gels systems: since δ is the angular displacement between the elastic and viscous response to an applied stress, *tan* δ values close to 0 point out a solid-like behaviour [17,125,147]. From a practical point of view, the classification of our formulations as strong gels means that the permanent bonds within the network yield gels with strong cohesion, able to maintain their shape, and even easily cut, manipulated, and removed in one piece without any additional mechanical action [17]. Experimental data from frequency sweep tests reveal no significant differences among the presented organogels: *Tab. 7.7* evidenced only slight discrepancies in G_p and *tan* δ values.

On the contrary amplitude sweep analysis, displayed in *Fig. 7.9*, indicate different behaviour between PEMA and PEMA/PEG gels. In particular we can appreciate a similar mechanical spectrum at small strain, (i.e. $G' >> G''$, typical of gel systems), but a very different strain dependence arises at larger applied deformation: the critical oscillation strain γ_c drastically drops as a consequence of the embedment of PEG linear chains in the PEMA 3-D network, from $\gamma_c = 20\%$ for ED50 to $\gamma_c \approx 1\% \div 2\%$ for PEMA/PEG gels. As above mentioned, γ_c is the upper limit of the LVE region: becoming the relationship between stress and strain non-linear for values greater than γ_c, it can be defined as the critical limit over which the applied strain causes irreversible modifications on the material that may eventually break [125,147,148]. According to literature, a more fluid-like behaviour at large deformations is distinctive of weak gels: increasing the applied strain, strong gels rupture and fail, while weak gels flow without fracture; in the latter case even a complete recovery of the gel-like characteristics may occur when the strain is removed [125,147,148]. Indeed our systems are not weak gels, as *tan* δ values reveal, but the embedment of PEG linear chains possibly bestows them a

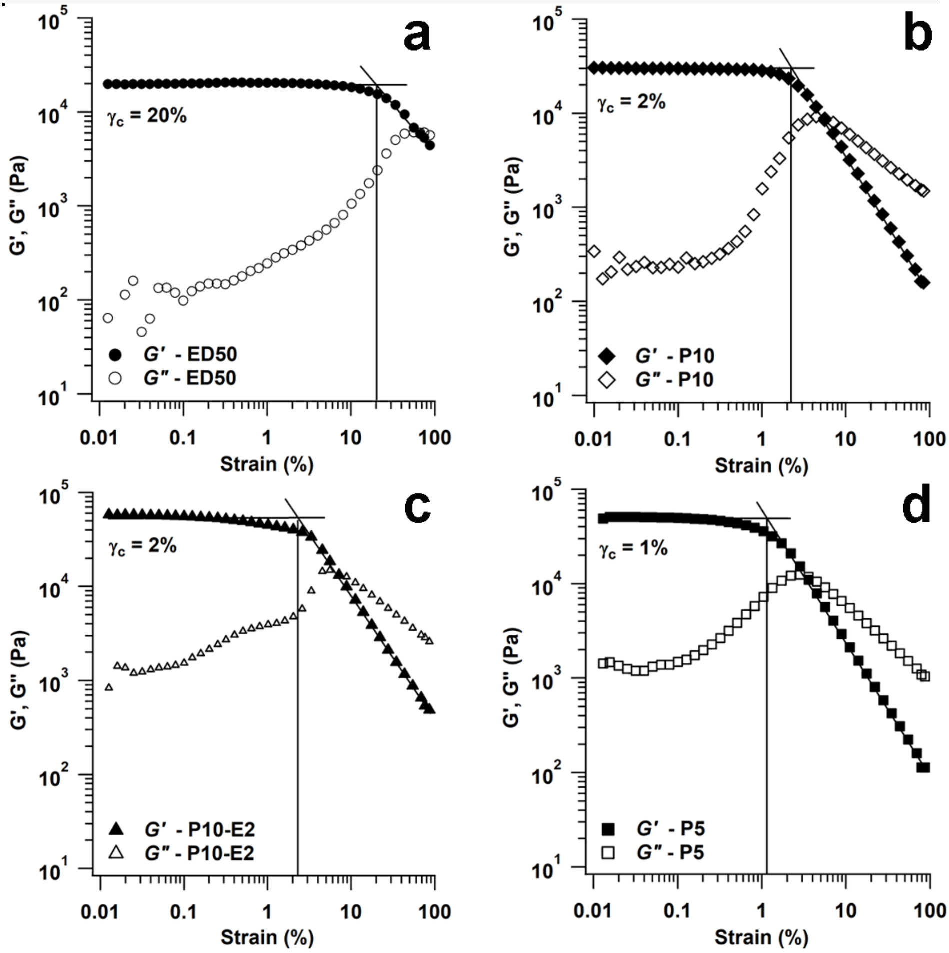

Figure 7.9 - Critical oscillation strain, γ_c, extrapolated from the amplitude sweep plot for each organogel: a) ED50, b) P10, c) P10-E2, d) P5; all plots report G' in filled markers, G" in empty markers

more fluid-like behaviour when exposed to large deformations. Macroscopically we noticed that PEMA/PEG systems are unquestionably more easily manipulated, less rigid, and less prone to rupture; moreover the enhanced flexibility of such gels represents an improvement since it further grants better adhesion to the non-planar surfaces.

Creep tests were then performed to assess the mechanical response of gels when exposed to a constant stress (see *Fig. 7.10*); the viscous reformation v_{ref}, that is the permanent deformation after compression, is reported in *Tab. 7.7*. Interestingly from creep plots, acquired at low induced strains located in the LVE range, we can notice a more solid-like behaviour of P10 and P10-E2 as compared to P5 and ED50. Actually ideal solids are characterized by an instantaneous jump to a constant strain value and complete recovery when the stress is removed; contrarily ideal fluids show a linear proportion between strain and time, and no recovery at all when the stress is removed; an intermediate behaviour among them is typical of viscoelastic materials, characterized by an instantaneous strain response followed by an apparent flow behaviour, and some recovery after the removal of the applied stress [147]. In our case ED50 and P5 shows the typical creep profile of viscoelastic materials, while P10 and P10-E2 reveal the instantaneous response distinctive of solids. Another really significant experimental data is the

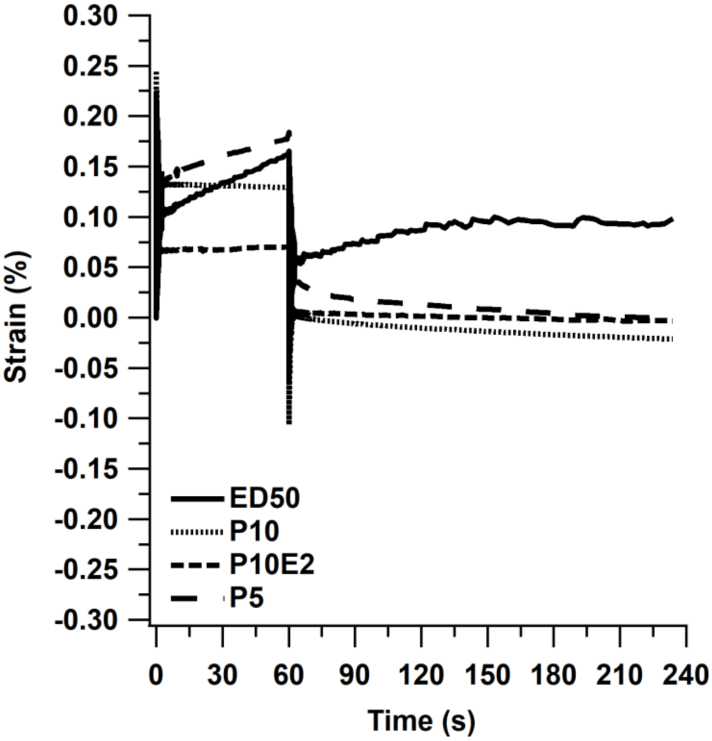

Figure 7.10 - Creep Test analysis performed on organogels: the first portion of each curve, up to 60 s, correspond to the compression time, the second part, from 60 to 240 s, to the relaxation period

absence of permanent deformation for all PEMA/PEG systems.

7.6 Loading PEMA based organogels with other solvents

As mentioned in previous *Chapters* (see *Ch. 1* and *4*), PSTs are made of a large number of different materials which had been changed over time; therefore during a PST removal intervention restorers could face very different issues. Actually we found the ability of DEC to interact with most of such compounds but, depending on both materials and their degradation, DEC is not always the best solution. In some case other organic solvents are rather more suitable, so we explored the possibility of their loading in PEMA based organogels.

Fig. 7.11 shows the equilibrium solvent content of different solvents loaded in P10 and P5 gels; the tested solvents were chosen among the ones commonly used in the restoration practice: water (H_2O), ethanol (EtOH), 2-propanol (2prOH), ethyl acetate (EA), acetone (Ac), methyl ethyl ketone (MEK), dimethyl carbonate (DMC), propylene carbonate (PC), and butyl acetate (BA).

The equilibrium solvent content here reported was assessed gravimetrically (i.e. *ESCg%*), as described in *Par. 6.3.3.1* for gels loaded with DEC; in this case, DEC swollen gels were dried and then immersed in the new solvent. We have to highlight that the results displayed in *Fig. 7.11* comes from preliminary tests; for comparison even the equilibrium solvent content of P10 and P5 formulations loaded with DEC is shown. From the histogram, we can notice the actual ability of PEMA/PEG systems to uptake other solvents: in particular ethyl acetate,

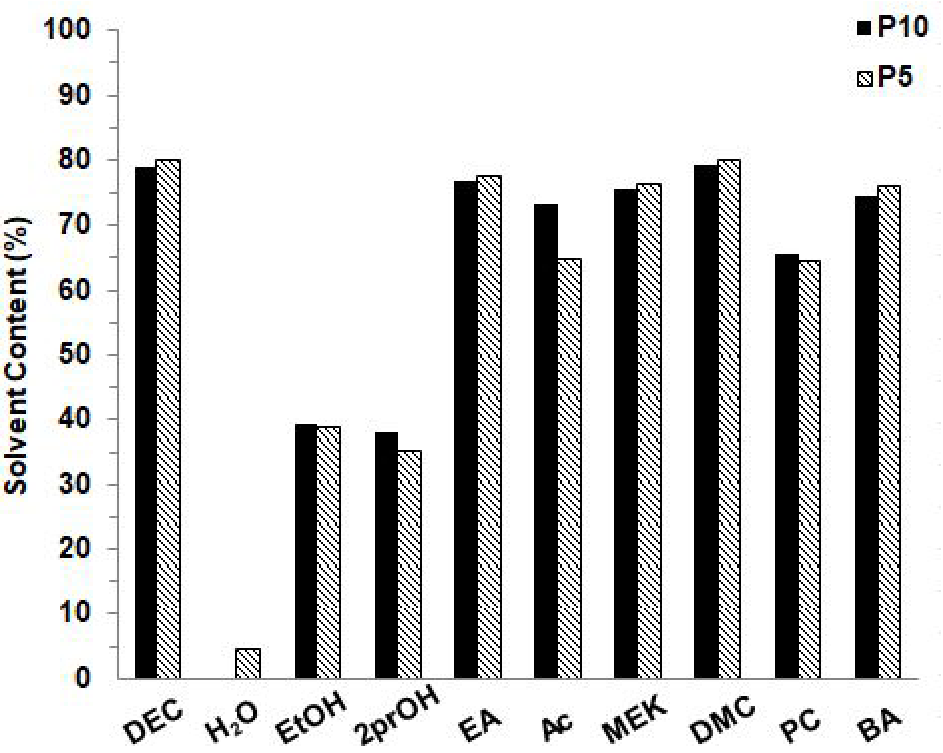

Figure 7.11 - Equilibrium Solvent Content assessed by gravimetric analysis for P10 and P5 formulations loaded with various organic solvents: diethyl carbonate (DEC), water, (H_2O), ethanol (EtOH), 2-propanol (2p-OH), ethyl acetate (EA), acetone (Ac), methyl ethyl ketone (MEK), dimethyl carbonate (DMC), propylene carbonate (PC), and butyl acetate (BA)

acetone, methyl ethyl ketone, dimethyl carbonate, and butyl acetate are characterized by high *ESCg%* values (e.g. 70 - 80%), similar to the ones registered for DEC. Conversely a scarce loading ability is registered for more polar solvents, i.e. ethanol and 2-propanol; water is not loaded at all.

Among these solvents, we focused on acetone and dimethyl carbonate due to their good loading in PEMA based gels and the great opportunities in their use in the restoration practice: acetone is already largely employed for the removal of hydrophobic grimes although lots of drawbacks related to the interaction with artistic media [8]; DMC is not yet so widespread but indeed it is able to interact with different kinds of unwanted materials on artworks [20]; furthermore preliminary tests revealed smaller side effect than acetone.

Tab. 7.8 and *Fig. 7.11* report the experimental results after repeated measures on P10 gels loaded with dimethyl carbonate and acetone: equilibrium solvent content, solvent release, and solvent evaporation rate were assessed (for experimental methods see *Par. 6.3.3* and *6.3.4*).

	ESCg1%	*Solvent Release (mg/cm^2)*
P10 - DMC	83 ± 1	3.5 ± 0.5
P10 - acetone	74 ± 1	1.5 ± 0.3

Table 7.8 – Gravimetrically assessed equilibrium solvent content (ESCg1%) and solvent release for dimethyl carbonate (DMC) and acetone loaded in P10 gels

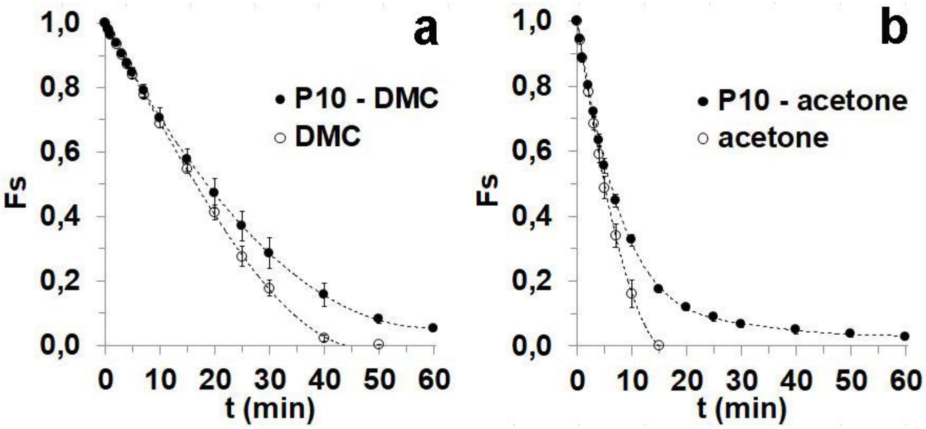

Figure 7.12 – Evaporation rate of dimethyl carbonate (DMC) and acetone from P10 gels; the kinetics of evaporation from the polymeric matrices are compared to the ones of bulk solvents; dashed lines are not fitting line but only a guide to the eye

Gravimetric analysis for the evaluation of the equilibrium solvent content confirmed data from preliminary tests: P10 gels are able to load a mass of DMC and acetone larger than 70% of their total weight. Concerning the solvent release on wettable substrates (i.e. Whatman®

paper samples), as we can notice from *Tab. 7.8*, P10 gels appear more retentive towards these two solvent as compared to DEC (i.e. *SR* for P10-DEC is 5.0 ± 0.1); anyway a possible systematic experimental error related to the very fast evaporation of DMC and acetone could have caused an underestimation of the real *SR* value for these two solvents [99,149].

From the solvent evaporation plots (*Fig. 7.12*) we can indeed notice the very fast drying kinetic of both DMC and acetone; furthermore we can observe the capability of P10 to retain these solvents and to limit their evaporation: particularly concerning acetone, the bulk solvent completely evaporates after 15 minutes, while the same amount of solvent retained in gels is not yet completely gone throughout 1 hour of exposure to the same room conditions.

PART IV

CLEANING

CHAPTER 8

Preliminary tests on mock-ups

In this *Chapter*, the application features of the selected organogels are evidenced through the use of representative mock-ups. This experimental step was furthermore essential in the tuning of procedures for intervention on real artworks.

8.1 Materials and methods

Before applying DEC-loaded organogels on real case studies their effectiveness in the removal of both tapes and adhesives was assessed. Even the absence of drawbacks both during and after treatments was evaluated. Six different PSTs (see *Tab. 8.1* and *Fig. 8.1*) were used as standard for experimental tests.

PSTs		**Company**	**Product Code**	**Composition**	
				Backing	**Adhesive**
Ordinary Tape	OT	Tesa	56100	poly (propylene)	acrylic copolymers
Brown Tape	BT	Tesa	64014	poly (propylene)	acrylic copolymers
Magic Tape	MT	Tesa	-	cellulose acetate	acrylic copolymers
Masking Tape	MKT	Tesa	4323 HM	paper	styrene-butadiene rubber
Filmoplast	FP	Neschen	Filmoplast® P	paper	acrylic copolymers
Insulating Tape	IT	Tesa	56193	poly (vinyl chloride)	styrene-butadiene rubber

Table 8.1 – Technical features of PSTs used for preliminary tests on mock-ups

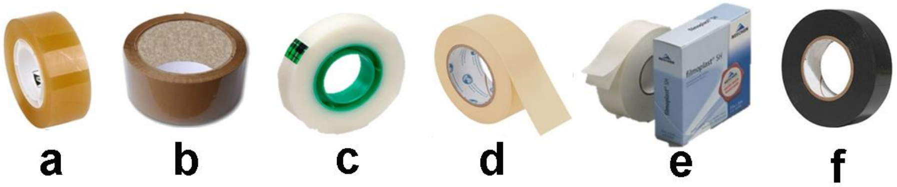

Figure 8.1 –Different kinds of PSTs used for experiments: a) Ordinary Tape, b) Brown Tape, c) Magic Tape, d) Masking Tape, e) Filmoplast, f) Insulating Tape

8.1.1 Visualising diethyl carbonate loaded gels on PSTs

The dynamic of interactions between the solvent-loaded polymeric gels and model PSTs were studied by means of Laser Scanning Confocal Microscopy (LSCM). For LSCM measurements a Leica TCS SP2 instrument equipped with a 20× air objective was used. Two different fluorescent probes were used to mark diethyl carbonate loaded within ED50 gels and PSTs adhesives: gels were equilibrated in an 100 µM solution of Coumarin 6 (Cou6, Sigma-Aldrich, purity ≥ 99%) in DEC; PSTs adhesives were labelled by immersion in 10 µM aqueous solution of Rhodamine B Isothiocyanate (RhBITC, Sigma-Aldrich, purity > 99%). 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 – 513 nm for Cou6 and 591 – 616 nm for RhBITC. The experimental setup was designed in order to mimic a real application: marked PSTs were attached on a sample carrier, and ED50 gels loaded with Cou6-labelled DEC were laid on them; each slice of gels was cut so as to match the shape of the analysed tape. To study the interaction between the solvent and PSTs, samples were visualized through confocal microscopy for up to one hour.

In order to check alterations in PSTs after treatments with gels, Field emission gun scanning electron microscopy (FEG-SEM) on the PSTs backing were carried out with a FEG-SEM ΣIGMA (Carl Zeiss, Germany). For the analyses an acceleration potential of 25 kV and a working distance of 1.8 mm was used; a gold-metallization of PSTs samples was performed with an Agar scientific auto-sputter coater.

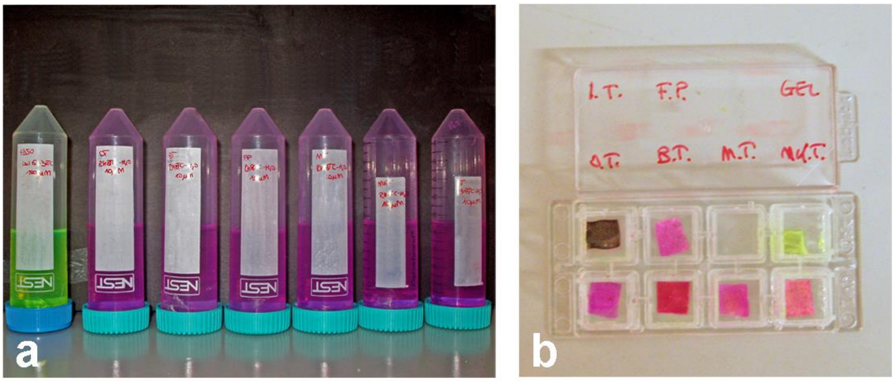

Figure 8.2 - Preparation of samples for Laser Scanning Confocal Microscopy (LSCM) analysis: gels and PSTs were immersed in solutions of fluorescent probes (Coumarin 6, Cou6, in DEC for ED50 gels, Rhodamine B Isothiocyanate, RhBITC, in water for PSTs) (8.1a); marked samples ready for analysis (8.1b)

8.1.2 Treating paper mock-ups with gels

Laboratory samples and preliminary tests for the assessment of the interactions of both bulk DEC and gels towards paper and inks were in part prepared in cooperation with the restorers Antonio Mirabile, Letizia Montalbano, i.e. manager of the High School of the *Opificio delle Pietre Dure*, and Maddalena Trabace, throughout the work related to her diploma.

The solubilising power of DEC towards common graphic media was preliminarily tested on coloured printing paper mock-up samples: inks used are displayed in *Tab. 8.2*. A drop of DEC was put on inked paper and then gently dabbed (*Fig. 8.3a* reports a typical inked mock-up used for tests). In the cases in which inks solubilisation took place, the effectiveness of DEC loaded PEMA based gels in limiting the spreading of artistic media was assessed; before gels application, the excess of solvent was gently removed with absorbent paper.

Ink medium	Color	Company
Ball point pen	Blue	BIC
	Red	Staedler
	Black	Pilot
Felt-tip pen	Blue	Giotto Turbo Color
	Green	Carioca Doodles Italy
	Pink	Tombow ABT Acid free
	Yellow	Swiss made Caran D'Ache
	Orange	Permanent Stabilo
	Red	OHPen universal

Table 8.2 - Inks used for realizing paper mock-ups

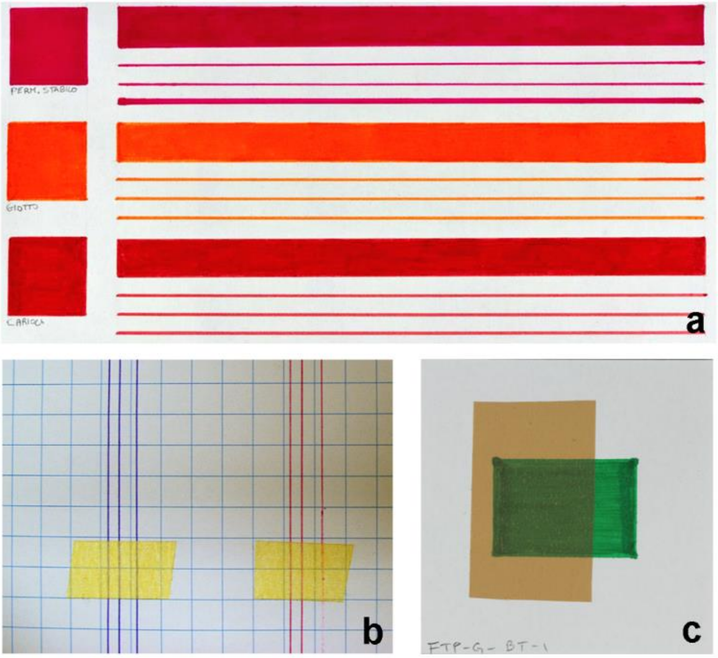

Figure 8.3 - Different kinds of mock-ups used for tests: 8.3a) felt-tip pens on printing paper; 8.3b) masking tape covering ballpoint pens on printing paper; 8.3c) brown tape on felt-tip pen inked printing paper

The ability of PEMA based organogels in the removal of PSTs from cellulosic samples was evaluated on. mock-ups realized by applying PSTs on printing paper; both inked and non-inked samples were prepared (for materials see *Tab. 8.1*, *8.2*, and *Fig. 8.3b, c*). In order to evaluate the capability of gels even in the removal of aged PSTs some samples underwent an artificial ageing process, described in *Tab. 8.3*.

Treatment	**Conditions**	**Time**
High humidity ageing	RH = 80%, T = 25°C	2 days
Thermal ageing	T = 80°C	4 days
High humidity ageing	RH = 80%, T = 25°C	2 days
Photo-chemical ageing	neon light – recto	4 days
High humidity ageing	RH = 80%, T = 25°C	2 days
Photo-chemical ageing	neon light – verso	4 days
High humidity ageing	RH = 80%, T = 25°C	2 days

Table 8.3 –Treatments listed in table represent one ageing cycle: it was repeated up to 6 times; between two cycles samples were put under weight for one week so as to restore their planarity. The RH value in the humidity chamber was kept by a glycerol aqueous solution (51% w/w). Photochemical ageing was performed with an illuminance of 11000 lux, and a continuous emission spectrum in the range 350 ÷ 650 nm

The cleaning effect carried out by PEMA based gels loaded with DEC was estimated by applying gels directly on the backing tape of PSTs: gels were shaped with a scalpel to match the dimension of the PSTs, and then applied on samples after having removed the excess of solvent on the gels surface. In order to prevent an excessive DEC evaporation, plastic foils were put on gels. ATR-FTIR spectroscopy was performed on samples treated with gels to assess their cleaning effectiveness (for instrumental set-up see *Par. 6.3.2*).

The possible drawbacks related to the use of gels in the long term period were assessed on Whatman® paper samples treated with DEC and then aged by the procedure described in *Tab. 8.3*. The characterization of mock-ups was performed by ATR-FTIR spectroscopy (*Par. 6.3.2*), pH analysis, and DTG measurements.

For the pH evaluation of cellulosic samples [1] the regulations of the *Technical Association of Pulp and Paper Industries* (TAPPI) were adopted [2] [150]. A cold extraction from paper samples was carried out by putting 125 mg of samples (cut into small pieces) in 9 ml of deionized water under stirring at room temperature; for pH measures a digital pH meter *Crison-Basic20*, equipped with a silver chloride electrode was used.

DTG measures were performed so as to assess the pyrolysis temperature (T_p) of mock-ups. Actually T_p is an index of the degradation level of cellulosic samples: a decrease in T_p of cellulose is observed when depolymerisation and swelling of cellulosic fibres take place [151,152]. Thermal analysis were performed on 5 ÷ 7 mg of samples, increasing temperature up to 500°C; for instrumental apparatus see *Par. 6.3.3.1*.

Further analyses were finally carried out on Whatman® and aluminium substrates so as to investigate the presence of gel residues after application of PEMA and PEMA/PEG gels: actually such residues may cause negative side-effects with the ageing of artefacts. Their possible presence was double-checked by means of ATR-FTIR spectroscopy (for experimental conditions see *Par. 6.3.2*). and 2D-FTIR imaging. In the latter case a Cary 620–670 FTIR microscope, equipped with an FPA 128

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[1] Strictly speaking we cannot talk about pH of cellulosic samples, being it appropriate only for aqueous solutions; anyway in the field of the restoration of cellulosic materials, an evaluation of their degradation due to acid or basic compounds is made by the assessment of the pH of their aqueous extractions

[2] TAPPI regulations require 1 g of cellulosic material, that is an excessive quantity in the restoration field; therefore conservation scientists usually employ moch smaller amounts

× 128 detector (Agilent Technologies) was used; spectra were recorded directly on the surface of samples (or of the Au background) in reflectance mode, with open aperture and a spectral resolution of 4 cm^{-1}, acquiring 128 scans for each spectrum; a “single-tile” analysis results in a map of 700 × 700 μm^2 (128 × 128 pixels), and the spatial resolution of each map is 5.5 µm (i.e. each pixel has dimensions of 5.5 × 5.5 μm^2); “mosaics” of 1400 × 2100 μm^2 were acquired to observe a larger field of view.

8.2 Experimental results

The procedures described in the previous sections let us to understand the way in which DEC loaded in the polymeric networks is able to interact with PSTs components, and even the applicative features of the developed systems. Even if these results are presented after *Ch. 7*, dedicated to gels characterization, clearly applicative tests addressed at each step modifications to the synthesis reaction: indeed they allowed us to understand which gels characteristics were really fundamental (e.g. tuneable retentiveness, flexibility) and which ones only desirable (e.g. transparency), so as to obtain gels able to match our aims.

8.2.1 Diethyl carbonate – Pressure Sensitive Tapes interactions

As extensively discussed in *Par. 5.1*, the proposed methodology for the detachment of PSTs from paper substrates consists in the application of DEC-swollen gels on the top of PSTs backing, so as to minimize the impact of the cleaning intervention on artworks. The effectiveness of this method depends on the ability of the solvent to penetrate the tape of

PSTs. To allow sufficient interaction between the solvent and the backing layer, gels must be able to release a proper amount of solvent while reducing its evaporation. As explained above, LSCM measurements were performed using an experimental setup that mimics real applications. Times for imaging acquisition are different for different PSTs samples: actually the kind of interaction strictly depends on the composition of the PST. Below results obtained are reported; in the acquired images the solvent (marked with Cou6) is displayed in green, the backing layer of the PST in black (not marked), the adhesive (labelled with RhBITC) in red. Due to the instrument configuration, in some cases gels applied onto the PSTs are not visible in the fluorescence images: since the visible laser comes from the bottom of the sample, if the PST backing is opaque, light is not able to cross it, reach the overlying gel, and so produce fluorescence. Therefore when gels were applied onto Brown, Masking, and Insulating PSTs, and on Filmoplast, only the red fluorescence of the adhesive is observable at time $t = 0$; the green marked solvent becomes visible only after DEC penetration.

Ordinary Tape

Fig. 8.4 shows the dynamic of the interaction between the PEMA-DEC gel ED50 and an Ordinary PST (OT), made up of a polypropylene backing and an acrylic adhesive, as listed in *Tab. 8.1*. At $t = 0$ the two fluorescent dyes used as markers for the solvent and the adhesive are well separated by the polypropylene backing layer showing no interaction between the solvent and the OT components (*Fig. 8.4a*). After 20 minutes, the RhBITC marked adhesive has lost its initial homogeneous appearance with a decrease of fluorescence intensity (*Fig.

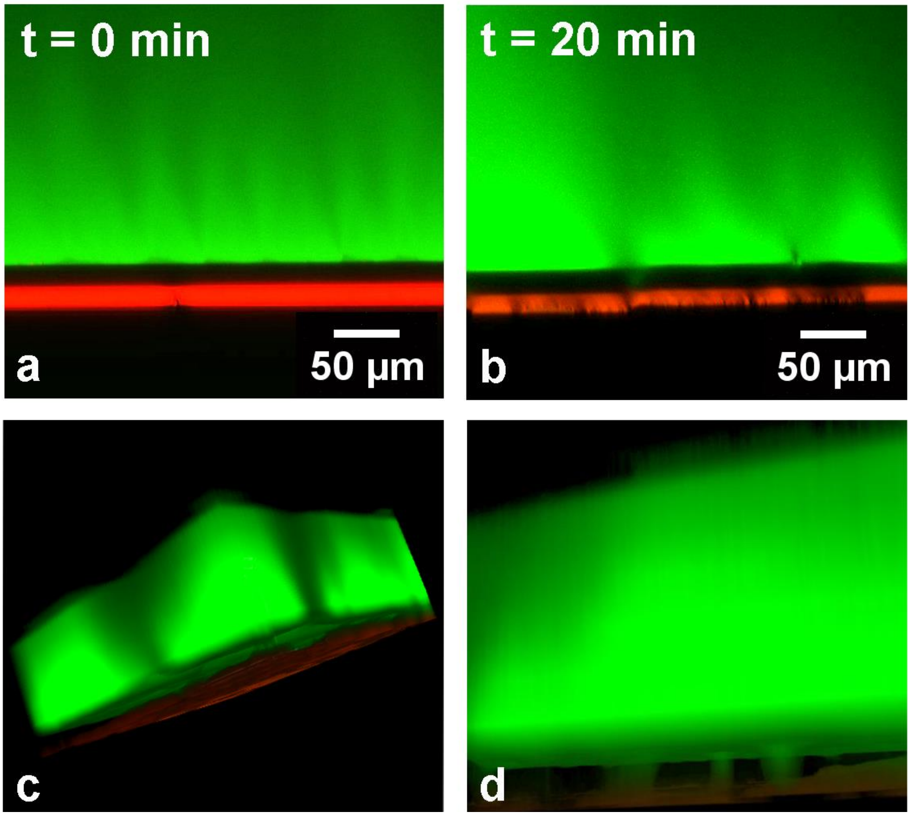

Figure 8.4 - Laser scanning confocal microscopy (LSCM) on the ED50-DEC gel applied on an Ordinary PST (OT, i.e. polypropylene tape, acrylic adhesive); DEC was marked green with Cou6, the acrylic adhesive red with RhBITC; the black layer corresponds to the polypropylene backing of the tape (not marked). At t = 0 the two fluorescent probes are well separated (8.4a) while after 20 minutes an evident penetration of the Cou6 dye through the OT backing is visible (8.4b-d); Fig. 8.4c,d show the 3-D reconstruction of internal portions of the gel lying on the OT

8.4b). As we can better notice in the detail of the 3-D reconstruction, *Fig. 8.4c*, the interaction between the solvent and the OT components does not occur through the penetration of a homogeneous solvent front moving from the upper PST surface towards the adhesive layer; instead the solvent apparently penetrates through some conduits in the plastic film. In order to verify their presence in the OT, FEG-SEM images of the backing were acquired: *Fig. 8.5* shows that the tape was actually altered after a 20 minutes interaction with DEC, but micron-sized conduits were observed neither before nor after the treatment. Thus, we concluded that

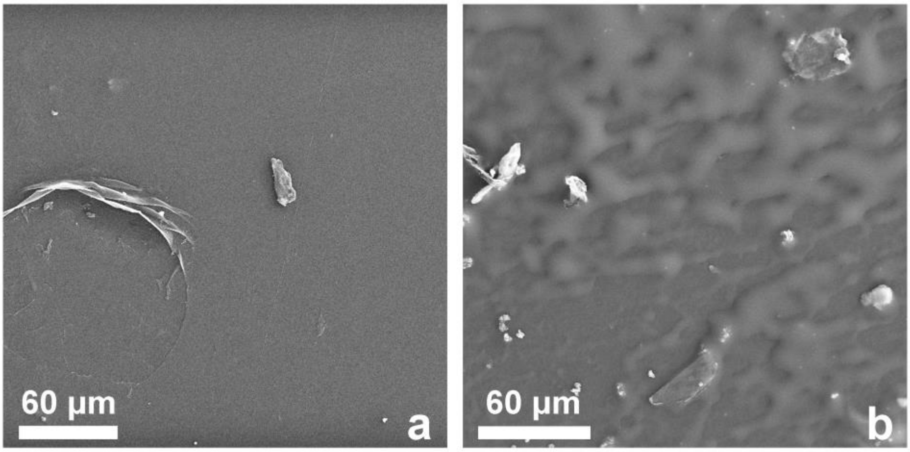

Figure 8.5 - Field emission gun scanning electron microscopy (FEG-SEM) images of the polypropylene backing of an Ordinary PST, before (8.5a) and after (8.5b) treatment with the ED50 gel (20 minutes application)

the solvent, gradually released by the gel, is able to partially swell the backing, forming conduits up to reach the acrylic adhesive layer.

Brown Tape

Due to the coloured tape of Brown PST (BT), as above explained, in *Fig. 8.6* only the adhesive layer is visible. Being BTs made up of polypropylene backing and acrylic adhesive like OTs, a similar behaviour was expected: actually the penetration of the solvent in the adhesive layer is evident in *Fig. 8.6b* after 20 minutes of application of the ED50 gel. Comparing *Fig. 8.4b* and *8.6b*, both acquired after 20 minutes of applications, the greater green fluorescence observable in the adhesive layer of the BT made us to conclude that a larger amount of DEC was penetrated in it as compared to the OT; differences in application times required to obtain a certain adhesive swelling degree may be related to the quality of the polypropylene tape used in the two PSTs.

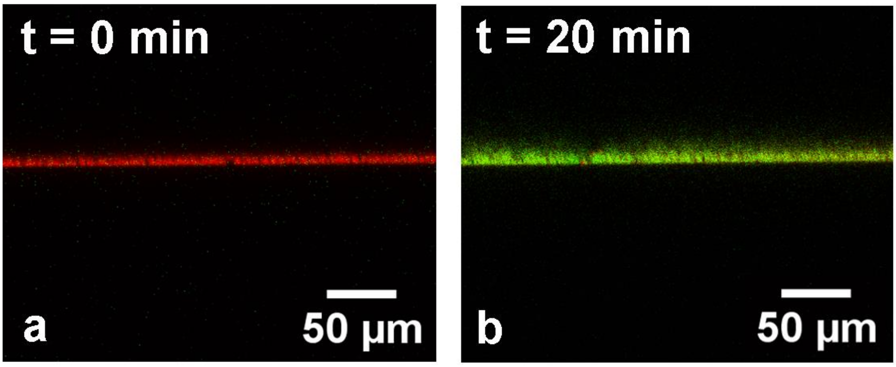

Figure 8.6 – LSCM images acquired on a Brown PST (BT) during the treatment with a ED50 gel loaded with DEC: the red fluorescence of the RhBITC marked adhesive (8.6a) is totally covered by the green fluorescence of DEC penetrated across the backing after 20 minutes of gel application (8.6b)

Magic Tape

A slower interaction was observed in the Magic PST (MT) case: from *Fig. 8.7* is evident that the penetration limiting step is the crossing of the backing (i.e. cellulose acetate). After a gel application of 5 minutes on the tape no penetration occurs, but an accumulation on its surface is evident (*Fig. 8.7b*); up to 10 minutes (image not displayed) the situation does not change. Nevertheless the green fluorescence in the backing layer in *Fig. 8.7c* acquired after 30 minutes points out a solvent penetration; moreover the adhesive appears significantly swollen. After 60 minutes (*Fig. 8.7d*) the accumulation of ,DEC in the backing, the solvent penetration in the adhesive and its swelling are more and more evident.

Masking Tape

A very fast penetration of DEC takes place through the paper backing of the Masking PST. As shown in *Fig. 8.8* at time *t = 0* the red signal from the adhesive (a styrene-butadiene rubber, see *Tab. 8.1*) is the only one visible: the paper tape stops the laser light so that no fluorescence from

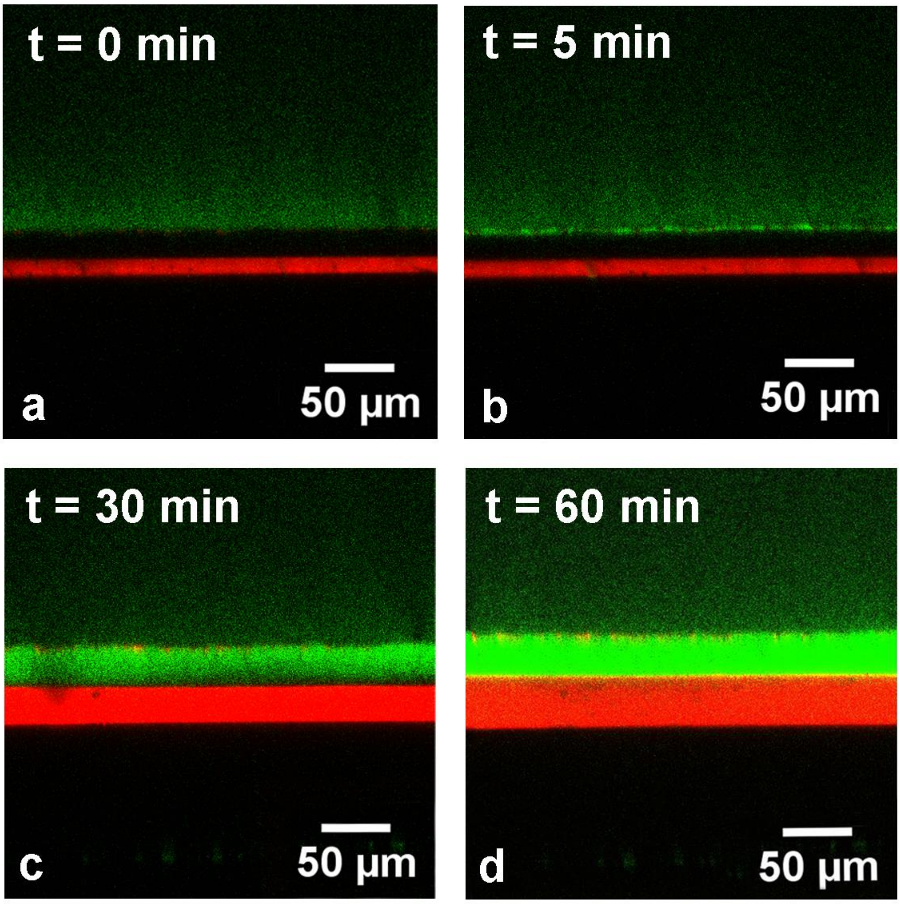

Figure 8.7 - Application of an ED50 gel loaded with DEC on a Magic PST (MT) visualized by LSCM: at t = 0 DEC is totally confined within the PEMA gel (8.7a); after 5 minutes of application an increase of the green fluorescence at the interface with the backing is observed (8.7b); a slow penetration of DEC across the backing is then visible in 8.7c,d, acquired respectively after 30 and 60 minutes; simultaneous decrease in the red fluorescence of the adhesive layer and its significant swelling are evident

the DEC-loaded gel is acquired. After a gel application of only 2 minutes the red fluorescence is completely covered by the green one of the solvent due to a copious penetration of the solvent.

Filmoplast

A very similar interaction dynamic occurs in the case of Filmoplast (FP), made up of a paper tape and an acrylic adhesive. After one minute of

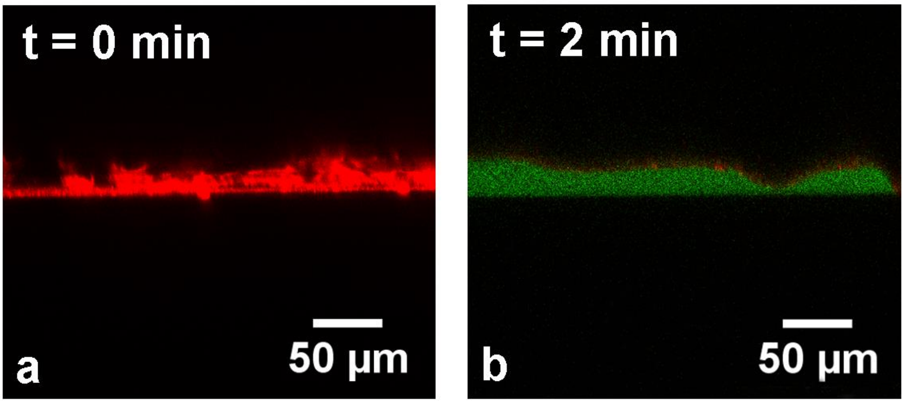

Figure 8.8 - LSCM analysis on a Masking PST (MT) treated with an ED50-DEC gel; at time t = 0 (8.8a) the red marked adhesive is visible; no signal from the gel is acquired due to the opaque backing layer; after a very fast gel application (only 2 minutes) the green fluorescence of the solvent is predominant in the adhesive layer (8.8b)

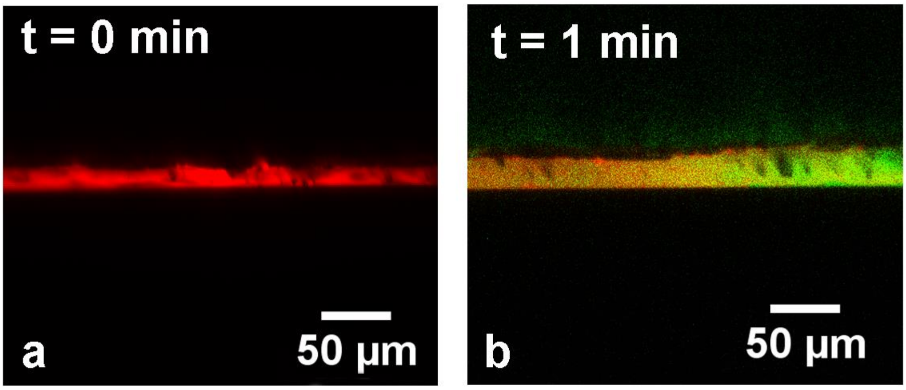

Figure 8.9 - Fluorescence images acquired by LSCM about the treatment of Filmoplast (FP) with an ED50-DEC gel; the acrylic adhesive layer is shown in 8.9a acquired at t = 0 (the gel applied above the tape is not visible due to the paper opaque tape); after 1 minute application the adhesive is already swollen due to the penetration of the solvent (8.9b)

application of a DEC loaded ED50 gel, the solvent is already penetrated and the adhesive is swollen (see *Fig. 8.9*).

Insulating Tape

Fig. 8.10 shows LSCM images acquired on the Insulating PST (IT) (i.e. poly vinyl chloride backing, styrene butadiene rubber); due to the black PVC tape, the DEC loaded gel applied on the top of the tape is not visible

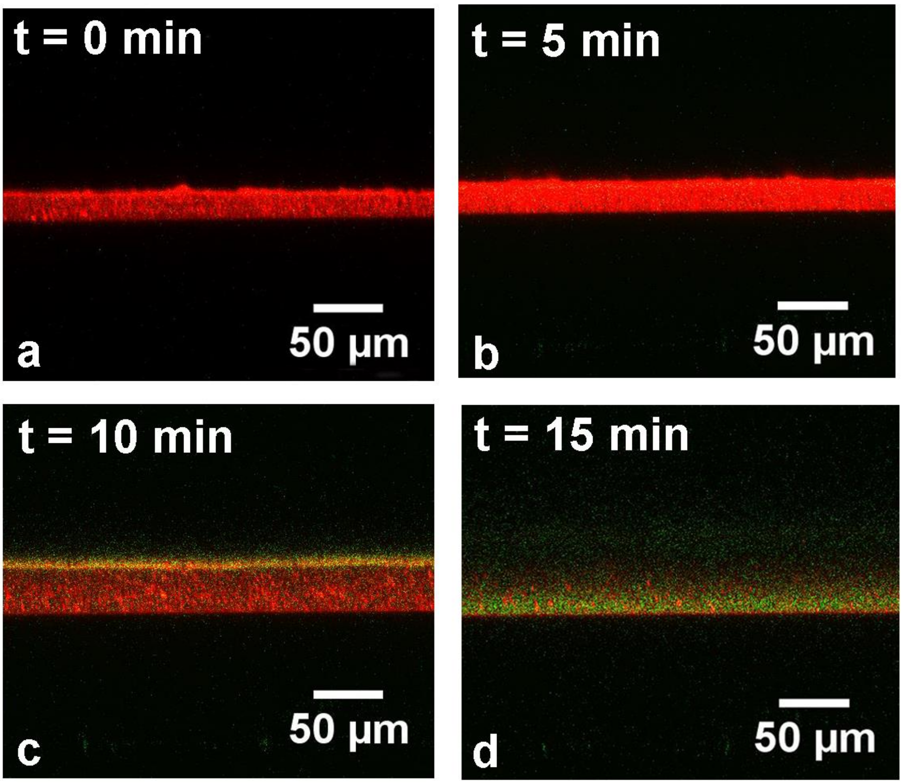

Figure 8.10 - Application of an ED50 gel loaded with DEC on an Insulating PST (IT); LSCM images show the gradual penetration of the green fluorescent DEC through the adhesive layer of the IT: at t = 0 (8.10a) only the red fluorescence from the adhesive is visible, due to the black PVC tape of the IT; after 5 minutes (8.10b) the red fluorescence decreases and the adhesive layer is slightly swollen; the swelling process proceeds after 5 minutes (8.10c) and 10 minutes (8.10d) of gel application

(*Fig. 8.10a*). After 5 minutes the penetration of the solvent through the backing and the simultaneous adhesive swelling are evident (*Fig. 8.10b*); these effects become more and more visible with time (*Fig. 8.10c,d*).

8.2.2 Removal of tapes with gels

The gels efficacy in removing adhesive tapes from cellulosic substrates was preliminarily assessed on paper mock-ups: as described in *Par. 8.1.2*, experimental tests were performed by applying DEC fully swollen gels on both inked and not inked samples covered by the PSTs listed in *Tab. 8.1*. Mock-ups were prepared the day before.

Fig. 8.11 shows the detachment of PSTs from a printing paper mock-up: results obtained when PSTs were removed in a traditional mechanical way, i.e. a scalpel (*8.11b 1*-7, left of pictures), are compared to the detachment of the tape after gel application (*8.11b 1-7*, right of pictures). The application time of gels on the PSTs backing were tuned depending on the kind of treated PST as expected from LSCM results: FP and MKT required about 3 minutes applications, IT about 10 minutes, OT and BT about 15-20 minutes, MT up to 30 minutes; in this time the penetration of DEC from the gel matrix through the PST causes the swelling of the

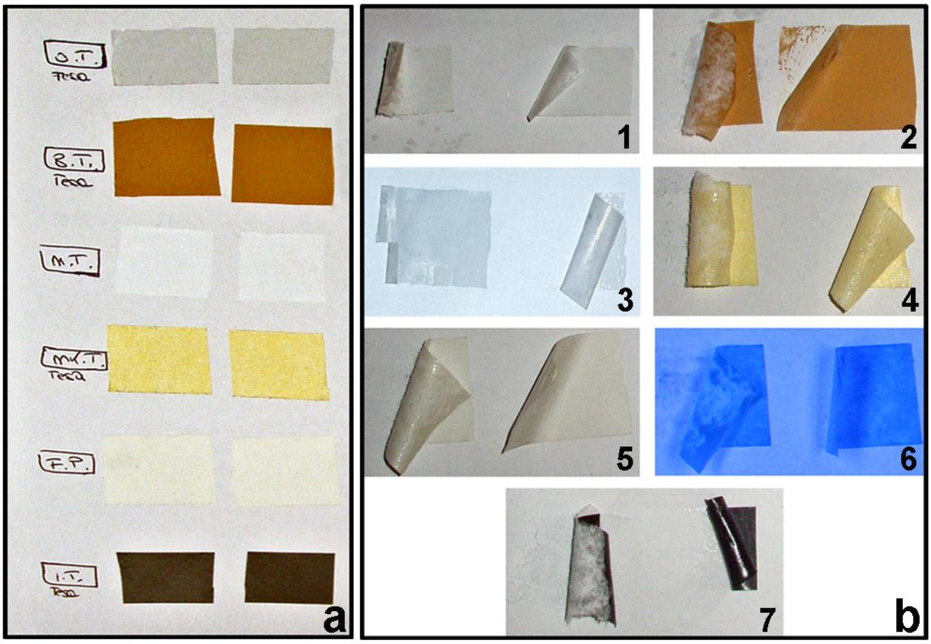

Figure 8.11 -Prepared printing paper mock-ups for the removal of PSTs (8.11a): from the top Ordinary Tape (OT), Brown Tape (BT), Magic Tape (MT), Masking Tape (MKT), Filmoplast (FP), and Insulating Tape (IT); Fig. 8.11b shows the comparison between results obtained without (on the left) and with (on the right) the application of gels for each PST: OT (8.11b-1), BT (8.11b-2), MT (8.11b-3), MKT (8.11b-4), FP (8.11b-5, Vis light; 8.11b-6, UV light), IT (8.11b-7); in each case there are some residues of paper on PSTs when gels were not used (in the case of Filmoplast such residues are evidenced in the UV image)

adhesive so that the backing can be detached by means of gentle mechanical action. On the contrary, when gels had not been applied, paper was very easily lacerated: lots of paper residues are visible on the mechanically detached PSTs.

Tests were also performed on inked samples. *Fig. 8.12* displays the removal of a MKT from an printing paper/ink (blue ballpoint pen) mock-up: following a 3 minute application of a DEC swollen P10 gel the tape was easily detached (*Fig. 8.12c, d*); trying to remove the MKT in a traditional mechanical way resulted in lacerating the paper (*Fig. 8.12b*).

In order to verify the effectiveness of gels in interacting also with old materials, some tests were performed even on aged inked samples (see *Tab. 8.3* for the ageing procedure). *Fig. 8.13* shows results obtained in the case of an aged OT/blue ballpoint pen/printing paper mock-up (*Fig.

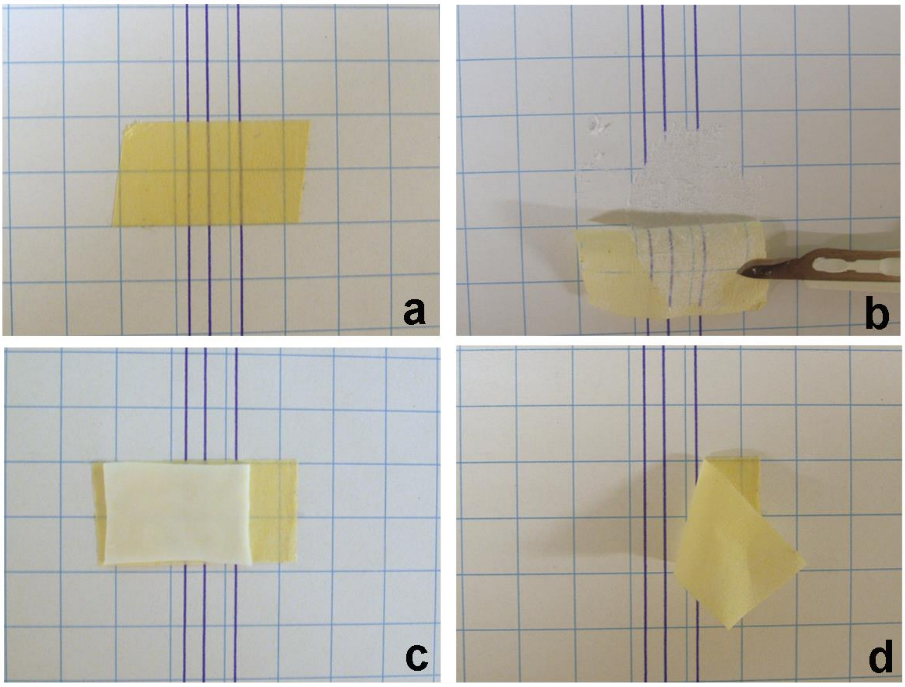

Figure 8.12 - Removal of a Masking tape (MKT) from an inked (blue ballpoint pen) printing paper mock-up (8.12a): the detachment of the tape with a mechanical method causes the laceration of paper (8.12b); after gel application (8.12c) the tape is safely removed (8.12d)

8.13b): a complete OT removal was achieved with two 15 minutes applications of an ED50 gel (loaded with DEC). After the first application the tape was removed but ATR-FTIR analysis, reported in *Fig. 8.13a*, pointed out a small IR absorbance at 1729 cm^{-1} (C=O stretching of the ester group [10]) ascribable to adhesive residues on the surface; the adhesive was then completely removed with a second gel application directly on the paper substrate, i.e. no band of the OT adhesive appears in the spectrum acquired on the paper sample after the second treatment. The assignment of such signal to some gel debris on paper was excluded due to its disappearance after the second treatment performed on the mock-up. Moreover it's worth noting that no tidelines or alteration of the ink were observed (*Fig. 8.13c*).

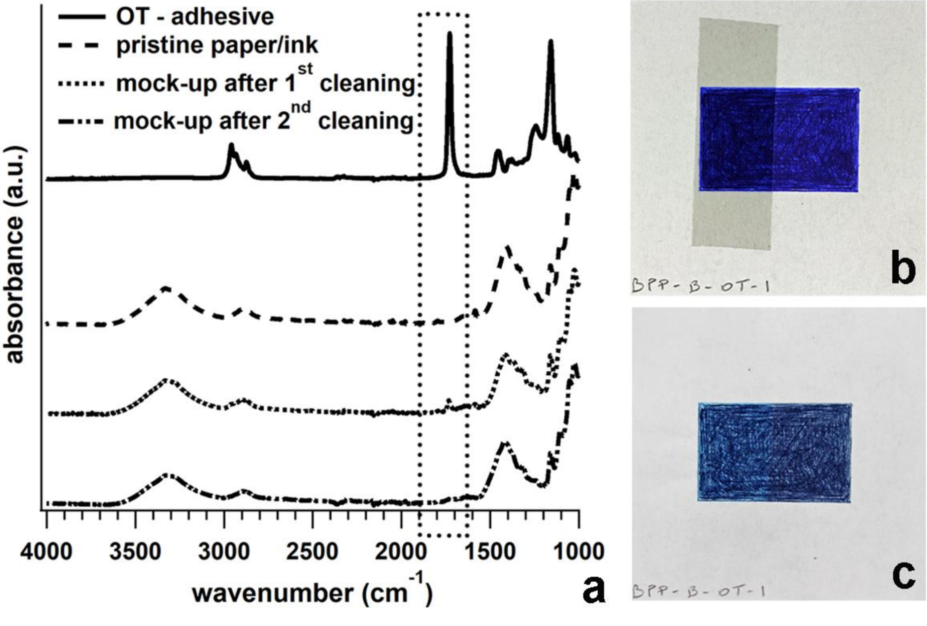

Figure 8.13 - ATR-FTIR spectra (8.13a) of (from top to bottom): the acrylic adhesive of the Ordinary PST (OT); the pristine paper/ink mock-up sample before the PST application; the paper/ink mock-up after the first gel application showing the removal of the OT backing and a small amount of adhesive residues (weak absorption band at 1730 cm^{-1}); paper/ink mock-up sample after the second gel application showing no bands of the adhesive. The pristine mock-up sample (8.13b), i.e. OT covering blue ballpoint pen on printing paper, underwent an ageing process (see Tab 8.3) before the removal of the OT by the use of an ED50 gel (8.13c)

8.2.3 Gel residues on mock-ups

The presence of gels residues on paper mock-ups was assessed by IR spectroscopy. *Fig. 8.14* shows the ATR-FTIR spectra of a Whatman® paper sample before and after application (15 minutes) and removal of gels, i.e. ED50 (*8.14a*), P10 (*8.14b*), P10-E2 (*8.14c*), and P5 (*8.14d*); for comparison, the spectra of gels are also displayed, their most diagnostic band being at 1721 cm^{-1} for PEMA and 1110 cm^{-1} for PEG (respectively the C=O stretching of PEMA and the C-O-C symmetric

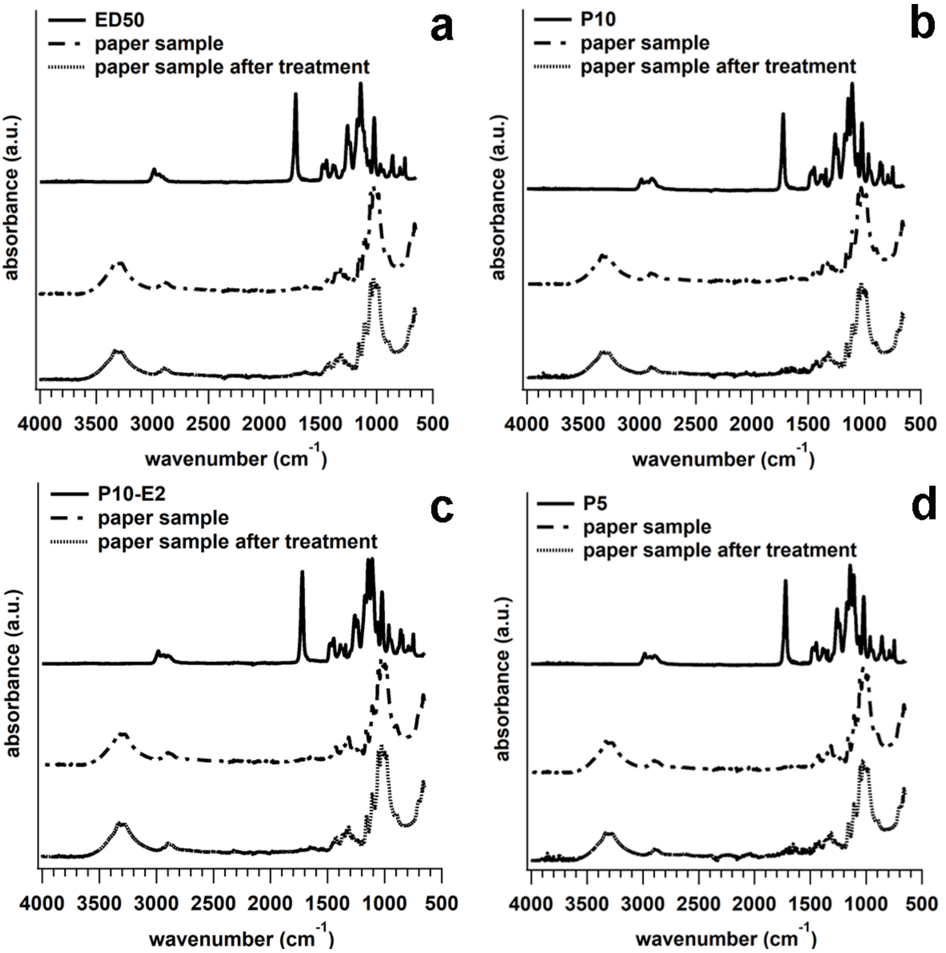

Figure 8.14 - ATR-FTIR spectra acquired on Whatman® paper mock-ups before and after application and removal of PEMA based gels for the assessment of gel residues: ED50 (8.14a), P10 (8.14b), P10-E2 (8.14c), P5 (8.14d); for comparison, the spectrum of gels is also shown

stretching of PEG) [127,128]. After gels application, no absorption ascribable to both PEMA and PEG appears in the IR spectrum of the treated paper sample.

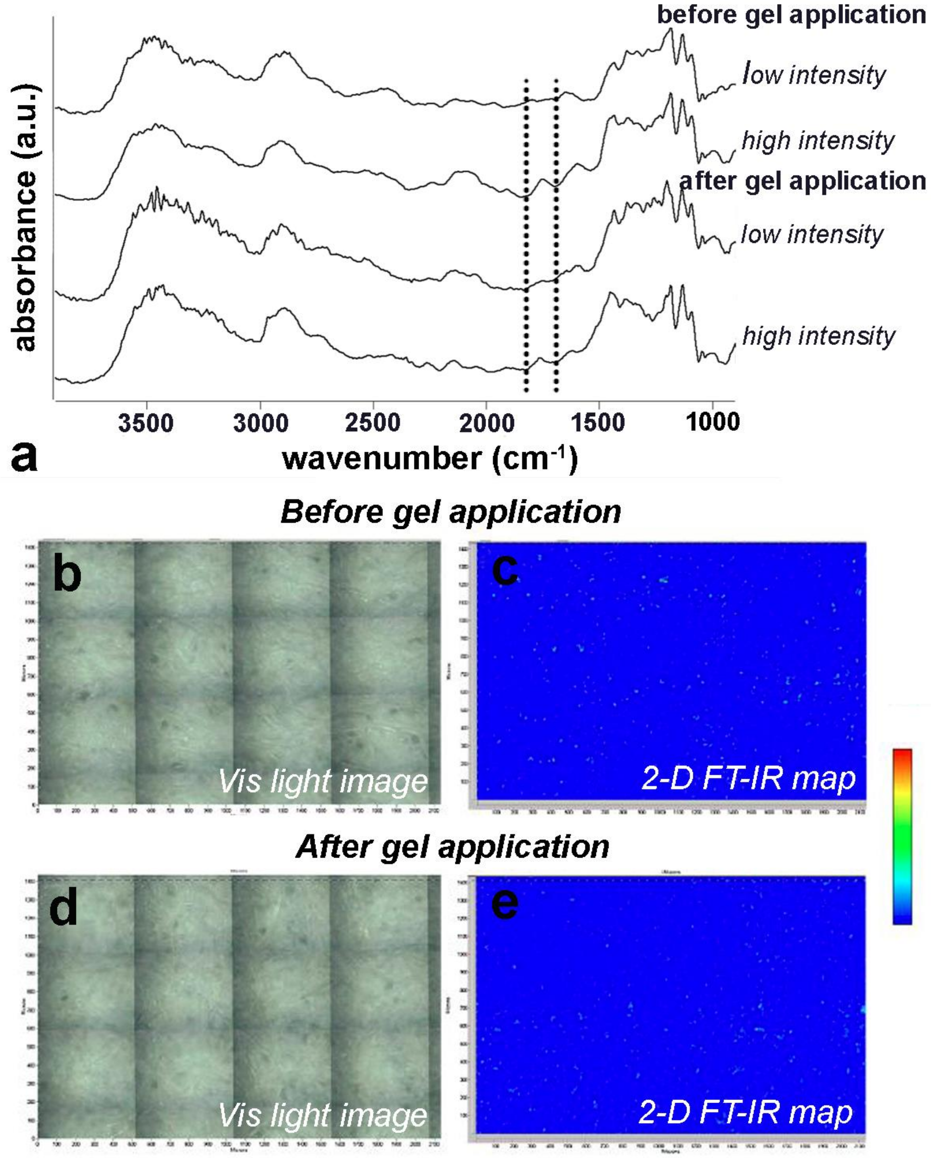

Figure 8.15 – FT-IR reflectance spectra (8.16a) of a Whatman® paper sample before and after application and removal of an ED50 gel. 8.16b and d are Vis light images, respectively acquired before and after gel application; 8.16c and e are the 2-D imaging maps, where the intensity of the spectra in the 1700–1790 cm^{-1}*range is imaged (highlighted by the dotted line in 8.16a). In the maps azure pixels correspond to high intensity signals, blue pixels to low intensity ones; all maps have dimensions of 1400 × 2100* μm^2

To double-check the presence of possible acrylate residues after the application of the ED50 gel, 2-D FTIR Imaging on the same Whatman® samples were performed (for the experimental set-up see *Par. 8.1.2*). Actually it is worth noting that the sensitivity level of an 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% [153]), owing to the possibility of detecting local (few μm^2) concentrations of analytes over large areas (mm^2). In *Fig. 8.15* the reflectance spectra of samples before and after gel application are displayed (*8.15a*), and the IR absorbance intensity in the range 1700–1790 cm^{-1} was imaged (*8.15c, e*). 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 such spectral region (blue pixels in the maps correspond to *low intensity spectra* in Fig. *8.15a*). Nonetheless some of the spectra in both maps show higher absorptions in the investigated IR range, with similar occurrence and intensity (azure pixels correspond to *high intensity spectra* in *Fig. 8.15a*): however such signals were ascribed to the presence of original oxidized groups of cellulose [154], and no relevant difference was noticed between the maps acquired before and after the application and removal of gels.

As a further proof of the absence of gels residues on treated substrates, additional IR measures were carried out on aluminium samples: such material was chosen since no IR absorption occurs in all the investigated range, thus helping in the discrimination of signals due to gels debris. As in the previous case, ATR-FTIR spectra were acquired on aluminium plates before and after gels application: ED50, P10, P10-E2, and P5 were all tested: as shown in *Fig. 8.16* no signals diagnostic for either PEMA and PEG were observed.

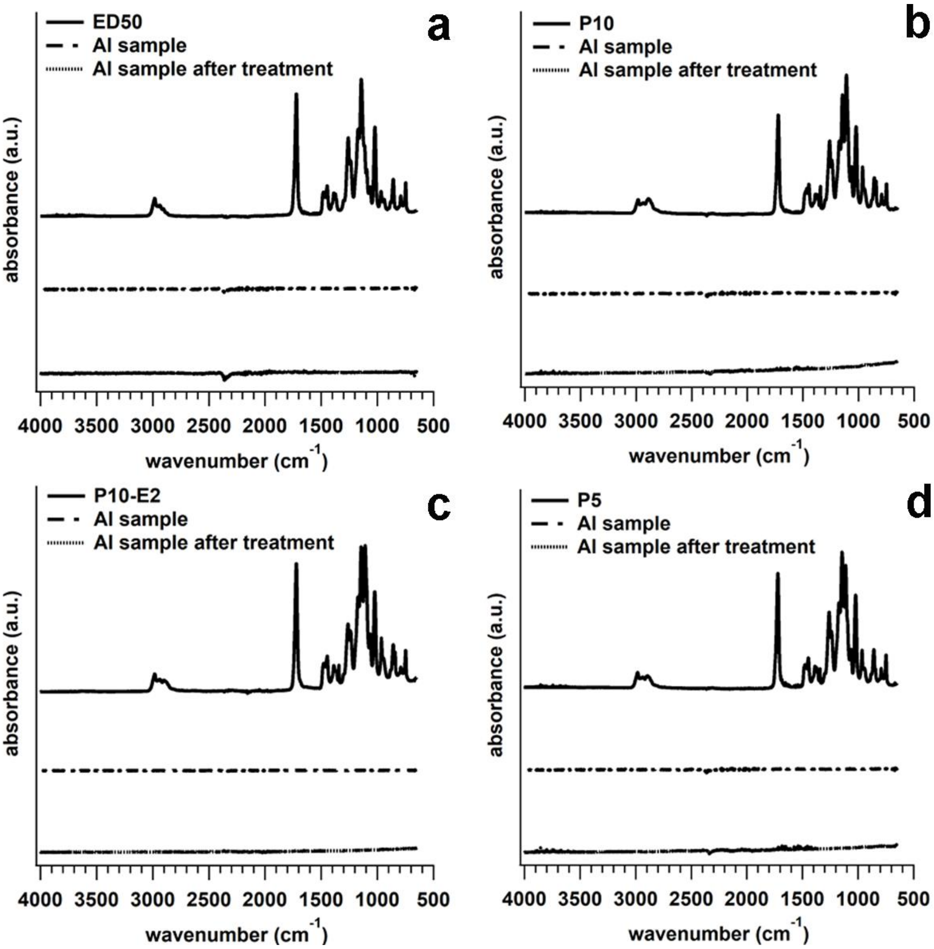

Figure 8.16 - ATR-FTIR spectra acquired on aluminium plates before and after application and removal of PEMA based gels for the assessment of gel residues: ED50 (8.16a), P10 (8.16b), P10-E2 (8.16c), P5 (8.16d); for comparison, the spectrum of gels is also shown

8.2.4 Diethyl carbonate on mock-up samples: evaluation in the short and long term period

Since DEC is not an organic solvent commonly employed in the restoration practice, we were interested in the assessment of possible drawbacks related to its use.

Preliminarily the solubilizing power of DEC towards a selection of inks and dyes was tested, as described in *Par. 8.1.2*. All the graphic media listed in *Tab. 8.2* were tested and most of them are not affected by the solvent: only the red Tombow ABT felt tip pen, the red BIC ballpoint pen, and the blue Staedtler and Pilot ballpoint pens undergo negative effects. In such cases the retentiveness of PEMA based gels were tested by their application on inked samples. The effectiveness of an ED50 gel loaded with DEC in preventing the spreading of a DEC sensitive ink is displayed in *Fig. 8.17*.

The effect of DEC on paper was also tested both in the short and long term period: actually before introducing this solvent into the restoration practice is important to know if it may induce degradation in paper substrates. For experimental tests three sets of samples were prepared:

1. aged Whatman® paper previously treated with DEC
2. not aged Whatman® paper treated with DEC
3. aged Whatman® paper

The followed ageing procedure is the one described in *Tab. 8.3*. *Fig. 8.18*

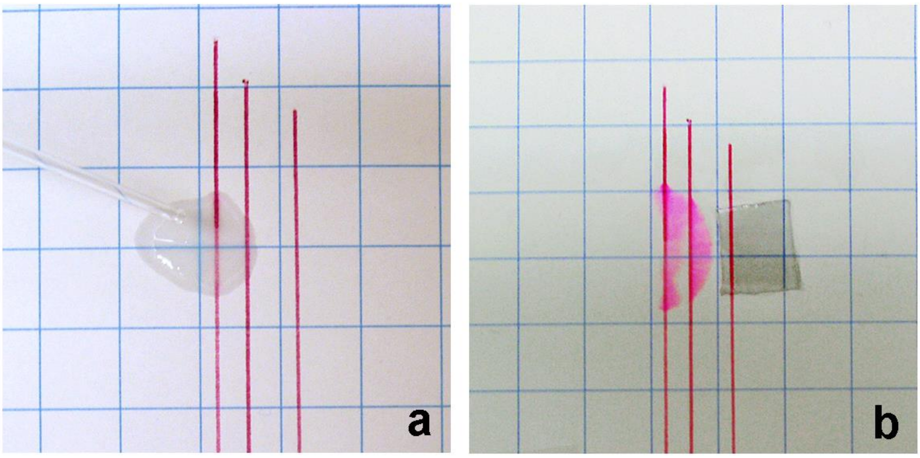

Figure 8. 17 - DEC solubility towards inks: spreading of a red ballpoint pen due to a drop of DEC (8.17a); when the solvent is retained in a PEMA based gel no drawback occurs (8.17b)

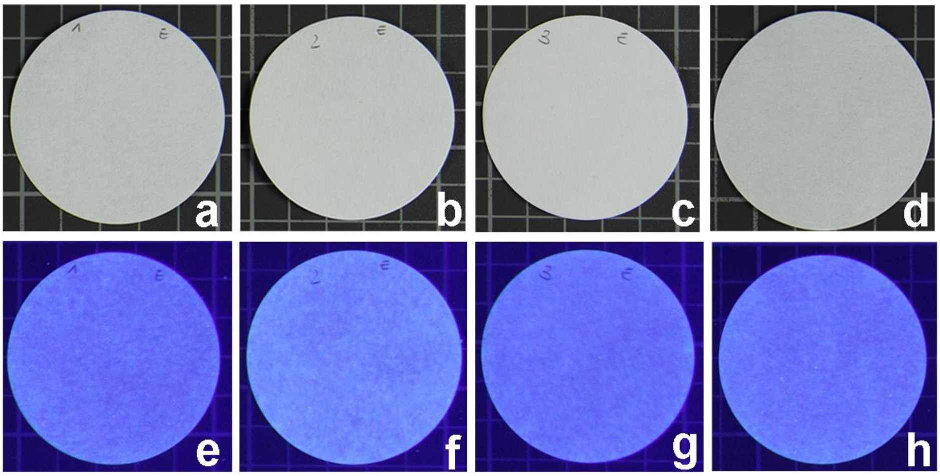

Figure 8.18 - Assessment of possible drawbacks related to the use of DEC in the long term period on Whatman® paper samples: Vis light images acquired on aged Whatman® treated with DEC (8.18a), not aged Whatman® treated with DEC (8.18b), aged Whatman® (8.18c), and pristine Whatman® (8.18d); 8.18e-h) same samples respectively acquired in UV light

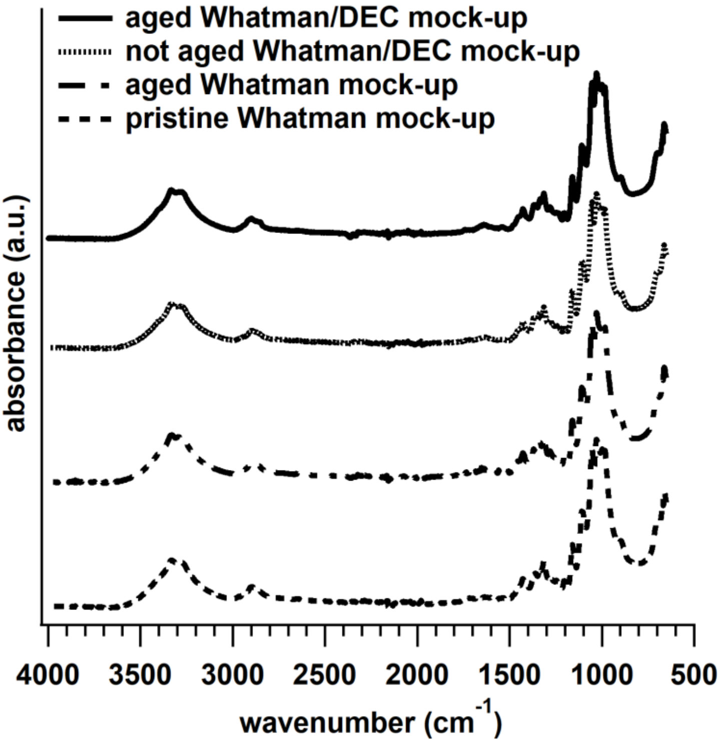

Figure 8.19 - ATR-FTIR spectra acquired on Whatman® paper mock-ups: for comparison both aged and not aged Whatman®/DEC mock-up, and both aged and pristine Whatman® samples are analysed; no significant differences among spectra are observed

shows the prepared mock-ups both in VIS and UV-light (also a pristine Whatman® paper samples is displayed for comparison): among them no significant macroscopic difference was detected. As expected, also ATR-FTIR spectra (reported in *Fig. 8.19*) does not show any changes after the samples treatment with DEC and the ageing process. In *Tab. 8.4* are reported experimental data concerning the assessment of the temperature of pyrolysis (T_p) of paper samples and the *pH* of the aqueous extracts from mock-ups.

Sample	T_p **(°C)**	***pH***
Aged Whatman®/DEC	357 ± 1	7.42 ± 0.03
Not aged Whatman®/DEC	363 ± 2	6.98 ± 0.03
Aged Whatman®	357 ± 2	6.63 ± 0.01

Table 8.4 – Temperature of pyrolysis (T_p) and pH of Whatman® paper mock-ups; presented data are the mean of at least three measurements. T_p and pH of pristine Whatman are: T_p =365°C , pH = 7.0

Comparing the results obtained on the not aged samples treated with DEC with the data of pristine Whatman® (T_p = 365°C, *pH* = 7.0), no significant difference appears. We can also notice that the procedure followed for the ageing is able to induce a small decrease in both T_p and *pH* of paper, thus indicating a slight degradation. Nevertheless T_p of aged mock-ups treated with DEC is consistent with T_p acquired for the aged/not treated sample, revealing no additional degradation induced by DEC. Moreover the *pH* of the extract from the aged Whatman®/DEC sample is significantly higher than 7, contrary to other mock-ups. This is an unexpected positive result: actually in the paper restoration practice a common treatment is the *deacidification*, a procedure (carried out in several different ways) that hinders the acidity of paper (i.e. the first cause of paper degradation) by increasing its *pH* up to 8 at most [155,156].

CHAPTER 9

Cleaning real artworks

This *Chapter* introduces the application of the developed tools to real artworks for the removal of both PSTs backing and adhesive residues, mainly form paper substrates; at the end of the *Chapter* a novel application of organogels for the restoration of photographic negatives is presented. All operations described below were designed and performed together with restoration professionals.

Testing our organogels in real case studies was extremely important to check their impact in the conservation and restoration field and to address our research to improve them: indeed each painted artefact is different from any other, thus having its own specific composition and degradation history, which could be very far from what can be reproduced by mock-ups in laboratory.

When possible, ATR-FTIR analysis were performed on samples collected from artworks: such measurements, carried out with the experimental set-up described in *Par. 6.3.2*, had a double aim: on the one hand to determine the chemical composition of unwanted materials, on the other to understand towards which compounds the tested solvents were effective. The cleaning level achieved on artworks was assessed only in one case (see *Par. 9.4*) by means of a 2-D FTIR Imaging technique (see *Par. 8.1.2* for experimental details) due to the impossibility of moving them to our laboratories.

9.1 Drawings by Federico Fellini from the *Municipal Rimini Film Library* (1987 - 1993)

The restoration of some drawings by Federico Fellini was performed in collaboration with *Opificio delle Pietre Dure* of Florence (i.e. Letizia Montalbano and Maddalena Trabace). The artworks, property of the *Municipal Rimini Film Library,* were realized between 1970s and 1990s with felt-tip pens and ballpoint pens on various kinds of paper; PSTs had been applied both on the *recto* and the *verso* of artworks, some even above graphic media, in order both to mend some lacerations and to mount drawings onto secondary supports [157].

Here the intervention on three artefacts is reported: *Anniversario: "14 Maggio 1957 – 14 Maggio 1987"*, 1987; *Titta e Federico davanti ai resti degli affreschi della Chiesa di S. Agostino di Rimini,* 1989; *Autoritratto con Oscar. "A Rinaldo, l'amico di sempre"*, 1993. Before operations on drawings, ATR-FTIR analysis were performed on PSTs samples collected from them: measurements were carried out by personnel from the *Opificio delle Pietre Dure,* and the experimental data were examined during this study. Preliminary tests concerning inks solubility due to DEC action were performed by restorer professionals [157].

9.1.1 Anniversario: "14 Maggio 1957 – 14 Maggio 1987", 1987

This artwork, acquired in 1997 by the *Rimini Film* from the *Anna Giovannini Fund Library* (Rimini Film Library code GR_13461/6), is realized on an industrial white paper sheet, 22.0 x 28.0 cm^2, with felt-tip pens, ballpoint pens and pencils; three similar PSTs (macroscopically paper PSTs) were applied on the *recto* side, even on artistic media, for mending some lacerations (see *Fig. 9.1*) [157].

ATR-FTIR analysis (see *Fig. 9.2*) carried out on samples collected from the PSTs on the artwork, despite their contaminations, confirmed a cellulosic backing layer (i.e. Masking Tape) [158]; the adhesive spectrum is consistent with an acrylic copolymer owing to the diagnostic peak at about 1730 cm^{-1} (due to C=O stretching of ester groups) and 1160 cm^{-1}

Figure 9.1- Anniversario: "14 Maggio 1957 – 14 Maggio 1987", F. Fellini, 1987; the artwork is shown before restoration

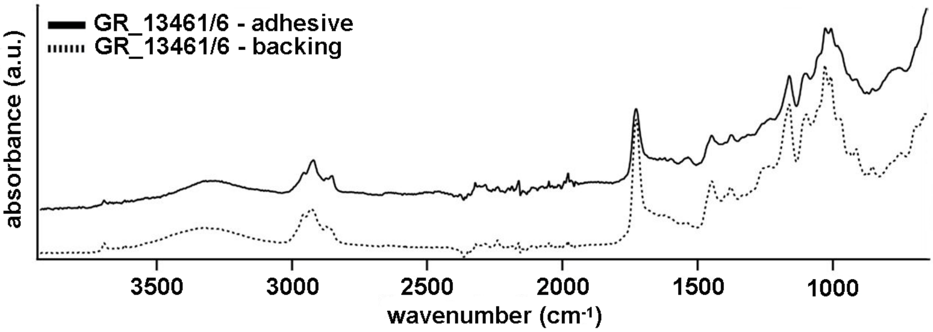

Figure 9.2 - ATR-FTIR analysis of a sample collected from PSTs on «Anniversario: "14 Maggio 1957 – 14 Maggio 1987"»: the spectra of both the adhesive and the backing layer of the PST are shown

(ascribable to the stretching vibration of C-C(=O)-O group), with an additional shoulder at 1240 cm^{-1} (originated from the C-O stretching) [10,11].

The removal of PSTs from the drawing was carried out by placing fully DEC swollen organogels directly on the top of each paper backings for 10 minutes. Before application ED50 gels were shaped with a scalpel to exactly match the dimension of PSTs; the excess of solvent was removed from gels surface with absorbent paper; in order to reduce solvent evaporation gels were covered with a polyester film throughout applications. As shown in *Fig. 9.3*, after 10 minutes an evident swelling of the adhesives occurred, thus allowing the detachment of PSTs backing by

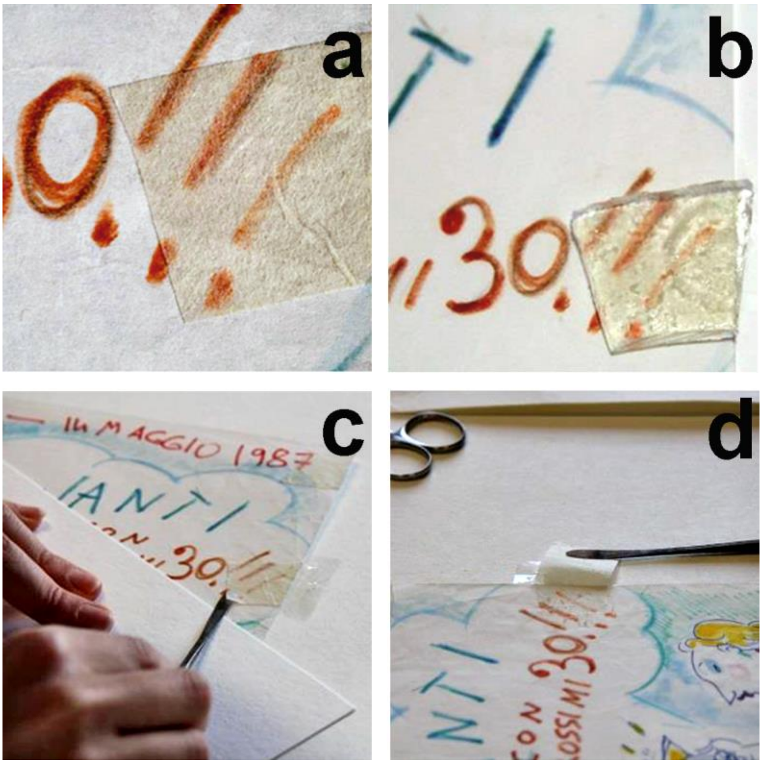

Figure 9.3 - Details of the intervention on «Anniversario: "14 Maggio 1957 – 14 Maggio 1987"»: a DEC loaded ED50 gel was placed onto the backing of the paper PST that covered the artistic medium (9.3a), for 10 minutes (9.3b); after the gel application, the PST was removed with a gently mechanic action (9.3c, d)

means of a spatula. Adhesive residues were then removed thanks to a cotton swab wetted with DEC.

Although systems able to retain solvents other than gels had been used in this intervention (i.e. cotton swab), we have to emphasize the significance of the use of gels in such a case study: PEMA based matrices are indeed essential in tape removal since they allow DEC to stay in contact with the tape for a sufficient time so as to penetrate it and swell the underlying adhesive, with a minimum impact towards the artwork; without the assistance of gels, feasible options are invasive and dangerous as mechanical ones (e.g. scalpel) or bulk solvents; in the latter case for tapes removal a really large amount of solvent should be used so as to grant the swelling of adhesive (e.g. for immersion), with related side effects like spreading of inks and waste of solvent.

9.1.2 Titta e Federico davanti ai resti degli affreschi della Chiesa di S. Agostino di Rimini, 1989

This artwork (see *Fig. 9.4*) comes from the *Luigi Benzi Fund*, childhood friend of Fellini and actual inspiration for the character of Titta in *Amarcord*, and therefore in this illustration [157,159,160]. The black ballpoint pen drawing is realized on a white paper sheet, 39.9 x 21.5 cm^2 (Rimini Film Library code GR_13461/9); two transparent PSTs were on the *verso* side, partially in correspondence with the pen line; the adhesive was strongly yellowed, being visible even on the *recto* of the artwork [157].

PSTs samples were collected and analysed by ATR-FTIR spectroscopy: IR spectra are shown in *Fig. 9.5*. Experimental data pointed out that PSTs applied on the drawing are Ordinary Tape made up of a polypropylene backing (diagnostic band of polypropylene at 2950 cm^{-1}, 2916 cm^{-1}, 2865 cm^{-1}, 2838 cm^{-1}; 1450 cm^{-1}, and 1375 cm^{-1} [10,11,161]) and a styrene modified rubber (peak at 699 cm^{-1} distinctive for the styrene [10,11,162,163]); IR absorptions located at about 1730 cm^{-1} can be ascribed to the C=O stretching in an ester group: ester tackifier are

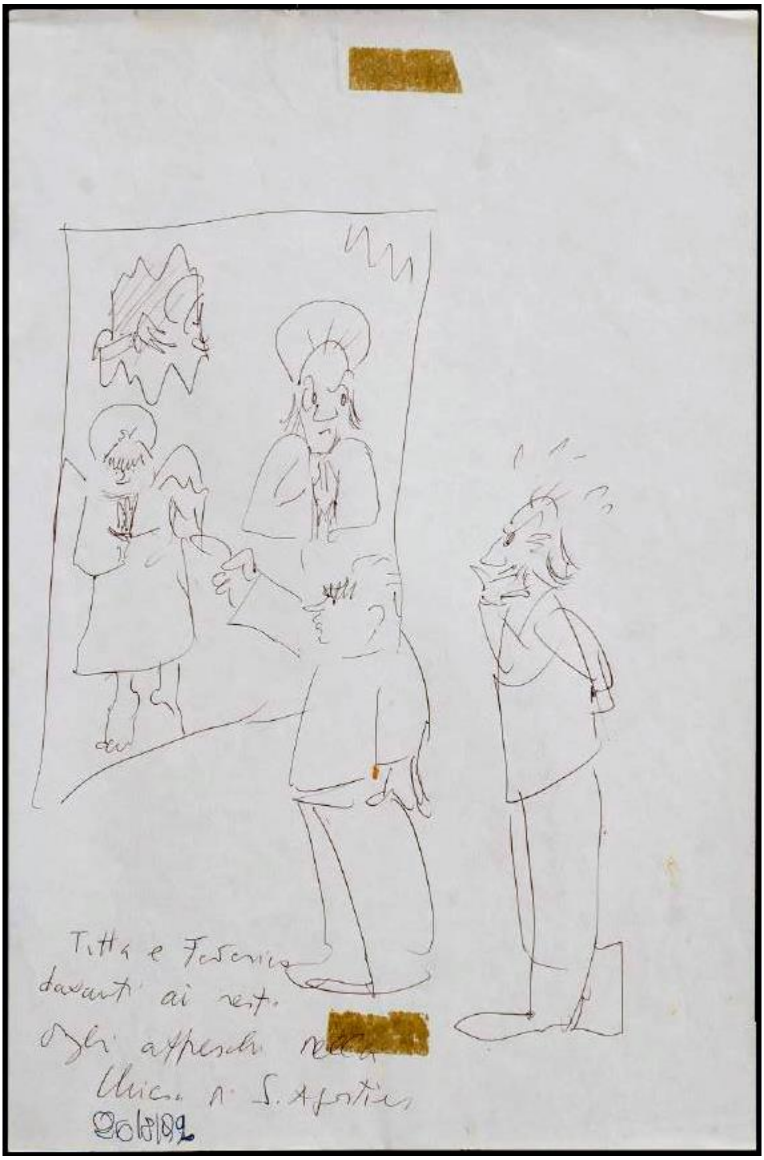

Figure 9.4 - Titta e Federico davanti ai resti degli affreschi della Chiesa di S. Agostino di Rimini, F. Fellini, 1989; brownish stain were visible before restoration on the recto side due to the penetration and oxidation of the PSTs adhesive applied on the verso

actually commonly used to improve the stickiness of adhesives [10,164].

In this case the removal of the two PSTs from the drawing was carried out in three steps, i.e. the detachment of the PST backing, the removal of superficial adhesive residues, followed by the elimination of the adhesive penetrated into the paper substrate. In *Fig. 9.6* we can notice the easy removal of the polypropylene backing tape after the PEMA-DEC gel application (10 minutes); adhesive residues were gradually eliminated by a cotton swab soaked in DEC and then by using bulk diethyl carbonate and ethyl acetate with the assistance of a suction table.

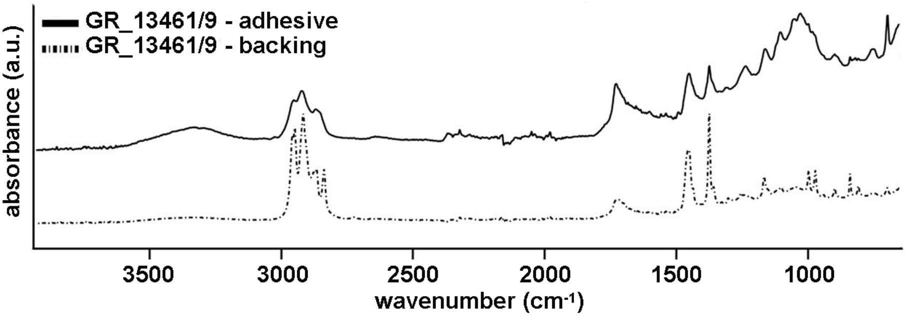

Figure 9.5 - ATR-FTIR spectra of both the adhesive and the backing layer of a PST sample from «Titta e Federico davanti ai resti degli affreschi della Chiesa di S. Agostino di Rimini»

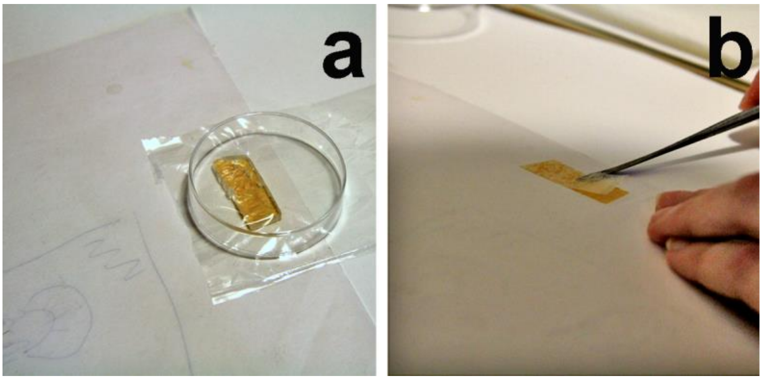

Figure 9.6 – The ED50 gel, fully DEC swollen, was applied onto the polypropylene backing layer of the PST, on the verso of «Titta e Federico davanti ai resti degli affreschi della Chiesa di S. Agostino di Rimini» (9.6a); after 10 minutes the PST backing was easily removed (9.6b)

9.1.3 Autoritratto con Oscar. “A Rinaldo, l’amico di sempre”, 1993

This artefact, shown in *Fig. 9.7*, was acquired from the *Rimini Film Library* in 1999 (code GR_13461/1) from the *Giuliano Geleng Fund*; this is the second of the two self-portrait with the Oscar dedicated to Rinaldo Geleng, co-worker and friend of Fellini [157,160]. The illustration is drawn by means of differently coloured felt-tip pens on an industrial white paper sheet, 30.2 x 21.5 cm^2. Inks faded over time due

Figure 9.7 - Autoritratto con Oscar. “A Rinaldo, l’amico di sempre”, F. Fellini, 1993; it is here displayed the condition of the drawing before restoration

to light exposure, and a significant washing away of inks occurred probably because of the drop of a liquid. The drawing was fixed on a support by means of four double sided PSTs, one on each corner on the *verso* side; due to adhesive penetration they became visible even on the *recto* of the artwork. At the bottom of the *verso* side there was even one transparent PST macroscopically consistent with a Magic Tape.

Fig. 9.8 and *9.9* display the ATR-FTIR analysis related respectively to the double sided PSTs, i.e. sample GR_13461/1 (1), and the transparent tape, i.e. sample GR_13461/1 (2). Concerning the former, IR spectra were collected from the adhesive residues on the cardboard at which the drawing was fixed, from the adhesive layer of the PST sample, and from the backing layer previously cleaned from most of the adhesive; IR measures are not decisive for the composition of the PST carrier, while the adhesive layer is presumably a styrene-butadiene rubber owing to the attribution of peak located at 964, 1449, 2844, and 2916 cm^{-1} to butadiene, and absorptions at 697 and 1601 cm^{-1} to styrene [10,11,162,163]; the peak at 1730 cm^{-1} is ascribable to an ester tackifier [10,164]. Analysis performed on the transparent tape confirmed it was actually a Magic Tape. The characteristic strong absorption band at about 1731 cm^{-1}, the broad peak at 1230 cm^{-1} and the strong absorption at 1159 cm^{-1} can be used to identify the acrylic composition of the adhesive [10,11]. The IR spectrum of the backing shows a very good overlapping with the one distinctive of cellulose acetate, peculiar of Magic PSTs: the peak at 1735 cm^{-1} (assigned to C=O stretching of the ester group), the band at 1367 cm^{-1}(due to deformation vibrations of CH_3 group), the strong absorption at 1216 cm^{-1} (attributed to C=O stretching mode of acetyl group), the broad band at 1031 cm^{-1} (C-O-C stretching of pyranose ring), and the weak peak at 900 cm^{-1} (probably

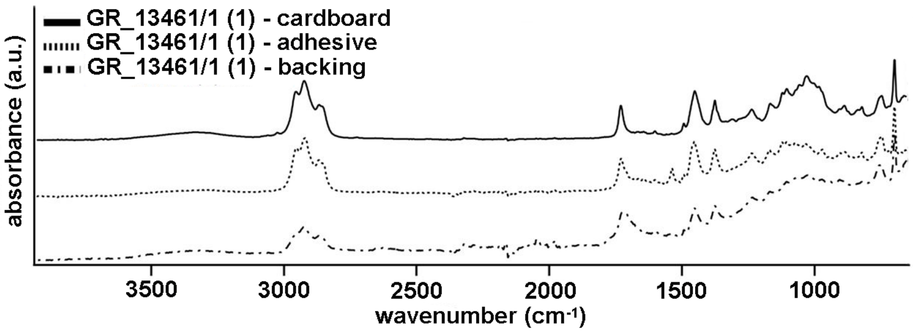

Figure 9.8 - ATR-FTIR spectra acquired on adhesive and backing layers of a sample collected from the double sided PST in «Autoritratto con Oscar. "A Rinaldo, l'amico di sempre"»; the IR spectrum of adhesive residues from the cardboard on which the drawing was mounted is also shown

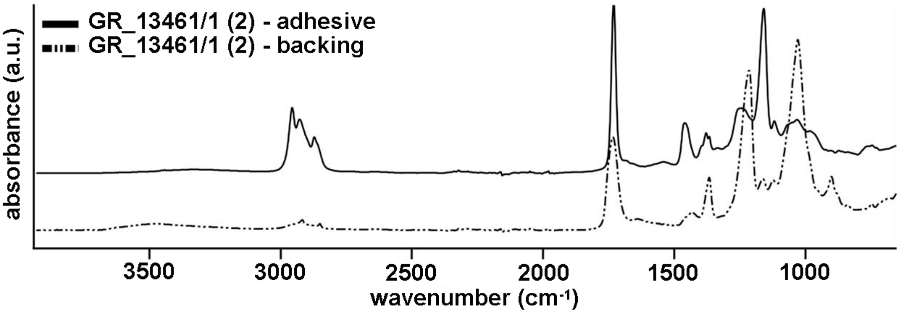

Figure 9.9 - ATR-FTIR spectra of both the adhesive and backing layer of a sample from the transparent PST in «Autoritratto con Oscar. "A Rinaldo, l'amico di sempre"»

due to C-H stretching deformation) can be undoubtedly assigned to cellulose acetate [10,11,165]

The removal intervention of the double sided PSTs was performed as shown in *Fig. 9.10,* with the same procedure as the one described for the two previous artworks: after 10 minutes of application of swollen PEMA-DEC gels on tapes, they were removed by simply lifting them with a spatula; adhesive residues were eliminated firstly with a DEC soaked cotton swab and then by dropping the solvent on stains with the assistance of a suction table.

Figure 9.10 – Application of the DEC loaded ED50 gel on the PST on the verso of «Autoritratto con Oscar. "A Rinaldo, l'amico di sempre"» (9.10a); detachment of the PST by means of a gentle mechanical action (9.10b)

9.2 *Untitled* by Keith Haring (1983)

In cooperation with the paper restorer Antonio Mirabile, we worked to the conservative intervention on the drawing realized by Keith Haring shown in *Fig. 9.11*. The artwork, black felt-tip on a 46.5 x 34.5 cm^2 paper sheet, was realized by the artist on the occasion of his first European exhibition in May 1983 at the *Lucio Amelio Gallery* in Naples [166]. As we can notice from *Fig. 9.11b*, the verso of the drawing presented six PSTs: four brown PSTs (B-PSTs) and two transparent tape (T-PSTs) had been applied for framing and mounting operations; two disfiguring yellowish stains are visible on the *recto* due to the penetration of the aged adhesive mass of the transparent PSTs, as can be better appreciated in *Fig. 9.12a*.

Prior to the intervention, preliminary micro-solubility tests were performed: they pointed out that the original ink was sensitive towards solvents commonly used for PSTs removal (i.e. ethyl alcohol, ethyl

Figure 9.11 - Untitled, K. Haring, 1983: recto (9.11a) and verso (9.11b) side before the restoration intervention

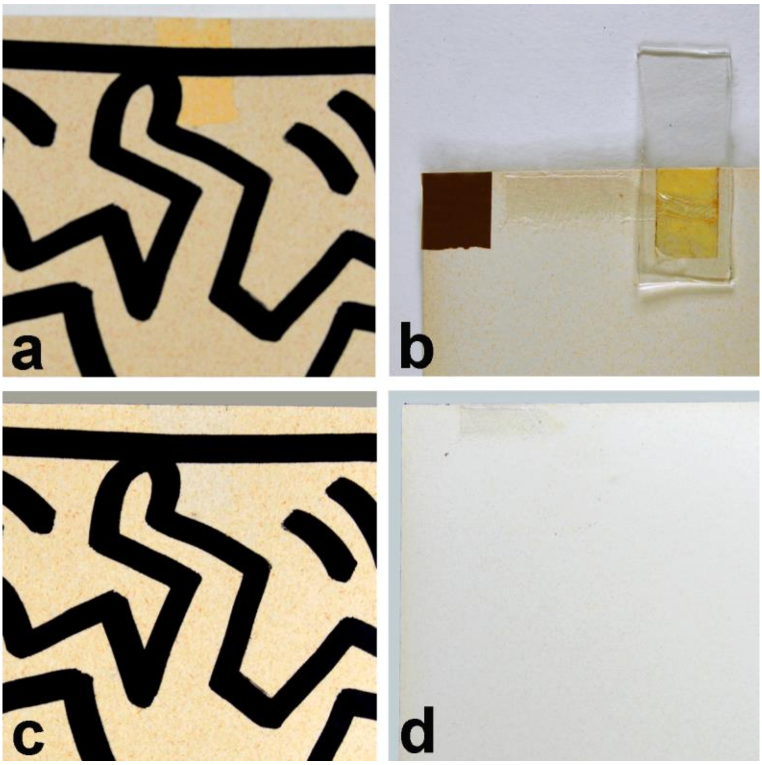

Figure 9.12 - Details of the drawing by K. Haring and the intervention for PSTs removal: a greasy yellowish stain (9.12a) is visible on the top right corner of the recto of the artefact owing to the presence of an aged transparent PST on the verso-side of the drawing (9.12b); ED50 gels, fully DEC swollen, were employed for tape removal (9.12b): the backing layer and the adhesive were removed from both the recto (9.12c) and the verso (9.12d) side of the drawing

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 removal of the adhesive. In the first step, ED50 organogels loaded with DEC were placed onto each of the six PSTs for a maximum of 30 minutes, covering them with a plastic film in order to prevent an excessive solvent evaporation; the detached backing was then simply removed with tweezers, with no damage or alteration of the inked artwork. In the second part of the intervention, the combination of a gentle mechanical action performed by means of a crepe-rubber eraser (a common

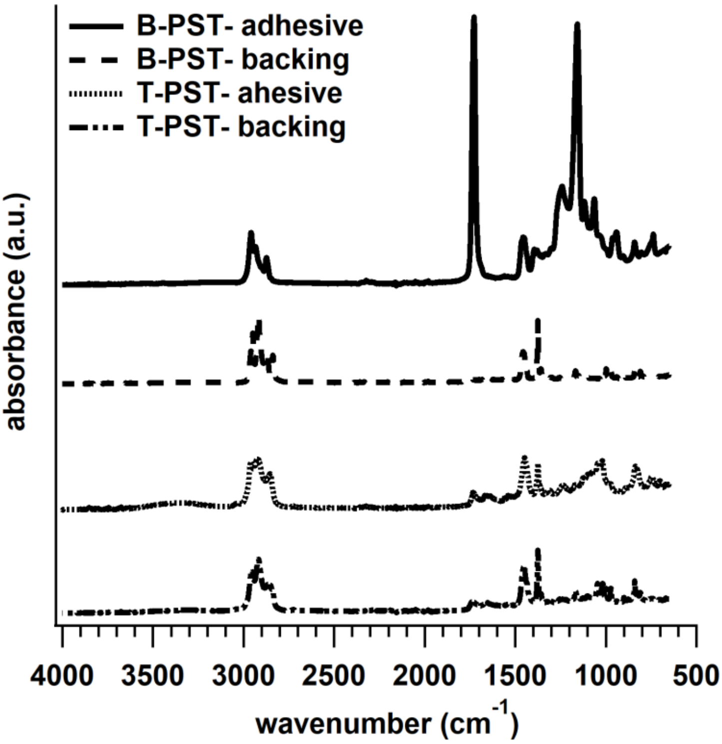

Figure 9.13 - ATR-FTIR spectra acquired on both the backing and the adhesive of the brown and transparent PSTs (B-PST and T-PST respectively), after their removal from the Keith Haring drawing

procedure in graphic arts) with the use of DEC, controlled by means of a vacuum suction table, was performed in order to remove the deeply ingrained adhesive residues. In *Fig. 9.12c* and *d* the state of the artwork after the restoration is shown.

After the removal of PSTs, ATR-FTIR analysis was used to assess their chemical composition: IR spectra displayed in *Fig. 9.13* revealed that the four brown PSTs (B-PST) and the two clear and transparent PSTs (T-PST) comprised identical polypropylene backing [10,11,161] but different adhesives, i.e. respectively acrylic copolymer [10,11] and natural rubber [163,167].

9.3 Drawings by Emilio Vedova from the *Foundation Emilio e Annabianca Vedova* (1943)

On the occasion of the exhibition *Post Zang Tumb Tuuum. Art Life Politics: Italia 1918–1943* (18 February – 25 June 2018, *Fondazione Prada,* Milan), three drawings painted by Emilio Vedova between 1943 and 1945 and an artist's sketchbook (1945) were exhibited. We cooperated with the restorer Vito Milo (*Studio C.R. Conservazione e Restauro,* Milano) for the restoration of two of this works: *Il padre morente,*1943, and *Natura morta con chicchere alle Zattere*, 1943.

Both this illustrations are pastels on thin paper sheets, glued on plywood supports; on the *recto* side some brownish stains were visible due to the penetration of the adhesive from aged PTSs that had been applied on the *verso* for a previous mounting. Preliminary tests showed that acetone was able to swell the glue and so promote the detachment from the support, nevertheless the artistic medium was sensitive towards it; on the contrary DEC was inert towards the pastel, but almost ineffective to both glue and the aged PSTs adhesive.

9.3.1 Il padre morente, 1943

In this artwork (see *Fig. 9.14*) greasy brownish stains were placed at three corners of the *recto* side; before the intervention was impossible to know if the aged PSTs were still present on the *verso*: the first step was then the detachment of the drawing from the plywood mounting, followed by the removal of adhesive residues due to PSTs.

As a results of preliminary tests, acetone loaded gels were used: ED50 and P10 gels were experimented. The estrangement from the support was achieved by applying gels along edges, as displayed in *Fig. 9.15*; in order to reduce the fast evaporation of acetone, gels were covered by a plastic foil. After 20 ÷ 30 minutes of application of ED50 gels, the swelling of the hardened glue occurred and the sheet detachment was achieved; P10 gels, being less retentive needed a shorter time, but in this case the risks of formation tidelines increased. However the use of the P10 formulation was preferable due to its better mechanical properties: actually the fast evaporation of acetone induces a deformation in both gels, but while the firmer ED50 completely fractures when removed from the application spot, P10 only slightly shrinks and totally recovers when immersed in the solvent (see *Fig. 9.16*). Noticeably the use of gels (both ED50 and P10) prevented the solubilization and spreading of pastel throughout the surface.

Figure 9.14 – Il padre morente, E. Vedova 1943; the drawing was framed without any superficial protection

After having separated the drawing from the wooden mounting, we could notice the actual presence of transparent PSTs on the *verso* of the artwork. The plastic tape was very easily removed mechanically (i.e. with the assistance of a spatula); in order to remove the greasy stains acetone-swollen PEMA based gels were applied on them for 10 minutes: a good bleaching level was achieved avoiding the solubilization and spreading of the graphic medium.

Figure 9.15 - Details of the intervention on «Il padre morente»: PEMA based gels loaded with acetone were applied all along the edges to detach the drawing from the mounting (9.15a, b); the state of the artwork after the restoration intervention is displayed in Fig. 9.15c

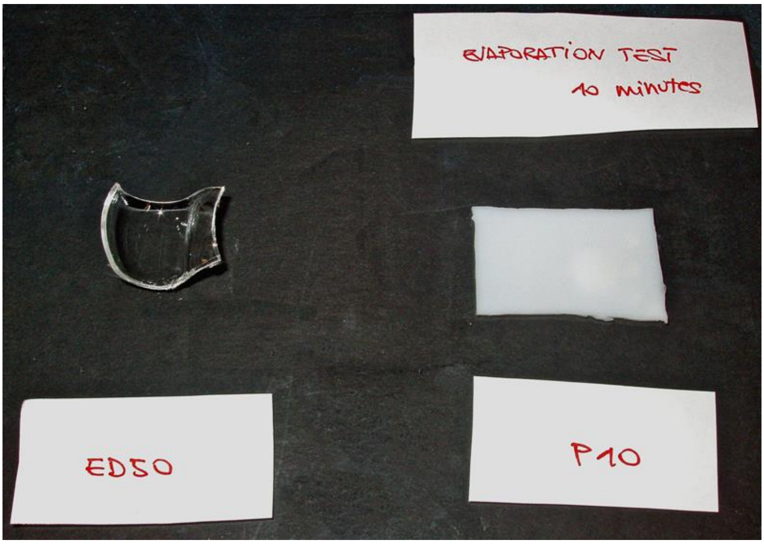

Figure 9.16 –Effects of solvent evaporation on ED50 and P10 gels: after ten minutes of exposition to room conditions ED50 gel is visibly out of shape contrary to P10

Samples of both the glue and PSTs applied on the verso of the drawing were collected for ATR-FTIR analysis; IR spectra are reported in *Fig. 9.17*. Concerning the transparent PSTs IR measurements pointed out a cellulose acetate backing, due to its most distinctive absorptions at 1019, 1234 and 1733 cm^{-1} [10,11,165]; the adhesive was instead not surely identified because of the strong overlapping with the cellulose spectrum: anyway two peaks, ascribable neither to paper nor to the cellulose acetate backing, arise at 1652 and 894 cm^{-1}, possibly indicating a natural rubber based adhesive [167,168]. Analysis of the glue used for mounting operations revealed a poly vinyl acetate adhesive, due to the strong acetate ester absorbance band at 1730 cm^{-1}, and other specific absorbance bands at 1431, 1372, 1226, and 1018 cm^{-1} [169].

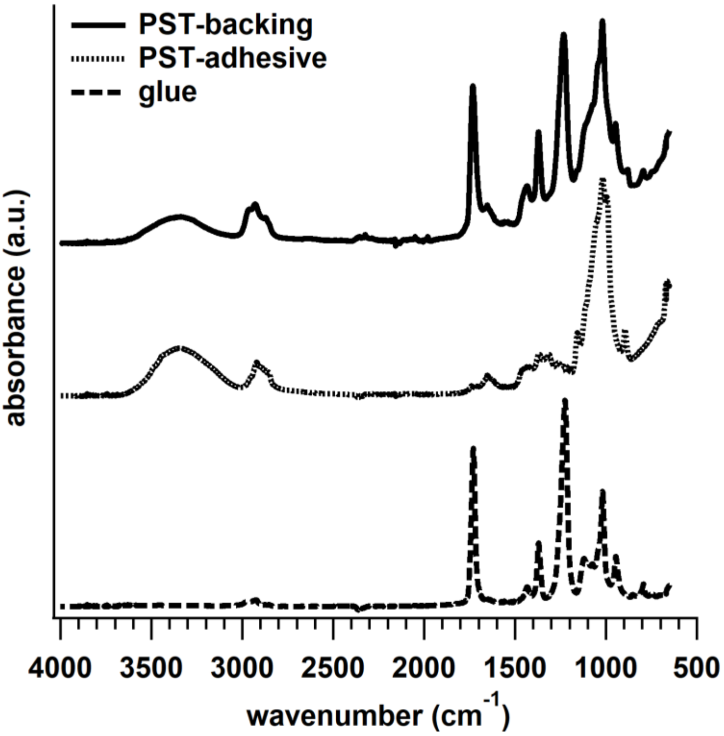

Figure 9.17 - ATR-FTIR spectra were collected on the removed transparent PSTs (both backing and adhesive) and on a sample from the adhesive used for gluing the drawing to the plywood support

9.3.2 Natura morta con chicchere alle Zattere, 1943

The state of the drawing before the restoration is shown in *Fig. 9.18*: two dark spots near the top corners and a long tear on the right are visible. Around the laceration a brownish stain widens, probably due to a PST used for mending in a previous intervention and a later attempt to remove it. Even in this case we could not know if PSTs were still present on the *verso*: therefore we proceeded by firstly detaching the drawing from the wooden support, and then bleaching the oxidized adhesive residues.

As in the previous case study, both ED50 and P10 gels loaded with acetone were used. The separation of the drawing from the glued plywood was achieved as a result of 20 minutes of gels applications; as we can notice from *Fig. 9.19a*, two slices of PSTs, macroscopically similar to Masking Tape, were found on the *verso* in correspondence with the laceration; they were later removed by swelling their adhesive thanks to the action of gels. The greasy stains were then weakened by repeated applications of acetone loaded gels (see *Fig. 9.19b, c*).

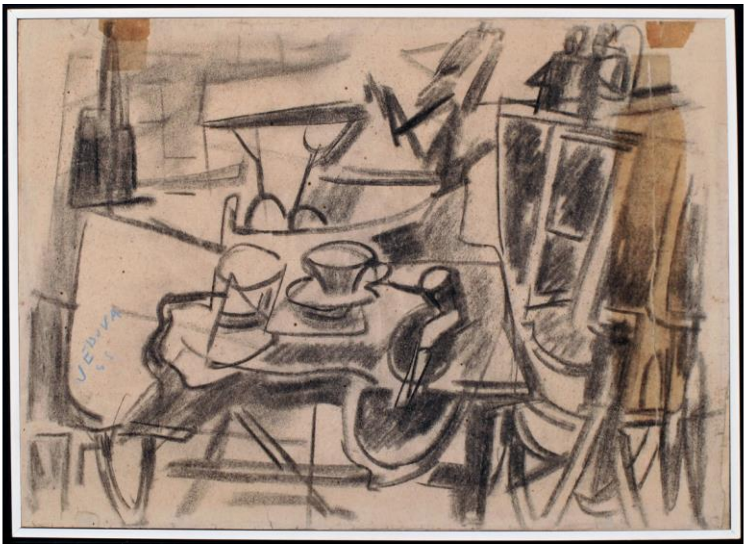

Figure 9.18 - Natura morta con chicchere alle Zattere, E. Vedova, 1943; the state of the artwork before the restoration intervention, framed and glued to the plywood mounting

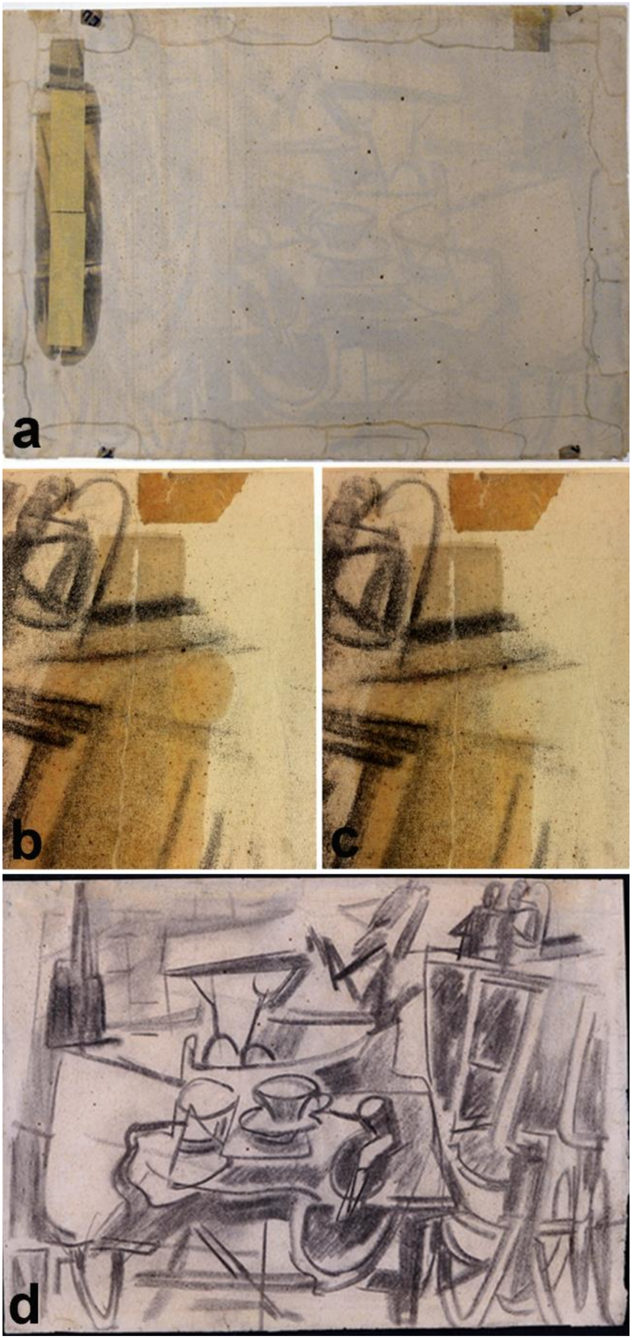

Figure 9.19 – Different steps of the restoration intervention on «Natura morta con chicchere alle Zattere»: 9.19a) the verso of the artwork after the detachment from the support: the PST used for mending the long laceration was still present; 9.19b) detail of the stain visible on the recto side due to the penetration and oxidation of the PST adhesive; 9.19c) after a 10 minutes application of an acetone loaded PEMA based gel the spot was significantly bleached; 9.19d) the state of the drawing after restoration

9.4 *Divina Commedia* (presumably end of XIX century)

In cooperation with the paper restoration laboratory *Restart* (e.g. Maria Diletta Pianorsi - PhD in Chemical Sciences, curriculum Science for the Conservation of Cultural Heritage -, and Lucrezia Vardaro - paper restorer), we worked on the restoration of a Divina Commedia (edited by Casa Editrice Sonzogno, Milano), illustrated by Gustavo Dorè and commented by Eugenio Camerini; the publication date is not indicated in the book, but probably it is datable between the end of the XIX century and the beginning of the XX.

The conservation state of the artefact is illustrated in *Fig.9.20*: an actual pervasive use of PSTs had been made in order to mount detached pages to the spine, and to fix the numerous tears. From a macroscopic standpoint, such PSTs are made up of a transparent backing; the adhesive, strongly yellowed, in most cases was completely dried so that the tape was easily detachable from paper, but some really sticky PSTs still strongly attached to pages were found. In such situations PEMA/PEG gels loaded with DEC were employed.

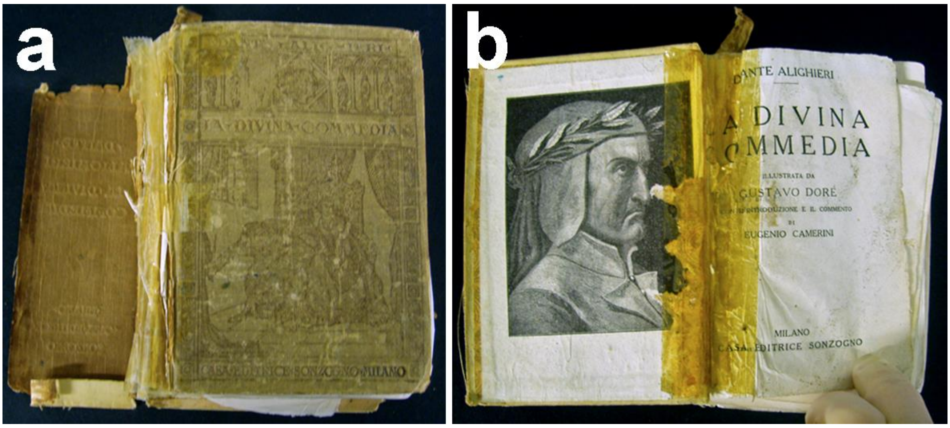

Figure 9.20 – Divina Commedia, Casa Editrice Sonzogno, Milano, presumably end of XIX century; PSTs were pervasively used to mend lacerations and reattach pages to the spine (9.20a, b)

Figure 9.21 - P10-DEC gels were used to remove PSTs from very fragile points: Fig. 9.21a and b show a fragment of paper attached to the page with PST; after having applied the gel (9.21c), covered with a plastic foil, the PST detachment was achieved

Figure 9.22 - Cleaning intervention for the removal of the adhesive penetrated into pores of paper; Fig. 9.22a and b show experimental tests performed with P10 gels loaded with both diethyl carbonate and acetone, the latter exhibiting greater effectiveness and extraction of the adhesive into the polymeric matrix (i.e. the P10-acetone gel acquired a yellowish colour after the treatment); Fig. 9.22c and d display the intervention on a shiny transparent yellow stain (no tape is still present in Fig. 9.22a) with a P10-acetone system; after 10 minutes of application most of the adhesive were removed and a clear recovery of paper appearance was achieved

Fig. 9.21 shows some step of the intervention for the removal of a sticky PST applied along all the edge of a page: DEC swollen P10 gels, were applied on the top of the backing for 15 minutes and covered with a plastic film to prevent excessive solvent evaporation (a glass plate or a plastic foil were used so as to protect pages below); since PSTs were placed on the two sides of the page, gels were applied both on the *recto* and on the *verso* to obtain a complete removal. The use of the P10-DEC formulation allowed the detachment of PSTs even from a very fragile point like the one showed in *Fig. 9.21b*.

However, the main issue related to the restoration of the *Divina Comedia* was the removal of adhesive residues, deeply penetrated into the pores of paper and highly disfiguring for the book due to their yellow appearance: as *Fig. 9.22* displayed, after the detachment of the tape greasy stains still persisted on pages. Cleaning tests were performed with P10 gels swollen in diethyl carbonate, dimethyl carbonate, and acetone (*Fig. 9.22b*): after 10 minutes of application, DEC loaded gels were ineffective and P10-DMC caused only a slight bleaching of the stain; on the contrary acetone released from gels was extremely operative: P10-acetone gels after the treatment were strongly yellowed, pointing out an extraction of the adhesive into the polymeric matrix; putting an absorbent paper sheet below the treated page resulted in an increase in the effectiveness of the cleaning, since the adhesive is partially caught by it, and in a reduction of the risk of tidelines formation. In some cases, as the one reported in *Fig. 9.22c*, the adhesive acquired even a shiny transparent appearance due to its degradation; acetone loaded P10 gels were proved to be effective even in these demanding situations: after only one application of 10 minutes, paper recovered its usual appearance due to the removal of most of the adhesive; repeated applications were performed in order to extract as many adhesive as possible.

ATR-FTIR measures were then performed for PST characterization: IR spectra collected on both the tape and the adhesive are shown in *Fig. 9.23*. Concerning the tape, both macroscopic observations and IR spectra pointed out a cellophane tape: the major IR bands assignments of cellophane are indeed quite similar to those of cellulose, that are a broad peak centred at about 3354 cm^{-1} (due to the stretching of OH groups), a smaller band at 2900 cm^{-1} (assigned to CH stretching vibrations), a signal at 1642 cm^{-1} (bending of absorbed water), a peak at 1364 cm^{-1} (ascribable to OH bending), a signal at 1314 cm^{-1} (assigned to CH_2

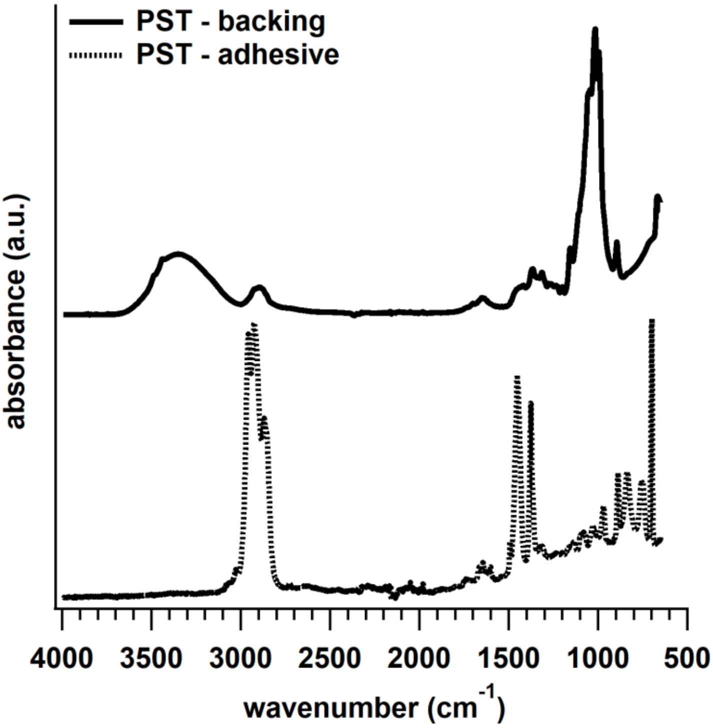

Figure 9.23 -ATR-FTIR analysis carried out on PSTs samples collected from «Divina Commedia»: IR spectra of both the backing and the adhesive are reported, thus revealing a cellophane base tape, and a styrene-butadiene rubber

wagging), the strong peak at 1016 cm^{-1} (attributed to C-O-C stretching) and a small band at 894 cm^{-1} (corresponding to the glycosidic C_1-H deformation) [10]. The adhesive spectrum perfectly overlaps the one of styrene-butadiene rubber, due to the sharp peak at 699 cm^{-1} (attributed to CH deformations), the signals at 1375 and 1451 cm^{-1} (distinctive of CH_3 deformations), the absorptions at 2868 and 2921 cm^{-1} (ascribed to CH stretching modes) [10,11,163].

Further analysis were performed on the *Divina Commedia* with a 2-D FTIR Imaging technique so as to check the cleaning level achieved by repeated applications of acetone loaded P10 gels on the shiny yellowish stains reported in *Fig. 9.22c* (for experimental set-up see *Par. 8.1.2*). *Fig. 9.24a* reports the reflectance spectra collected on two different areas of the page, i.e. the impregnating adhesive, a clean paper spot, and the same zone of the first acquisition after the cleaning procedure. The absorbance intensity in the range 1620 ÷ 1820 cm^{-1} (highlighted in *Fig. 9.24a* by the dotted lines) was imaged in the maps displayed in *Fig. 9.24b*, *d*, and *f*. Here red pixels correspond to *high intensity spectra*, while blue ones to a *low intensity* in the imaged spectral region. The maps of paper covered by the adhesive (*Fig. 9.24b*) points out a significant absorbance within this IR range; instead the map related to pristine paper (*Fig. 9.24d*) exhibits a large majority of blue pixels: green and azure ones, which corresponds to *high intensity spectra* acquired on pristine paper (*Fig. 9.24a*) might be due to contaminations, to additives in the processing of paper, or to its degradation; actually absorptions between 1720 and 1760 cm^{-1} can be ascribed to the presence of original oxidized groups of cellulose [154]. Measures performed on the cleaned area reveal that repeated treatments of the P10-acetone gel lead to a good cleaning level: the map reported in *Fig. 9.24f* is characterized by a larger

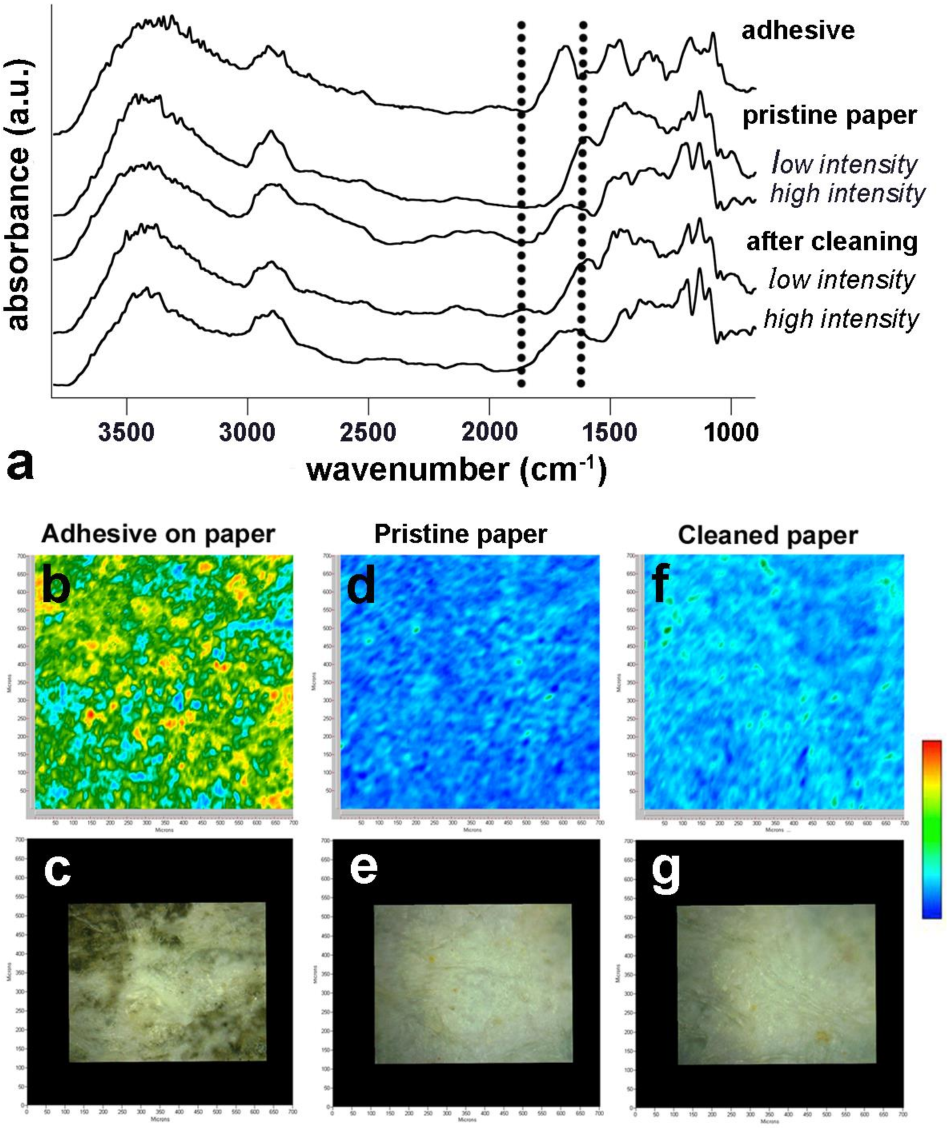

Figure 9.24 - FT-IR reflectance measures carried out on the «Divina Commedia»: IR spectra (9.24a) were acquired on a spot of the book completely filled with the adhesive, on a pristine paper zone, and on an area cleaned with acetone loaded gels; dotted lines in 9.24a highlight the IR absorption band (1620 ÷ 1820 cm^{-1}*) diagnostic for the presence of the adhesive and therefore imaged: in the IR reflectance maps (9.24b, d, f) red pixels correspond to high intensity signals, blue pixels to low intensity ones (maps are 1400 × 2100 µm*^{2}*); also Vis-light images are acquired in the mapped areas (9.24c, e, g)*

number of azure pixels as compared to pristine paper, but we can undoubtedly assert that most of the degraded adhesive penetrated in the pores of the cellulosic substrates was removed by means of a slightly intrusive treatment; unfortunately in such cases the complete removal of unwanted materials is quite impossible, even as a result of highly invasive procedures, like the immersion in organic solvents.

9.5 Gels for the cleaning of photographic and cinematographic films

The *Opificio delle Pietre Dure* of Florence, and particularly the two restorers Barbara Cattaneo and Giulia Fraticelli, presented us a conservative issue related to the restoration of materials other than the paper ones PEMA based organogels had been developed for: i.e. photographic and cinematographic films.

Both of them are multilayer objects in which emulsion films and protective layers are coated on polymer supports: the emulsion is mainly constituted by animal gelatine containing light-sensitive compounds; the protective layer, that prevents the emulsion from dust deposition and scratches, is a polymeric compound, e.g. gelatine, acrylic polymers, etc; as support layer several materials had been used over time, like cellulose nitrate, which was progressively replaced by cellulose acetate due to its flammability, and polyester, that became prevalent in 1990s because of the strong deformations induced in cellulose acetate supports by the "vinegar syndrome" (i.e. release of acetic acid) [165,170–173]. Actually such artefacts often exhibit PSTs applied for masking during photographic development, and mounting operations of animated motion picture productions; a removal intervention may be requested owing to their degradation or degradation of substrates.

Prior to operating directly on films, ATR-FTIR analysis were carried out on both substrates and PSTs (some samples could be easily collected without causing any damage). Moreover preliminary tests were performed on supports so as to assess if the selected organic solvents (i.e. diethyl carbonate, dimethyl carbonate, and acetone) may provoke negative drawbacks.

9.5.1 Photographic films

In this *Paragraph* the intervention on three negatives from the *Villani Fund* of *Fratelli Alinari I.D.E.A. S.p.A.*, datable around 1970s, is introduced. Their conservative state before restoration is reported in *Fig. 9.25* (*9.25a*, *b*, and *c* are named respectively «negative1», «negative2», and «negative3»): they all are characterized by the pervasive presence of

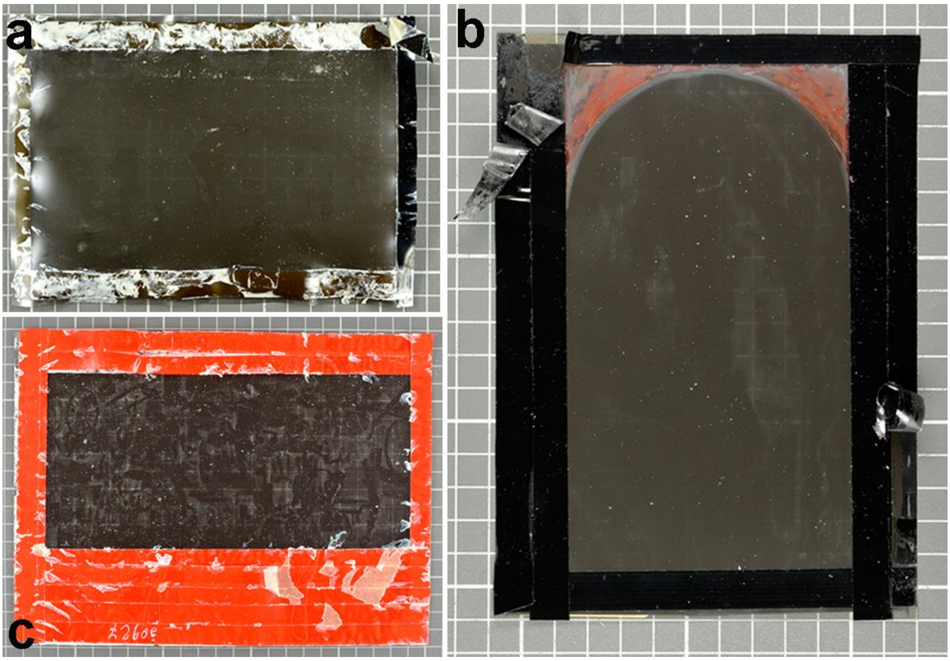

Figure 9.25 - Photographic films from the Villani Fund of Fratelli Alinari I.D.E.A. S.p.A.: «negative1», «negative2», and «negative3»are respectively reported in Fig. 9.25a, b, and c

PSTs used for photographic masking; macroscopically all PSTs looks like lithographic tapes, usually characterized by a poly (vinyl chloride) backing; the adhesive looks white and tough in «negative1» and «3», black and still sticky in «negative2».

On account of the production period of negatives and the sign “safety film” impressed on them we hypothesized cellulose acetate supports. All the same ATR-FTIR analysis (*Fig. 9.26*) performed on a representative negative evidenced in both the support and emulsion layer a gelatine film, therefore employed even as protective coating: the two sharp peaks located at about 1630 and 1535 cm^{-1} are assigned respectively to the C=O stretching mode of amide I and II, absorption at about 1240 cm^{-1} is ascribable to NH vibrations in amide III, and the band at 1084 cm^{-1} is related to CO and C-O-C stretching of carbohydrate moieties [174,175]. IR spectra acquired on both adhesive and backing layers of PSTs from the three negatives are reported in *Fig. 9.27*: concerning adhesives, ATR-FTIR measures pointed out a natural rubber adhesive for «negative1» and «3» and a styrene modified rubber, added with an ester tackifier, for «negative2» [10,11,162,167,168,176]; the backing was confirmed to be in all cases a poly (vinyl chloride) film due to the characteristic C-Cl stretching absorption located at about 690 cm^{-1}, the band at 960 cm^{-1} assigned to CH_2 rocking, the two peaks at 1329 and 1253 cm^{-1} attributed to CH bending of CH-Cl group, the signal at 1426 cm^{-1} related to CH_2 bending, and bands at 2849 and 2915 cm^{-1} ascribed to CH_2 stretching mode; owing to the stronger signal at 1730 cm^{-1}, «negative2» is characterized by a greater amount of ester plasticizer [10,177,178].

Preliminary tests on a negative samples were performed with DEC, DMC, and acetone on a representative negative: no macroscopically

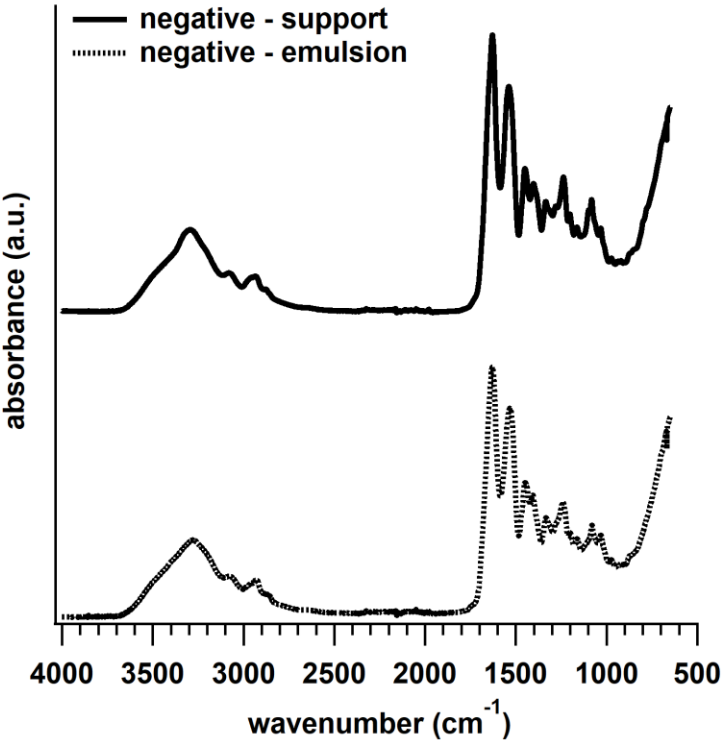

Figure 9.26 - ATR-FTIR spectra acquired on the support and emulsion side of a representative negative

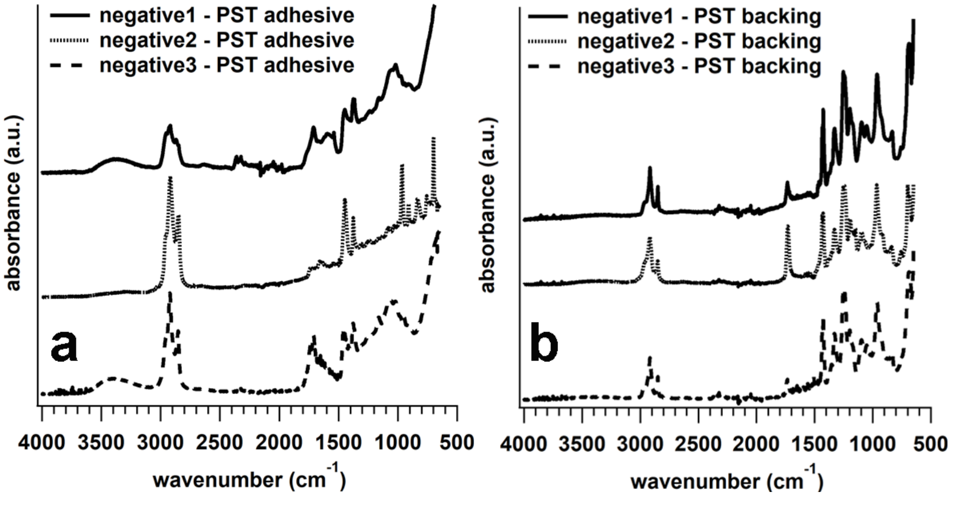

Figure 9.27 - PST samples from the three negative films were analysed by ATR-FTIR spectroscopy: IR spectra of both adhesive (9.27a) and backing layers (9.27b) are reported

evident damages to substrates arose from experimental tests carried out by means of both cotton swabs wetted with organic solvents and PEMA base gels (applications lasted 30 minutes at most).

Fig. 9.28, *9.29*, and *9.30* report interventions carried out respectively on «negative1» , «negative2» , and «negative3». Due to the large amount of adhesive to remove from photographic films, the less retentive gel formulation, P10, was taken into account.

P10 gels loaded with acetone and DMC were tested for the deletion of adhesive residues from «negative1»; in this case the PST carrier could be easily removed mechanically. Gels were cut with scalpel or scissors to match the proper dimension and shape, dabbed with absorbent paper to remove the excess of solvent, then applied on the unwanted layer and covered with a plastic foil. After 20 minutes gels were lifted, and the swollen adhesive was easily removed with the gentle mechanical action of a cotton swab soaked with the organic solvent. Both acetone and DMC proved their effectiveness in the removal of the natural rubber based adhesive, even though acetone provoked also the deletion of the yellow patina along the edge of the negative, thus resulting too aggressive (see *Fig. 9.28a* and *b*). As clear from *Fig. 9.28c* «negative1» was strongly affected by the “vinegar syndrome” that had caused serious distortions of the film and its wavy appearance: the flexibility of the PEMA/PEG gels are therefore here of paramount relevance since they grant a perfect adaptability to irregular surfaces.

The intervention on «negative2» was carried out in two steps: the removal of the PST tape, and the elimination of the sticky synthetic adhesive. Fully swollen DEC and DMC P10 gels were experimented by

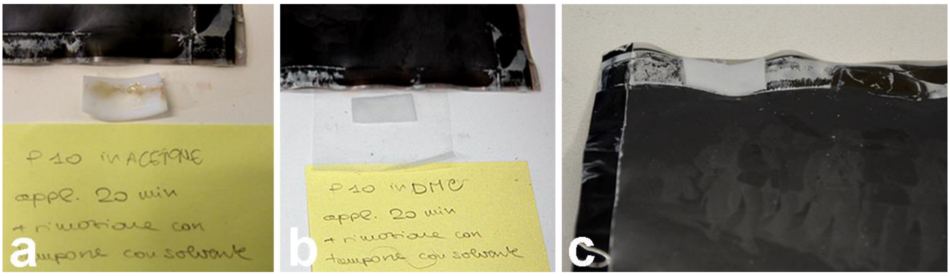

Figure 9.28 – Removal of PST backing and adhesive in «negative1»: 9.28a) after a 20 minutes application of a P10-acetone gel the adhesive was easily removed by a soaked cotton swab; 9.28b) an analogous result was obtained with a P10-DMC gel; 9.28c) the flexibility of P10 gels is of paramount importance to grant adhesion to non-planar surfaces

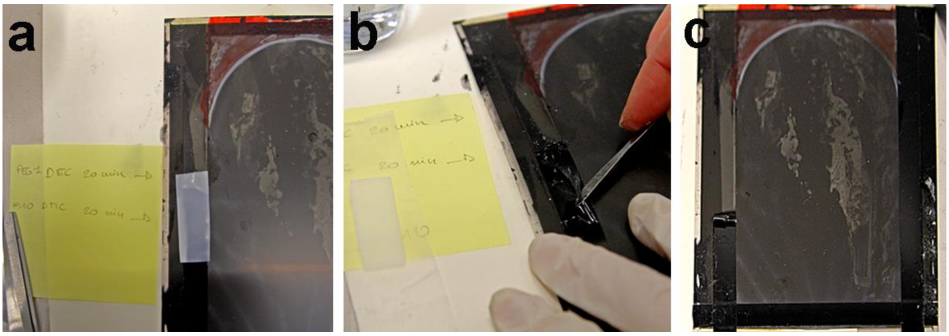

Figure 9.29 – A P10-DMC gel was used to detach the PST tape from «negative2» where it was not in correspondence with the red dye (9.29a, b); contrarily the complete removal of the adhesive covering the red ink was achieved with a P10-DEC gel avoiding solubilization of the graphic medium (9.29c)

Figure 9.30 – An almost uniform layer of white dried adhesive was under the red backing PST applied on «negative3» (9.30a); it was removed thanks to numerous applications of DMC loaded organogels (9.30b) and the gentle action of a DMC soaked cotton swab(9.30c)

20 minutes applications. Concerning the treatment of the backing, unexpectedly DEC resulted ineffective: indeed LSCM measurements, reported in *Par. 8.2.1*, showed the capability of DEC in gradually penetrating PVC films; maybe, in the present case study, the processing of the tape or its degradation are able to affect DEC-polymer interactions. DMC instead is able to distinctly swell the backing layer, as displayed in *Fig. 9.29b*. Nevertheless experimental tests pointed out that the removal of adhesive residues applied in correspondence with the red dye by means of DMC is dangerous owing to ink solubilization; conversely DEC was proved to be effective in adhesive swelling and even inert toward the dye.

In *Fig. 9.30* we can appreciate the complete removal of the homogenous white dried natural rubber layer on «negative 3» by means of DMC loaded gels; the red tape was previously eliminated by means of a weak mechanical action.

9.5.2 Cinematographic films

Animated motion picture production on which we intervened comes from the private collection of Marco Pagni Fontebuoni (*FILM Ferrania S.r.l.*). The two films, from the ‘90s, are a black and white (i.e. b/w) and a color one (c.); they are signed as “Kodak safety film”, thus pointing out a cellulose acetate support. Many PSTs, macroscopically consistent with Ordinary Tape, were applied on them for mounting operations.

ATR-FTIR analysis, reported in *Fig. 9.31*, were performed on the two films and PSTs samples collected from them. Both the artefact resulted to be made up of a cellulose acetate substrate (possibly cellulose triacetate in view of the low intensity of the IR band centred at about 3500 cm^{-1} due to small absorptions by hydroxilic groups) [10,165] and a gelatine emulsion [174,179]; the presence of a small peak located at 1732 cm^{-1} in both the spectra of the emulsion layer might be related to the presence of an ester additive in it (assuming that the points selected for ATR-FTIR analysis were not contaminated by the PST adhesive) [170,171]. Measures performed on PSTs show a clear overlap with the IR spectrum of acrylic copolymer adhesives, and polypropylene for what concern the backing layer [10,11].

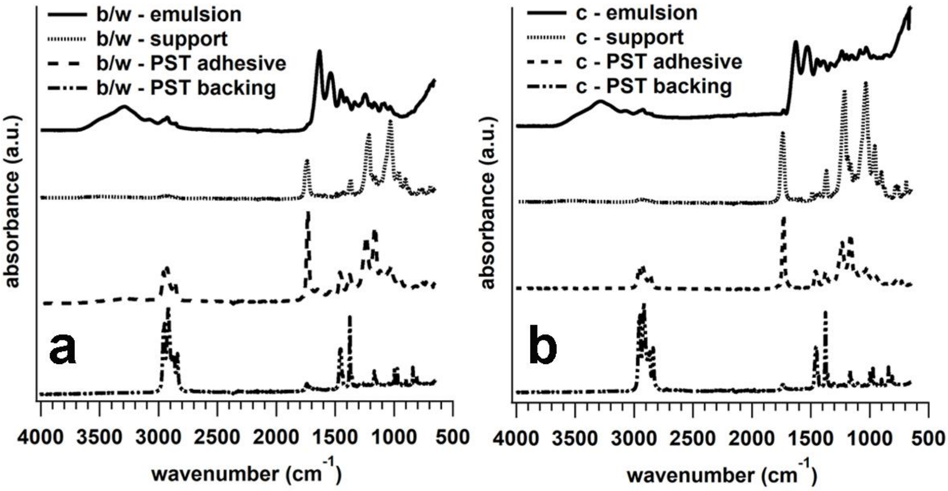

Figure 9.31 – ATR-FTIR analysis were carried out on films (i.e. emulsion layer and support) and PSTs collected from them (i.e. adhesive and backing side): IR spectra related to the b/w film are in Fig. 9.31a, to the color one in Fig. 9.31b

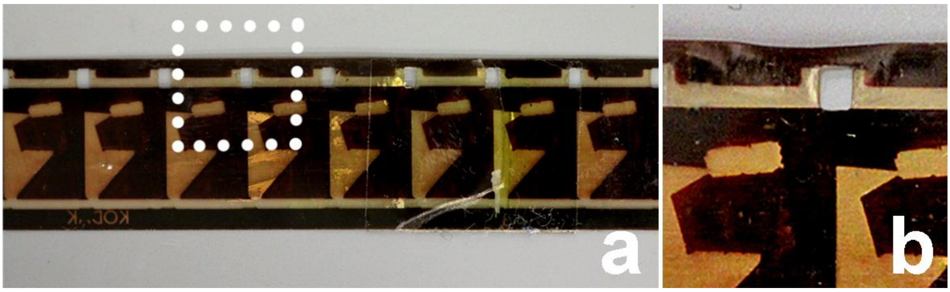

Figure 9.32 –Preliminary tests on the color film: 9.32a) the state of the object before the test (dotted lines highlight the application area); 9.32b) after a 2 minutes application of a P5-DMC gel a clear deformation occurred

Solvent-substrate interactions were assessed by means of preliminary tests carried out on representative samples with PEMA based gels loaded with DEC and DMC. *Fig. 9.32* shows the effects of 2 minutes of application of a P5-DMC gel (i.e. the more retentive formulation) on a color film: unexpected evident deformations occurred due to the swelling of the substrate, both on the emulsion and the support layer. Indeed some drawbacks towards the support layer (i.e. cellulose acetate) may be hypothesized, since cellulose acetate tapes had been removed thanks to DMC loaded gels; instead the clear swelling of the emulsion layer was totally unforeseen as gelatine had proved to be inert towards

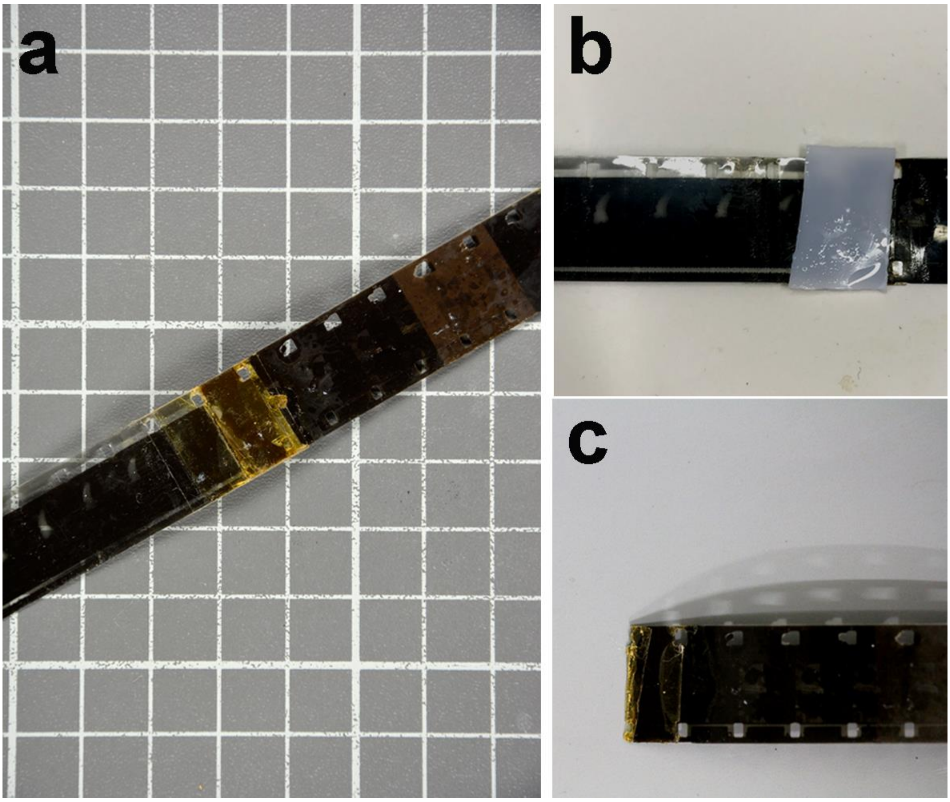

Figure 9.33 - Details of operations on the b/w film: the aged PST (9.33a) was treated with a P10-DEC gel for20 minutes for tape removal (9.33b); then a 10 minutes application was carried out to promote the deletion of adhesive residues (9.33c)

DMC in previous tests; this behaviour may be related to additives and plasticizers in the film formulation, e.g. ester ones, as possibly pointed out by ATR-FTIR spectroscopy. Contrarily, repeated applications of P10-DEC gels (less retentive) up to 20 minutes did not reveal any distortion both in the emulsion and the support film, even if DEC had been proved to penetrate cellulose acetate tape from LSCM analysis. Tests performed on a b/w film gave the same results.

Therefore the PSTs removal intervention was carried out on both artefacts with the DEC-swollen P10 formulation: gels, properly cut and shaped were applied on PST tapes for 20 minutes, thereafter the backing was easily detached; for the deletion of adhesive residues a further 10 minutes application was performed so as to swell the acrylic copolymer, then removed with a DEC soaked cotton swab.

Conclusions

The *cleaning* of cultural heritage artefacts is one of the most controversial procedures in the restoration practice due to its intrinsic irreversibility and invasiveness. Efficacy, high selectivity, controllable action, and low toxicity are the essential features that a system should have to grant an efficient ad safe cleaning performance. The use of non-confined organic solvents in cleaning procedures is considered to be too invasive nowadays, due to the lack in control of solvents penetration and spreading on artistic matrices, and to the insufficient selectivity that can lead to dissolution and swelling of compounds from the original substrate.

In this thesis the development of innovative tools for the removal of *Pressure Sensitive Tapes* (PSTs) and adhesive residues from artworks is introduced: poly (ethyl methacrylate) (PEMA) based organogels loaded with proper solvents were realized as a new strategy for overcoming issues related to traditional methods. These gelled systems can be easily shaped with a scalpel or scissors to exactly match the dimension of the PST to remove, and applied on its top surface; after that, the confined solvent is released from the polymeric matrix, penetrates the backing layer, and then swells the underlying adhesive, so that the tape can be simply removed with a gentle mechanical action. Clearly the chosen cleaning fluid loaded within the gelled system has to be able to interact with PSTs components: to this aim diethyl carbonate (DEC) was selected as benchmark solvent, due to its solubility parameters, inertness towards most common inks and dyes, and classification as *green* solvent.

The actual effectiveness of DEC in positively interacting with PSTs components was assessed by means of Laser Scanning Confocal Microscopy: depending on the kind of PST different times of application are required, but in each case DEC is proved to be able to penetrate the carrier (e.g. polypropylene, paper, cellulose acetate, polyvinylchloride) and swell the adhesive (e.g. acrylic co-polymers, styrene-butadiene rubbers). DEC inertness towards paper mock-up samples was also assessed both in the short and long term period: pH analysis of aqueous extracts, evaluation of the pyrolysis temperature, and IR spectroscopy were performed on Whatman® paper samples.

PEMA organogels were synthesized by means of a solution polymerization performed in presence of a cross-linker so as to obtain chemically bonded 3-D network: in this way strong gels should be realized, easily applicable on surfaces to be treated and scarcely prone to the leaving of residues. In order to obtain gels characterized by satisfying mechanical properties and tuneable release several attempts were made: both reaction parameters and chemicals were changed, but the most significant improvement was achieved by blending PEMA with poly (ethylene glycol) (PEG): specifically semi-interpenetrating (semi-IPN) systems were realized by cross-linking ethyl methacrylate (EMA) in presence of PEG linear chains, whose permanence in the PEMA network was assessed by means of IR spectroscopy. The embedment of PEG within the PEMA network allows a significantly enhanced elasticity and flexibility of gels, at the meanwhile preserving the high solvent content and gradual release of PEMA gels. PEMA/PEG systems are characterized by an easy manipulation and high adaptability to non-planar and rough surfaces, that permits them to be applied even on warped surfaces (e.g. degraded photographic negatives), the edge of framed drawings, or the spine of books.

Solvent content and gels retentiveness were deeply investigated. Thermal analysis were used for the evaluation of the amount of solvent confined in the polymeric matrices, and the quantity of free and bound solvent; gravimetric measures allowed to assess the mass of released solvent, DEC evaporation rate, and its uptake from dried matrices. The synthesized gels was all proved to be able to load large amount of DEC (70 ÷ 80% of the total gel mass), and to slow down its evaporation; an almost quick uptake of solvent from the dried gels occurs up to complete solvent recover, thus pointing out no irreversible wreckages over dying; owing to this feature PEMA based gels may be classified as reusable systems. Furthermore experimental tests showed that a tuneable gel release can be attained by varying cross-linker and PEG concentration in pre-gel formulations: a correlation between the quantity of solvent released on wettable substrates and the amount of the free DEC retained in the polymeric matrices was observed. Eventually the gels capability in loading other solvents potentially useful in the restoration practice (e.g. acetone, methyl ethyl ketone, dimethyl carbonate) was assessed.

Following the good results obtained in the removal of PSTs from laboratory samples, PEMA based gels were used in the conservative intervention of real artworks: PEMA-DEC gels were used for the removal of tapes from drawings by Federico Fellini, and an illustration by Keith Haring; PEMA and PEMA/PEG systems loaded with acetone were used for the deletion of greasy stains from two drawings by Emilio Vedova and a XIX century Divina Commedia. Finally even a case-study distant from our initial purpose was taken into account: the cleaning of photographic and cinematographic films from PSTs and adhesive was also achieved by means of applications of PEMA/PEG systems loaded mainly with diethyl and dimethyl carbonate.

Acknowledgments

With these few lines I would like to express my thankfulness to all people close to me throughout the accomplishment of this long path.

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ANNEX

List of publications

P. Ferrari, D. Chelazzi, N. Bonelli, A. Mirabile, R. Giorgi, P. Baglioni, *Alkyl carbonate solvents confined in poly (ethyl methacrylate) organogels for the removal of pressure sensitive tapes (PSTs) from contemporary drawings*, Journal of. Cultural Heritage, 2018, *article in press*

M. Trabace, A. Mirabile, L. Montalbano, R. Giorgi, P. Ferrari, *An innovative method to remove Pressure Sensitive Tape from contemporary felt-tip pen and ballpoint pen drawings on paper. The case studies of Federico Fellini from Rimini film library*, in Scienza e Beni Culturali, Le nuove frontiere de restauro - Trasferimenti, Contaminazioni, Ibridazioni, Edizioni Arcadia Ricerche, 2017, pp. 849-859

M. Trabace, A. Mirabile, L. Montalbano, R. Giorgi, N. Bonelli, M.D. Pianorsi, P. Ferrari, *Un metodo innovativo per la rimozione di nastri autoadesivi da disegni contemporanei su carta. I casi studio di Federico Fellini della Cineteca di Rimini*, in OPD Restauro, n.29, 2017, pp. 259-266

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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 artefacts 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 controlled. In order to optimize the processing costs and final properties of the gels, three formulations of poly (ethyl methacrylate)-diethyl carbonate (PEMA-DEC) organogels were synthesized, using different diluents and additives. A thorough physicochemical 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.

1. 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 artefacts. 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 copolymers, 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 loss of adhesiveness and color changes (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

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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 confined 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 investigated the penetration of the solvent into the polypropylene backing layer of a model PSTs (PP-PST), so as to provide 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_{1000}) 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) was carried out to evidence structural changes induced by the use of different diluents or by the addition of PEG_{1000}.

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 × 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. Fourier transform infrared spectroscopy (FTIR) was used to assess the removal of the PSTs and the absence of gel residues after treatment.

2. Experimental

2.1. Materials

Ethyl 2-methylprop-2-enoate (EMA) (Sigma-Aldrich, purity ≥ 98.5%), 2-(2-methyl-acryloyloxy)ethyl 2-methylacrylate (EGDMA) (Sigma-Aldrich, purity ≥ 99%), 2,2′-Azobis(2-methylpropionitrile) (AIBN) (Fluka, purity > 98%), polyethylene glycol (average Mw ≈ 1000 kDa) (PEG_{1000}), diethyl carbonate (DEC) (Sigma-Aldrich, purity ≥ 98.5%), and 2-propanol (IP) (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 ≥ 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® (product code 56100), blue ball-point pen ink was from Bic®.

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

	Monomer(w/w %)	Solvent(w/w %)		PEG_{1000}(w/w %)
ED50	50	DEC	50	–
EI50	50	IP	50	–
EI50P10	40	IP	50	10

2.2. 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_{1000} 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.

The presence of monomer in the refreshed solvent was checked with FTIR measurements: a BioRad FTS-40 spectrometer recorded spectra from 4000 to 400 cm^{-1}, at 4 cm^{-1} 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, FTIR grade ≥ 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_{1000} was considered):

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

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.

2.3. Physicochemical 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:

$$ESC\% = \frac{W_s}{W_g} \cdot 100 \tag{2}$$

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 (Ø = 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 20× 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 cover glass, and a gel sample loaded with Cou6-labelled DEC was laid 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 ΣIGMA (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 °C, 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:

$$F_s = \frac{M_t}{M_{inf}} \tag{3}$$

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^{-3} 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.

2.4. Removal of PSTs from paper artefacts

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 form 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. Attenuated total reflectance FTIR spectroscopy (ATR-FTIR) 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^2), averaging 128 scans in the 4000–650 cm^{-1} range, with a spectral resolution of 4 cm^{-1}. 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 128 × 128 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 cm^{-1}, acquiring 128 scans for each spectrum. A "single-tile" analysis results in a map of 700 × 700 μm^2 (128 × 128 pixels), and the spatial resolution of each Imaging map is 5.5 μm (i.e. each pixel has dimensions of 5.5 × 5.5 μm^2). "Mosaics" of 1400 × 2100 μm^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.

3. 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 were obtained as 1–2 mm thick sheets 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 adding 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.

Fig. 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 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.

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_{1000} into the reaction mixture noticeably reduces the reaction yield (down to 65%), probably due to the lower amount

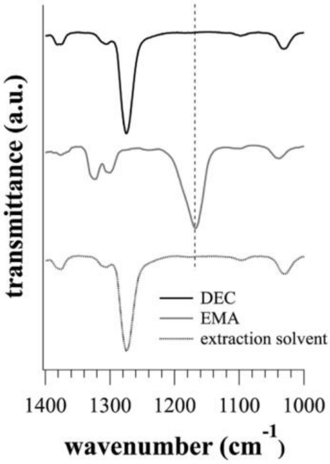

Fig. 1. FTIR spectra (1400–1000 cm^{-1}) of diethyl carbonate (DEC), pure ethyl methacrylate (EMA) monomer, and DEC used as exchange solvent (24 h) after preparation of the gels and extraction of 24 h in DEC.

Table 2
Reaction yield, equilibrium solvent content (*ESC%*), residual solvent fraction (F_s) after 1 hour evaporation, time required to reach *ESC%* for completely dried gel samples (t_f), 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.

	Yield (%)	*ESC* (%)	F_s (60 min)	t_f (h)	*SR* (mg/cm^2)
ED50	73 ± 3	76 ± 3	0.70 ± 0.03	5	1.7 ± 0.4
EI50	72 ± 2	79 ± 2	0.44 ± 0.04	4	1.4 ± 0.1
EI50P10	65 ± 3	86 ± 2	0.53 ± 0.03	4	1.8 ± 0.6

of monomer used, and to possible interference of PEG$_{1000}$ with the gelation process; moreover, not all PEG$_{1000}$ might be efficiently embedded into the PEMA polymeric network.

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 1.6 mg/cm^2. 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. Fig. 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 (Fig. 2a). After 20 minutes, the RhBITC marked adhesive layer has lost its initial homogeneous appearance with a decrease of fluorescence intensity (Fig. 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 (Fig. 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 Fig. 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.

Thus, the use of gels is necessary to decrease the evaporation rate of DEC, and promote its interaction with the PST, even when limited amounts of solvent are used. Fig. 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 ± 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 Fig. 4 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].

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 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

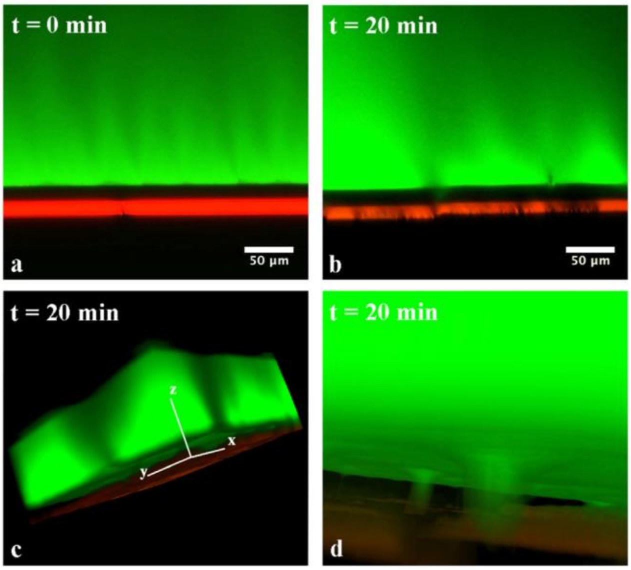

Fig. 2. Laser scanning confocal microscopy (LSCM) measurements on the ED50 gel loaded with diethyl carbonate (DEC) (solvent marked green with Cou6) and applied on a polypropylene (PP)-pressure sensitive tape (PST) (acrylic adhesive marked red with RhBITC); the black layer corresponds to the polypropylene 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); Fig. 2c shows the 3-D reconstruction of 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.

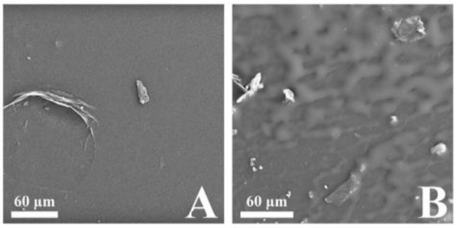

Fig. 3. Field emission gun scanning electron microscopy (FEG-SEM) images of the polypropylene backing of a pressure sensitive tape (PST), before (A) and after (B) treatment with the ED50 gel (20 minutes application).

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 cross-linking 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].

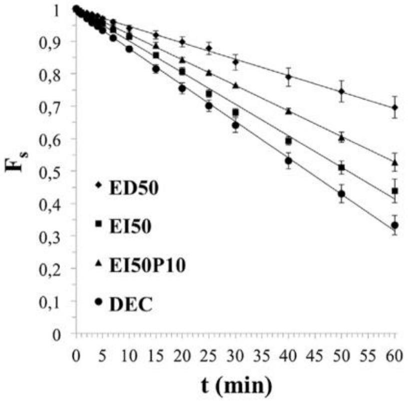

Fig. 4. Evaporation kinetics of diethyl carbonate (DEC) confined in the three gel formulations, compared to bulk solvent. F_s indicates the residual solvent fraction.

The 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. Fig. 5A 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) reached their *ESC%* value. During the process, all gels turned from a glassy polymer into a rubbery one; at the same time an increase in gels volume is observed. The diffusion

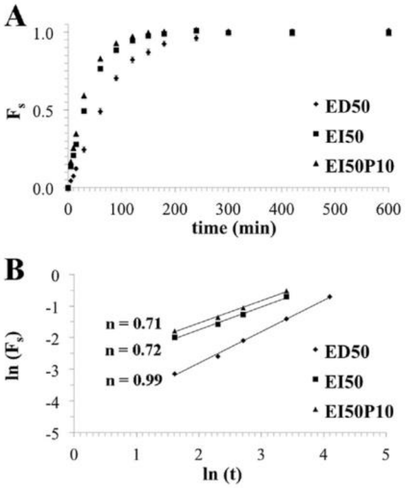

Fig. 5. A. Solvent uptake plots of F_s versus time for the three selected PEMA-DEC organogels; gel samples were completely dried previous to solvent uptake measurements. B. Log-log uptake kinetic plots for $F_s < 0.6$, and linear fitting ($R^2 > 0.99$ for all systems); for each gel formulation the obtained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

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:

$$F_S = kt^n \tag{4}$$

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_S) versus ln(t) plot (see Fig. 5B) 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 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.

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 γ_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 γ_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; γ_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 γ_c is expected to decrease as the cross-linking density increases [28]. Table 3 shows γ_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 γ_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 γ_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).

Fig. 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' » G'' over the entire range of investigated frequencies [29–32]. Moreover, the loss tangent values ($tan\partial = G''/G'$) 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

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

	G' (kPa)	$tan\delta$	γ_c (%)
ED50	37.7	0.010	20
EI50	27.2	0.006	6
EI50P10	16.7	0.003	22

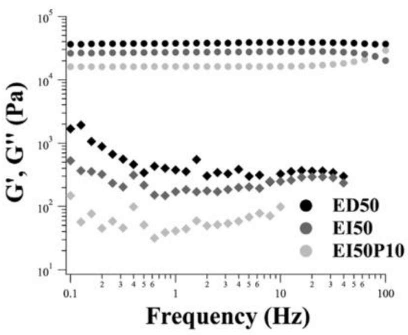

Fig. 6. Frequency dependence of G' (circles) and G'' (diamond) for the three investigated gel formulations.

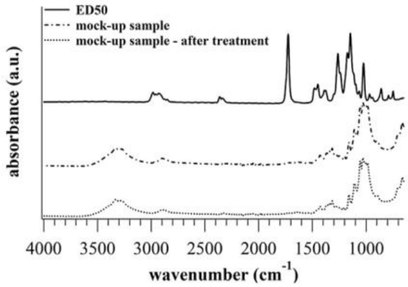

Fig. 7. ATR-FTIR spectra of a Whatman® paper sample before and after application and removal of an ED50 gel; for comparison, the spectrum of the ED50 gel is also shown.

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 ($tan\partial = 0.003$).

3.1. 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.

Fig. 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 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. 8 shows the 2D FTIR Imaging of the same Whatman® samples, were the intensity of the reflectance spectra in the 1790–1700 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 Fig. 8). Some of the spectra in both maps show higher absorptions, with similar occurrence and intensity for both samples, between 1720 and 1760 cm^{-1} (azure pixels, "high abs." spectra in Fig. 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 an 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 μm^2) concentrations of analytes over large areas (mm^2).

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 Fig. 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.

Figs. 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 Fig. 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 removal 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 Fig. 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 comprised identical polypropylene backing [35,36] but different adhesives, i.e. respectively acrylic copolymer [35,37] and natural rubber [35,36].

4. 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 that include 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 sheets of ca. 2 mm thick, with suitable properties 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

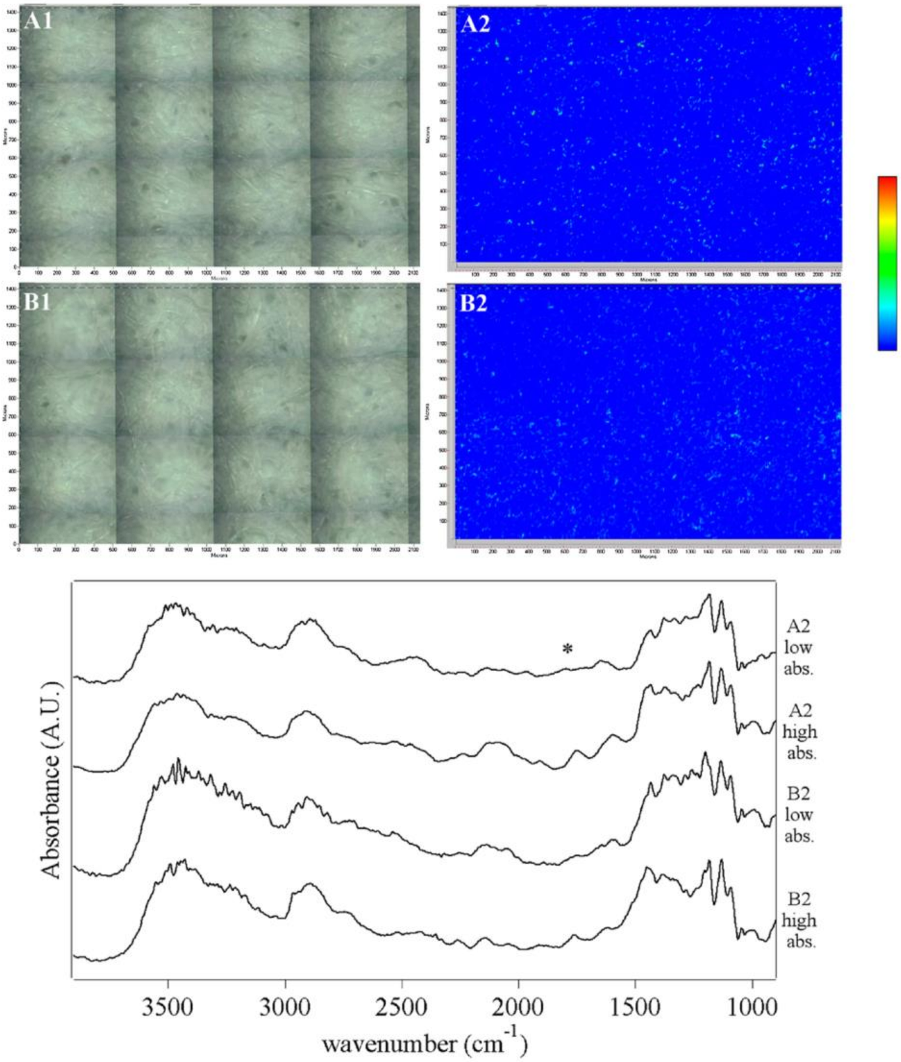

Fig. 8. FTIR 2D imaging (using an FPA detector) of a Whatman® paper sample before (A1–2) and after (B1–2) application and removal of an ED50 gel. A1 and B1 are Vis light images. A2 and B2 show the 2D Imaging maps, where the intensity of the spectra in the 1790–1700 cm^{-1} range was imaged. All maps have dimensions of 1400 × 2100 μm^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.

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 the 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$_{1000}$ (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

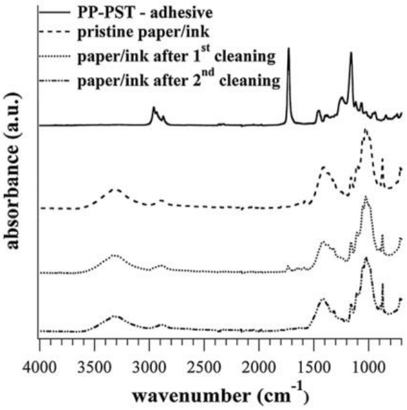

Fig. 9. ATR-FTIR spectra of (from top to bottom): the acrylic copolymer-based adhesive of the polypropylene (PP)-pressure sensitive tape (PST); the pristine paper/ink mock-up sample (printing paper/blue ball-point pen), i.e. before PST application; the paper/ink mock-up sample after the first gel application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

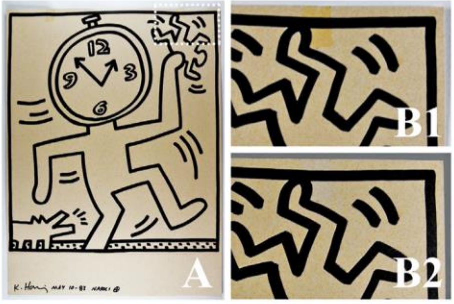

Fig. 10. (A) *Untitled*, K. Haring, 1983 – recto of the artwork, rectangle indicates the area with a greasy stain due the presence of the aged pressure sensitive tape (PST) on the verso-side of the drawing; (B1) detail of the stain before and (B2) after cleaning.

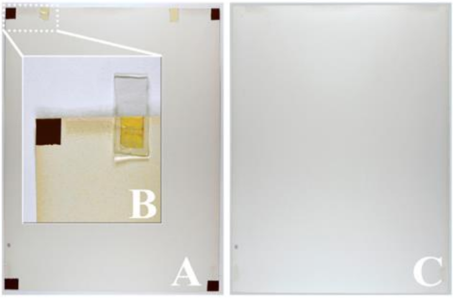

Fig. 11. A. Verso-side of the artwork by K. Haring before restoration showing the presence of the pressure sensitive tapes (PSTs). B. Detail showing the application of a PEMA-DEC organogel. C. Verso-side of the artwork after removal of the PSTs.

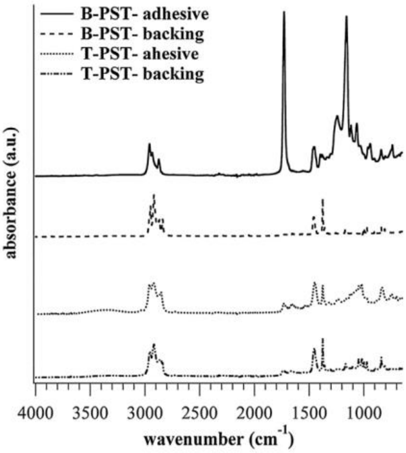

Fig. 12. ATR-FTIR spectra acquired on both the backing and the adhesive of the brown (B-PST) and transparent pressure sensitive tape (T-PST), after their removal from the Keith Haring drawing.

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 × 128 array) with spatial resolution of 5.5 μm.

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.

Acknowledgements

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SCIENZA E BENI CULTURALI.2017

AN INNOVATIVE METHOD TO REMOVE PRESSURE-SENSITIVE TAPE FROM CONTEMPORARY FELT-TIP PEN AND BALLPOINT PEN DRAWINGS ON PAPER. THE CASE STUDIES OF FEDERICO FELLINI FROM RIMINI FILM LIBRARY

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The removal of aged Pressure-Sensitive Tape (PST) is one of the most common issues during the restoration of drawings, as aged PST on paper can damage or negatively affect the artwork.

The removal of these materials, especially when applied on contemporary inks such as felt-tip pen, has to be considered carefully as it can present challenges that might not be successfully resolved using established approaches and materials. Conservators are familiar with many tape-removal methods including: mechanical action, immersion, poultices; each method however presents some associated risks, which may result in undesirable changes of the artwork (e.g.media bleeding, tidelines).

The purpose of this study is to develop a safe method to remove PSTs from works of art with felt-tip pen and ballpoint pen technique.

The study commenced with the preparation of test samples, exposed to accelerated aging treatment, choosing PSTs and techniques similar to those of the drawings by Fellini examined as case studies in this research.

Organogels based on the crosslinking of poly(methyl methacrylate) and poly(ethyl methacrylate) loaded with diethyl carbonate have been tested as a new removal system, made of gel and a non-toxic solvent. Applied directly on the PST, they led to removal of the backing and the adhesive of the PST.

The positive results obtained on test samples have been applied on Fellini's works, representing the first case of removability of PST from felt-tip pen and ballpoint pen artworks.

Key-words: Pressure-sensitive tape (PST), Tape stain removal, Felt-tip pen, Ballpoint pen, Organogel

1. Introduction

Pressure-sensitive tapes (PSTs) consist of four component layers: the backing, the adhesive mass, the release coat and the primer coat.

The development of the pressure-sensitive tape industry started around 1845 in the medical field with the production of adhesives and sticking plasters [1]. Starting from 1920, PSTs were mainly used in the auto industry; in 1925 Richard Gurley Drew invented masking tape, a PST with a paper backing and a rubber based adhesive. Gradually the natural rubber adhesive component was replaced with synthetic based mixtures, and with a new transparent backing, cellophane.

Originated in the context of the economic crisis that hit America at the end of the 20s, PSTs soon became a highly successful product.

PSTs have been erroneously used to repair tears or for mounting drawings on paper supports. Applied on paper they can damage and negatively influence the perception of the artwork: over time in fact they deteriorate differently according to the kind of backing and adhesive.

The chemical and physical damages that PSTs produce over time on paper supports are various, and can increase considerably if the PSTs are applied on paper and contemporary techniques, such as felt-tip pen and ballpoint. The physical damages include deformations and undulations, which generally occur in the case of PSTs with a backing-film; for example polyethylene, whose morphology is different from paper, under even a minimal thermo-hygrometric variation tends to move in a different way, creating tensions which can originate undulations (Fig. 1).

Chemical damages are due to the oxidation of the adhesive which, partially penetrating within the paper support, causes a visible alteration, resulting in a dark stain as can be seen for example in one of the case studies, partly above the drawing medium (Fig. 2).

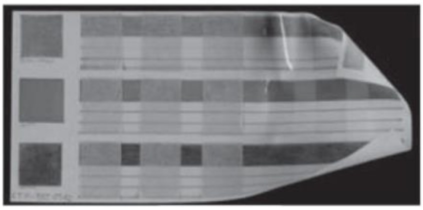

Fig.1

In the case of PSTs with an acrylic adhesive, the adhesive's solvent can interact with inks, such as those of ballpoint pens, causing alterations that can be under the form of chromatic variations and colour migration (bleeding) (Fig. 3).

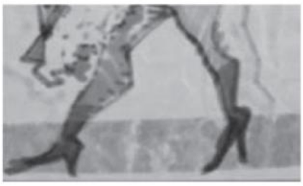

Fig.2

Fig.3

The most common removal methods of PSTs including both dry techniques (use of heat, silicone paper, spatulas and erasers) and wet cleaning, mainly using solvents [2].

Heat induced onto the PST's surface allows its detaching from the paper support, softens the adhesive and thus facilitates the removal with tweezers. This technique allows to remove the backing and part of the PST's adhesive. The simultaneous use of heating tools and tweezers does not however allow a perfect control of the artwork being treated, making the intervention difficult.

Teflon spatulas and erasers, such as the crepe rubber eraser squares, based on natural latex, are generally used for the removal of residues of active (sticky) adhesive, but the friction can often cause tears or creases especially on low weight papers. Solvents that can be used for the removal of PSTs are: water, ketones (acetone), esters (ethyl acetate), alcohols, cyclic ether (tetrahydrofuran), and aliphatic hydrocarbons (cyclohexane). Many of these products can however solubilize some contemporary artistic techniques, such as felt-tip pen and ballpoint pen. The only solvent stable towards these techniques is cyclohexane.

In this study a new removal method will be presented - "Organogels in DEC" - to remove PSTs from works of art with felt-tip pen and ballpoint pen technique.

The organogels in DEC were applied on both model and on Fellini's drawings.

2. New methods for the removal of PSTs: Organogels in Diethyl carbonate

Organogels are a chemical kind of gel, capable of loading solvents or mixtures of solvents in their polymeric network and releasing them gradually onto the surface of the artwork. Their confinement avoids an uncontrolled release of the solvent, which can cause problems such as the migration of the artistic technique; moreover, confining the solvent within the gel guarantees the decrease of the solvent's evaporation and therefore also reduces harmful risks for the operators' health.

This new method for PST removal from contemporary drawings on paper with felt-tip pens and ball-point pen has been developed and experimented, in the framework of the NANORESTART project (H2020-NMP-21-2014/646063), at the Research Centre CSGI, Florence University Chemistry Department, in close collaboration with Antonio Mirabile. It is based on the use of organogels loaded with diethyl carbonate (DEC), considered to be a "green" solvent, never used before in the field of restoration.

The synthetized organogels can be considered more or less retentive according to their graduality of releasing the solvent; the more they are retentive, more the solvent is released gradually and in less quantity.

The organogel used for the removal of PSTs are based on poly(methylmetacrylate) (PMMA) [3] and poly(ethylmethacrylate) (PEMA) [4].

Three gels, containing DEC and at different retention capacity, were synthetized: 1) PMMA E2: ESC=85%, 2) PMMA E2.5: ESC=84%, 3) PMMA E3: ESC=75%. Amongst these the third formulation (PMMA E3) is the most retentive. Two organogels made of PEMA were also tested: ED50 with ESC=82% and EEA50 (containing ethyl acetate) with ESC=73%. ED50 is more retentive than EEA50.

The Equilibrium Solvent Content (ESC) indicates the mass of solvent in the gel at equilibrium (after a prolonged immersion in the solvent) in relation to the total mass of the gel.
Organogels present good transparency optical properties and good mechanical properties due to the formation of a three-dimensional network between the polymeric chains. These properties allow an easy removal without leaving residues on the artwork’s surface. The absence of residues has been previously investigated by means of IR Spectroscopy (ATR-FTIR).

DEC: A new green solvent
Diethyl carbonate (DEC) is a green solvent; its constitutional formula is $O=C(OCH_2CH_3)_2$ [5]. The idea of ‘‘green’’ solvents expresses the goal to minimize the environmental impact resulting from the use of solvents in chemical production. [6]. DEC is part of the family of alkyl carbonates, and is a polar aprotic solvent, it is also called ethyl carbonate or carbonic acid diethyl ester [7]. It can soften natural and synthetic polymeric substances and be considered a valid green alternative to esters and ketones, which have been used for the removal of PSTs [8]. Amongst green solvents, DEC is the one that has shown the best results in terms of solubility on PST adhesives and stability towards all the artistic media used in the samples prepared for this study, reason why the organogels used for this experimentation were loaded mainly with this solvent.

2.1. Removal tests with Organogels in DEC on the samples

Choice and realization of the samples
The materials used in the realization of the samples were chosen in order to create samples similar in their paper support, artistic technique and PSTs to those of several drawings by Federico Fellini realized with felt-tip pens and ballpoint pen from the Film Library of Rimini, the case studies of an OPD diploma dissertation in which organogels were applied and experimented [9].
Thanks to the collaboration of Roberto Mannoni, a close collaborator of Federico Fellini, it was ascertained that Fellini used the following brands of felt-tip pens: Tombow AB and Swiss made Caran D’Ache.
Comparing Tombow felt-tip pens used by Fellini with those currently on the market, the first ones are called “Tombow AB”, the latter “Tombow ABT Acid free”. This leads to hypothesize a different formulation, which needs to be further understood, analysing and comparing the components of the original drawing lines with those realized with the current Tombow felt-tip pens.
Another important aspect taken into account in our research on felt-tip pen medium is the solubility of their ink, in water or in organic solvents, based on which felt tip

pens are divided into two classes: water soluble felt-tip pens and solvent soluble felt-tip pens.
For our study the following brands were chosen: Giotto Turbo color, Carioca Doodles Italy, Tombow ABT Acid free, Swiss made Caran D'Ache, Permanent Stabilo, OHPen universal. These are all water soluble, with the exception of Permanent Stabilo OHPen, soluble in organic solvents.
For the realization of the samples with ballpoint medium (the original typology was not ascertained) three different ballpoint pen brands were selected, in use between the 70s and 80s of the 20th century: Bic148, Staedtler noris stick 434 M, both with oily inks, and Pilot G-2 07 with fluid so-called "gel" inks.
The choice of PSTs fell upon the two main kinds of adhesives and backings generally applied on artworks to repair tears or for mounting systems: rubber and acrylic for the adhesives, cellulose and polypropylene for the backings. The chosen PSTs are: masking tape (paper backing and natural rubber adhesive) and ordinary tape (polypropylene backing and acrylic adhesive).
The following samples on paper (similar to office paper sheets used by Federico Fellini, produced by Cartiere Miliani Fabriano) were therefore prepared, with PSTs both on the rear and the front:

- Sample 1: Fabriano paper, Permanent Stabilo, Giotto and Carioca, masking tape (MKT) and ordinary tape (OT)
-Sample2: Fabriano paper, Tombow ABT, MKT, OT
-Sample3: Fabriano paper, Swiss made Caran D'Ache, MKT, OT
-Sample4: Fabriano paper, Bic, Staedtler noris stick 434M, PilotG-2 07, MKT, OT.

Removal tests – Application method

The PST removal tests were realized with organogels in DEC, cut to the size of the PST to remove; the gel was applied onto the PST and covered with a melinex sheet and a glass plate in order to create a confined environment and avoid the evaporation of the solvent. The gels were applied (for a maximum of 30 minutes) and subsequently removed without leaving any residues (Fig. 4). The action of the gel allows a softening-swelling of the PST and the following mechanical removal with a scalpel.

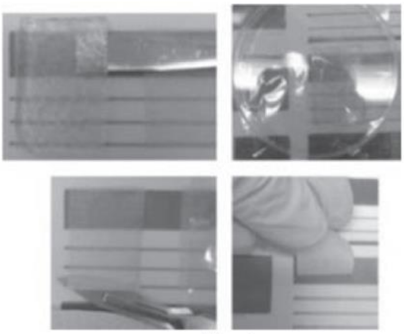

Fig. 4

2.2 Results and discussion

The removal tests on unaged samples revealed that the organogels in DEC work well in the removal of both kinds of PSTs used on the samples. On the treated samples, in the case of both masking tape and ordinary tape, it is possible to observe that there are no residues of adhesive and the paper supports and the artistic media are stable.

The organogels that gave the best results for the removal of masking tape were PMMA E3 and PEMA ED50 in DEC, and on ordinary tape PMMAE2 in DEC.

On the artificially aged samples the adoption of these new systems gave good results for the removal of ordinary tape. The best result was obtained with PMMA E3 EA 5% v/v in DEC, with the removal of the backing and of most of the adhesive.

The macroscopic observation of the aged masking tapes reveals that the backing appears rigid and tends to detach with simple mechanical action. A layer of deteriorated adhesive remains on the surface, covering the graphical strokes and it has partially penetrated into the paper matrix.

In the tests carried out, the main problem was the spreading of the deteriorated adhesive, which produced a visible stain over the artistic media. The best result in the adhesive removal was obtained with the most retentive gel, PMMA DEC E3%.

3. Case studies: the drawings by Federico Fellini of the Film Library of Rimini

The drawings by Federico Fellini subject of this study were realized on various kinds of paper, with felt-tip pens and ballpoint pen as artistic media.

Coming from different graphical collections, the drawings were acquired by the Municipal Film Library of Rimini between 1995 and 1997. A few of these drawings have been restored by the Department of Conservation and Restoration of Paper and Membrane materials of the Opificio delle Pietre Dure (OPD), Florence.

The works are: *Self portrait with the Oscar. "To Rinaldo, friend forever"*, 1993; *Anniversary: "14 May 1957 – 14 May 1987"*, 1987; *Titta and Federico in front of the remains of frescoes in the Church of Sant'Agostino, Rimini*, 1989. The drawings present damages due to the application of various kinds of PSTs, applied both on the back and front of the artworks, some above the artistic media and some only on the paper support, to fix some tears or to mount the drawings onto secondary supports.

3.1 Diagnostic Analyses on the PSTs

In order to analyse the typologies of PSTs present on the artworks, as well as photographs in visible light and observations under the stereo-microscope, useful for monitoring the conservation conditions and phases of the intervention on the PSTs, attenuated total reflection infrared spectroscopy in Fourier transform (ATR-FTIR) was used to identify the chemical nature of the PSTs (backing and adhesive).

Federico Fellini, *Self portrait with the Oscar. "To Rinaldo, friend forever"*, 1993, felt-tip pens on paper, Giuliano Geleng Collection (2^{nd})

The verso of the drawing is fixed with PSTs along its four corners to a secondary support in cardboard (fig. 5), applied after the realization of the artwork.

The macroscopic analysis of the front of the drawing reveals the presence, in correspondence of the four corners, of rectangular shaped dark brown stains (fig. 6), indicating an oxidation layer of the PSTs' adhesive, penetrated within the paper matrix. After the removal of the secondary support, it could be observed that on the rear of the drawing the PSTs' adhesive was still active (sticky) (fig. 7): this confirms the presence of double sided PSTs.

From the analyses in IR Spectroscopy (ATR-FTIR) performed on a fragment of PST (Sample GR_13461/1(1)), it was ascertained that the adhesive is compatible with a synthetic rubber Styrene-Butadiene-Styrene (SBS) segment butadiene: 1449, 964, 2916, 2844 cm-1; segment styrene: 697, 1601 cm-1 (fig. 8).

Fig. 5

Fig. 6

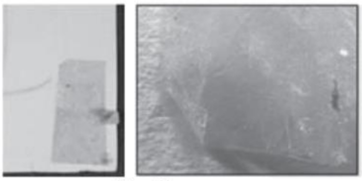

Fig. 7.

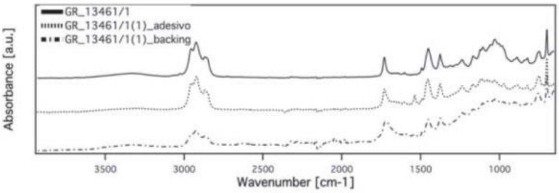

Fig. 8

Federico Fellini, *Anniversary: "14 May 1957 – 14 May 1987"*, 1987, felt-tip pens and ballpoint pen on paper, Anna Giovannini Collection

This artwork presents PSTs of the same typology, some also above the artistic media and some only on the paper support (Fig. 9). On the front three PSTs are visible: one on the upper right edge above the artistic medium, on the red number seven and on some of the light blue speech bubble strokes; another, in the central part of the same edge, covers red exclamation marks and is folded onto the back of the drawing. The third is on the left hand side of the lower edge, it covers pencil strokes and is folded onto the back; the PSTs were probably applied to repair tears visible on the artwork.

Fig. 9.

From the analyses in IR Spectroscopy performed on a fragment of PST (Sample GR_13461/6), it was ascertained that the adhesive is compatible with an acrylic adhesive (ca. 1730 cm-1, 1160 with a shoulder at 1240 cm-1) and the backing is compatible with a cellulose based compound (Fig. 10).

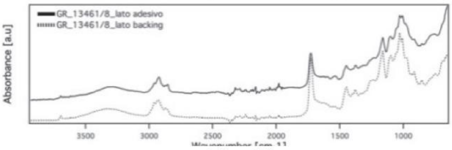

Fig. 10

Federico Fellini, *Titta and Federico in front of the remains of the frescoes of the Church of Sant'Agostino, Rimini*, ballpoint pen on paper, 1989, Benzi Collection

On the back of the drawing, above the paper support and the artistic medium are two PSTs, whose adhesive has penetrated within the paper matrix (Fig. 11).

The analyses in IR spectroscopy carried out on a fragment of PST (Sample GR_13461/9) reveal that the backing consists of polypropylene (2950, 2916, 2865, 2838 cm-1; 1450 and 1375 cm-1) whilst the adhesive is a synthetic rubber SBS (Fig. 12).

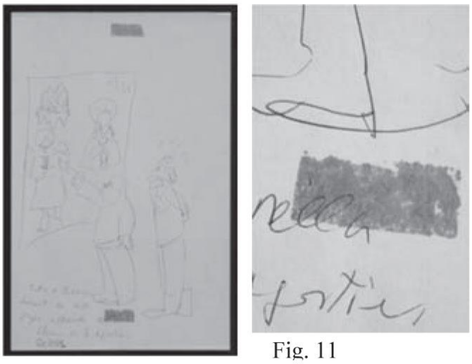

Fig. 11

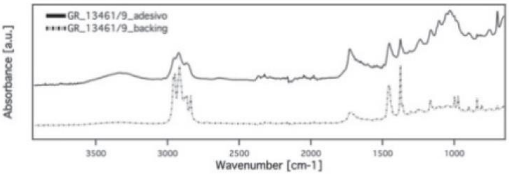

Fig. 12

3.2 Removal of the Pressure-sensitive tapes with organogels in DEC

After the positive results of the experimentation on the samples we proceeded to the PST removal from Federico Fellini's drawings.

Before this step, some preliminary operations were necessary: the detaching of the drawings from the secondary support, cleaning with dry techniques, stability tests on the paper support and solubility tests on the artistic media. The tests were realized to verify the interactions between the paper supports, the artistic media and the chosen removal methods.

The intervention of removal of the PSTs was articulated in two phases: 1) removal of the backing and of the adhesive; 2) removal of the adhesive penetrated within the paper support. During the first phase the backing and a part of the adhesive layer were removed with the organogels in DEC, the only non-toxic solvent revealed to be stable towards almost all of the artistic media analysed (Fig. 13).

For the tests on the artworks the most retentive organogels were chosen, as these had given the best results in terms of removal, stability towards the artistic media and the paper supports: PMMA E3 with ESC 75% and ED50 with ESC 82%.

These systems were used both on PSTs applied in correspondence of the artistic media and in areas where no artistic media were present. The gels were applied for a maximum of ten minutes, as established during experimental tests on the samples. The mechanical removal of the adhesive residues was done by dabbing with the solvent DEC on a cotton swab and with the aid of a Teflon spatula and tweezers.

In the second phase we removed the adhesive penetrated within the paper matrix with a low pressure table and using the pure solvents DEC and EA (Ethyl Acetate). This operation was necessary for the PSTs with a synthetic rubber SBS based adhesive, differently from acrylic adhesives which have proved to be more viscous and with less tendency to penetrate into the support.

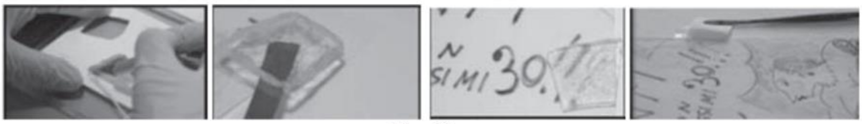

Fig. 13

3.3 Results and discussion

Federico Fellini*, Self portrait with the Oscar. "To Rinaldo, friend forever"*, 1993, felt-tip pens on paper, Giuliano Geleng Collection (2nd)

The first phase of PST removal was realized by using an organogel in DEC 100% v/v which allowed to remove the backing and a partial removal of the adhesive, slightly lightening the stain.

The second phase showed a complete asportation of the adhesive penetrated within the paper support, with a significant reduction of the stain (Fig. 14).

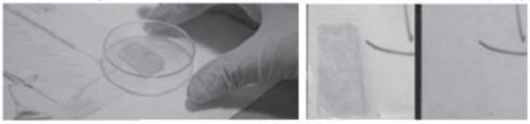

Fig. 14

Federico Fellini, *Titta and Federico in front of the remains of the frescoes of the Church of Sant'Agostino,* Rimini, black ballpoint pen on paper, 1989

This intervention was particularly delicate due to the presence of PST above the artistic media; in the first step the organogel PMMA E3 in DEC 100% v/v was used (Fig. 15), allowing to remove the backing and the surface layer of the adhesive with a slight reduction of the stain, attenuated more in a second step using a suction table and the pure solvents DEC and EA (Fig. 16)

Fig. 15

Federico Fellini, *Anniversary: "14 May 1957 – 14 May 1987"*, felt-tip pens and ballpoint pen on paper, 1987, Anna Giovannini Collection

In this case study the removal of PSTs was even more delicate due to two PSTs on the front of the drawing above the felt-tip pen medium; in this case also we used the most retentive organogel, allowing the removal of the backing and the adhesive (Fig. 17).

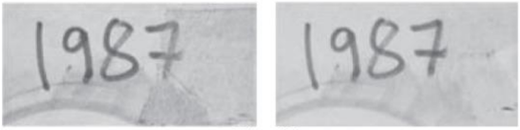

Fig. 17

Conclusions

This study presents a new approach for PST removal on contemporary artworks, in this case felt-tip pen and ballpoint pen on paper, with technical methods less invasive than those used so far, as well as effective.

The combined use of organogels and the non toxic solvent DEC proved to be a valid alterative to the traditional PST removal methods.

The results obtained on Federico Fellini's drawings have demonstrated this method's efficacy: the application of the organogels allowed the complete removal of the backing and of part of the PSTs' adhesive layer. In the case of adhesive penetrated within the paper support, the organogels in DEC contributed to the partial removal of the adhesive and the attenuation of the stains, further reduced with the use of the suction table and the solvents DEC and EA. This method proved effective also on stains above the artistic media, which resulted stable.

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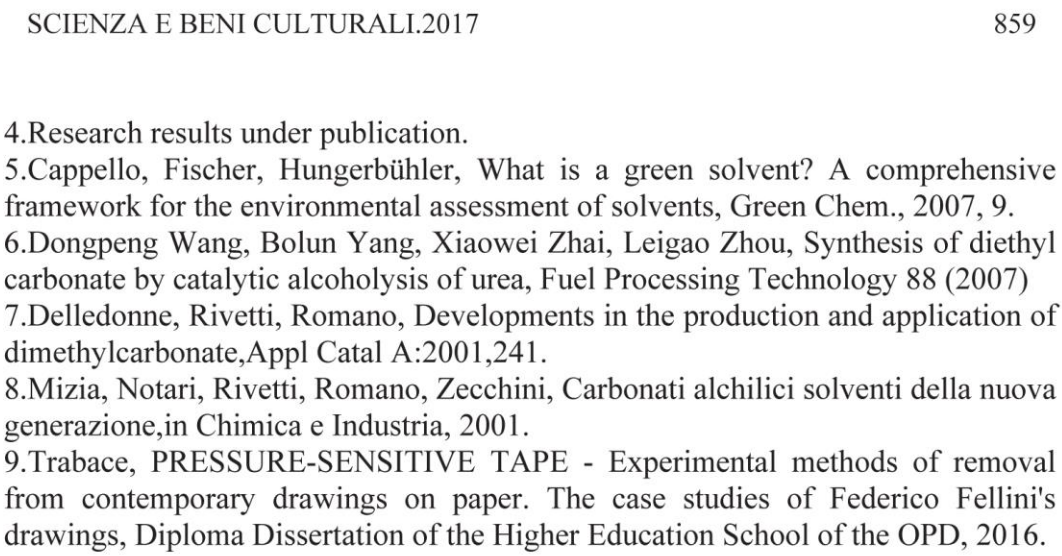

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Un metodo innovativo per la rimozione di nastri autoadesivi da disegni contemporanei su carta. I casi studio di Federico Fellini della Cineteca di Rimini

Maddalena Trabace, Antonio Mirabile, Letizia Montalbano, Rodorico Giorgi, Nicole Bonelli, Maria Diletta Pianorsi, Pamela Ferrari, Piero Baglioni

I nastri autoadesivi

I nastri autoadesivi, conosciuti in vari Paesi come *pressure-sensitive tape*, *adhesive tape*, *self-stick tape*, *sticky tape* o semplicemente come scotch, sono prodotti largamente diffusi nella vita quotidiana. Purtroppo a partire dalla loro piena introduzione negli anni sessanta del secolo scorso, sono stati utilizzati anche per risarcire strappi o incollare supporti secondari su opere grafiche, in particolar modo su quelle prodotte nel XX secolo. La novità, la praticità e soprattutto l'essere in gran parte trasparenti, hanno così creato la falsa illusione di poter restaurare la carta facilmente e in modo veloce, senza pensare al futuro degrado di questi nuovi materiali, che in breve tempo si deteriorano lasciando macchie e residui di collanti sui supporti con cui vengono a contatto. Allo stato attuale, i danni da nastri autodesivi possono essere considerati tra le maggiori cause di degrado delle opere grafiche contemporanee.

Pressure-sensitive tapes (PSTs) è la denominazione maggiormente ritrovata in ambito scientifico, e come tale è quella utilizzata nel presente studio.[1]

I PSTs si compongono generalmente di quattro strati: *backing*, adesivo, *release coat* e *primer coat* (fig. 1). Sono in particolare il *backing* e l'adesivo a provocare danni fisici e chimici sui materiali di contatto, supporti e tecniche artistiche (soprattutto quelle contemporanee, come penne a sfera e pennarelli di cui si parla nel presente studio).

Tra i danni fisici si riscontrano spesso deformazioni e ondulazioni, che si verificano generalmente in presenza di PSTs costituiti da film di *backing* (per esempio il polietilene) morfologicamente differenti dalla carta e sensibili alle variazioni termoigrometriche, tanto da creare facilmente tensioni e contrazioni in grado di deteriorare il supporto (fig. 2). I danni chimici sono dovuti invece all'ossidazione dell'adesivo che, penetrando parzialmente all'interno del supporto cartaceo, provoca macchie di color giallo-bruno, particolarmente difficili da rimuovere (fig. 3).

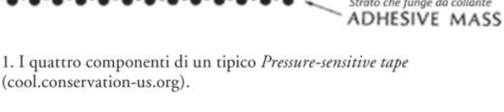
Inoltre i PSTs costituiti da adesivi acrilici contengono un solvente che può interagire con gli inchiostri, provocando alterazioni evidenti come variazioni cromatiche, sbiadimenti e perdita di definizione, in particolare sui tratti delle penne a sfera.

Nell'ambito del restauro della carta, la rimozione dei PSTs e dei residui di adesivo si effettua sia con metodologie a secco (calore, carta siliconata, spatole e gomme) sia con solventi.[2]

Il calore in particolare, indotto direttamente sulla superficie del PST, agevola il distacco del nastro dal supporto cartaceo, ammorbidisce l'adesivo e ne facilita la rimozione meccanica; nonostante ciò questo metodo non permette comunque un perfetto controllo dell'opera su cui si lavora, rendendo difficoltoso l'intervento.

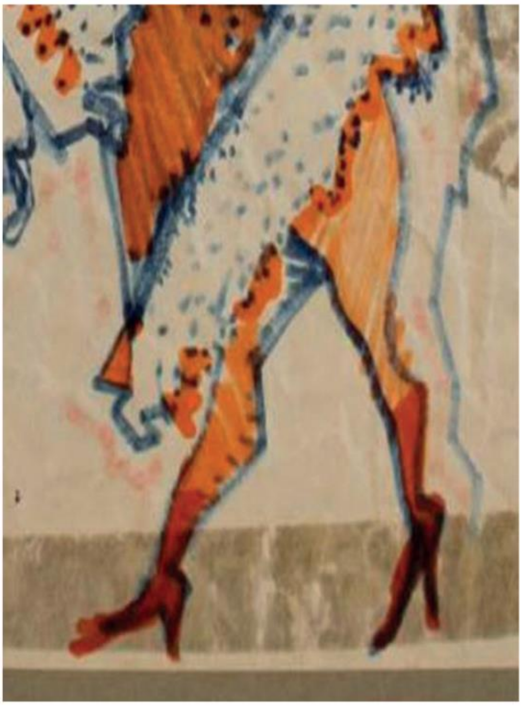
Per la rimozione dei residui di adesivo ancora attivo (appiccicoso) sono solitamente utilizzate spatole e gomme, ma in molti casi la frizione può causare strappi soprattutto su carte a bassa grammatura.

I solventi più in uso per la rimozione dei PSTs sono: l'acqua, gli idrocarburi alifatici (cicloesano), i chetoni (acetone), gli esteri (etilacetato), gli alcoli e gli eteri ciclici (tetraidrofurano). La maggior parte di queste sostanze però sono tossiche, tendono a solubilizzare i media grafici, soprattutto i pennarelli e gli inchiostri; ecco dunque che la ricerca si sta indirizzando verso prodotti alternativi, i cosiddetti solventi *green*, più sicuri sia per i materiali che per gli operatori.



1. I quattro componenti di un tipico *Pressure-sensitive tape* (cool.conservation-us.org).

2. Le ondulazioni prodotte dalla contrazione del *backing* di polietilene su uno dei campioni eseguiti in laboratorio.



3. Federico Fellini, *Il Casanova. Un personaggio di profilo*, disegno a pennarelli su carta bianca, Rimini, Cineteca. Particolare con macchia giallo-bruna prodotta dall'adesivo in corrispondenza dei tratti grafici.

Un nuovo metodo di rimozione dei PSTs: gli *organogels* in DEC

Gli *organogels* sono gel di tipo chimico, in grado di caricare nel network polimerico solventi o miscele di solventi e di rilasciarle in maniera graduale sulla superficie dell'opera d'arte. Il confinamento evita un rilascio incontrollato del solvente, che potrebbe causare problematiche come la migrazione dei media; inoltre, garantisce la riduzione dell'evaporazione del solvente e quindi una diminuzione dei rischi per la salute degli operatori.

Questo nuovo metodo per la rimozione dei PSTs da disegni contemporanei su carta eseguiti a pennarelli e penne a sfera è stato formulato e sperimentato nell'ambito del progetto NANORESTART (H2020-NMP-21-2014/646063), dal Consorzio CSGI dell'Università di Firenze, ed è basato sull'uso di *organogels* caricati con Dietilcarbonato (DEC), considerato un solvente *green*.

Gli *organogels* sintetizzati possono essere considerati più o meno ritentivi in base alla gradualità di rilascio del solvente; più sono ritentivi e più il solvente viene rilasciato in maniera graduale e in minor quantità.

Le tipologie di gel utilizzate per la rimozione dei PSTs sono due: *organogel* di polimetilmetacrilato (PMMA) e *organogel* di polietilmetacrilato (PEMA).[3]

Per la prima tipologia sono stati sintetizzati in DEC tre gel con tre livelli di ritenzione:

1) PMMA E2: ESC% = 85%, 2) PMMA E2.5: ESC% = 84%, 3) PMMA E3: ESC% = 75%. Tra questi la terza formulazione (PMMA E3) è la più ritentiva.

Per la seconda tipologia è stato sintetizzato in DEC l'ED50; ESC% = 82% mentre l'EEA50 con EA; ESC% = 73%. Tra i due il primo (ED50) è il più ritentivo.

L'*Equilibrium Solvent Content* (ESC) indica la massa di solvente nel gel all'equilibrio (dopo immersione prolungata nel solvente) rispetto alla massa totale del gel.

Gli *organogels* presentano buone proprietà ottiche di trasparenza e buone proprietà meccaniche dovute alla formazione di un reticolo tridimensionale tra le catene polimeriche. Tali proprietà permettono una semplice rimozione senza rilascio di residui sulla superficie dell'opera d'arte.

DEC: A new green solvent

Il Dietilcarbonato (DEC) ($C_5H_{10}O_3$) fa parte della famiglia dei carbonati alchilici,[4] è un solvente polare aprotico di natura esterea. È in grado di ammorbidire sostanze polimeriche di origine naturale e sintetica, può essere considerato una valida alternativa agli esteri e ai chetoni, da sempre utilizzati per la rimozione dei PSTs.

Il DEC è tra i solventi *green* che hanno dato i migliori risultati di solubilità dell'adesivo dei PSTs e di stabilità di tutte le tecniche artistiche adoperate per i campioni, per questo motivo gli *organogels* utilizzati sono stati caricati principalmente con questo solvente.

Prove di rimozione sui campioni - *Organogel* in DEC

Scelta e realizzazione dei campioni

Per mettere a punto un metodo valido e testare gli *organogels*, con l'obiettivo di utilizzarli su una serie di disegni di Federico Fellini, provenienti dalla Cineteca Comunale di Rimini, particolarmente degradati da PSTs di vario tipo e che rappresentano i casi studio di una tesi di laurea della Scuola di Alta Formazione e di Studio dell'OPD, è stato necessario realizzare dei campioni simili per supporto cartaceo, *medium* grafico e tipologia di PSTs.[5]

La ricerca si è incentrata, per prima cosa, sul reperimento di informazioni sul modo di lavorare di Fellini e sui prodotti usati. Fondamentale è stato il contatto con Roberto Mannoni, direttore di produzione del regista dal 1967, che ha fornito informazioni in particolare sulla marca di pennarelli usati, ossia brand del tipo Tombow AB e Swiss made Caran D'Ache.[6]

Mettendo a confronto i pennarelli Tombow utilizzati da Fellini con quelli in commercio attualmente, risulta che i primi sono denominati Tombow AB e i secondi Tombow ABT Acid free. Questo fa ipotizzare una differente formulazione, che andrebbe indagata mettendo a confronto i materiali originali con quelli attualmente in commercio.

Un altro aspetto fondamentale considerato per la scelta dei pennarelli è la solubilità dell'inchiostro, in acqua o in solventi organici, che divide i pennarelli in due classi: *water soluble felt-tip pen* e *solvent soluble felt-tip pen.*

Sulla base di questa analisi sono stati scelti i seguenti brand: Giotto Turbo color, Carioca Doodles Italy, Tombow ABT Acid free, Swiss made Caran D'Ache, Permanent Stabilo, OHPen universal. Sono tutti solubili in acqua tranne i Permanent Stabilo OHPen, solubili in solventi organici.

Per la realizzazione dei campioni con penne a sfera sono stati selezionati tre differenti brand di penne a sfera: BIC 148, Staedtler noris stick 434 M, costituite da inchiostri oleosi, e Pilot G-2 07 costituita da inchiostri fluidi detti 'gel'.

I PSTs sono stati selezionati in relazione a quelli maggiormente riscontrati sulle opere d'arte per risarcire strappi o per sistemi di montaggio: gomme e acrilici per gli adesivi, cellulosa e polipropilene per i *backing.* I PSTs scelti sono: *masking tape* (*backing* di carta e adesivo a base di gomma naturale) e *ordinary tape* (*backing* in polipropilene e adesivo acrilico).

Prove di rimozione - Metodologia di applicazione

Le prove di rimozione dei PSTs sono state eseguite con gli *organogels* in DEC, ritagliati a misura dei PSTs e applicati sul PST da rimuovere, coperti con Melinex e piastra di vetro per creare un ambiente confinato ed evitare l'evaporazione del solvente. Sono stati applicati (tempo massimo di 30 minuti) e successivamente rimossi senza rilasciare residui. L'azione del gel comporta l'ammorbidimento del PST e ne permette la rimozione meccanica (fig. 4).

Risultati

Dalle prove di rimozione effettuate su campioni non invecchiati emerge che gli *organogels* in DEC, riescono a rimuovere tutte le tipologie di PSTs applicate sui campioni: non si evidenziano residui di adesivo, i supporti cartacei e i media grafici rimangono stabili. Nei PSTs con *masking tape* invecchiati invece, il *backing* risulta rigido e tende a staccarsi con una semplice azione meccanica. Ciò che rimane sulla superficie è lo strato di adesivo degradato che ricopre la tecnica artistica e che in parte risulta penetrato nella matrice cartacea.

Dalle prove effettuate, la problematica maggiore risulta lo spandimento dell'adesivo degradato che tende a creare gore. Il risultato migliore in questo caso si ottiene con il gel più ritentivo, il PMMA E3 in DEC 100% v/v (fig. 5).

I casi studio: i disegni di Federico Fellini della Cineteca di Rimini

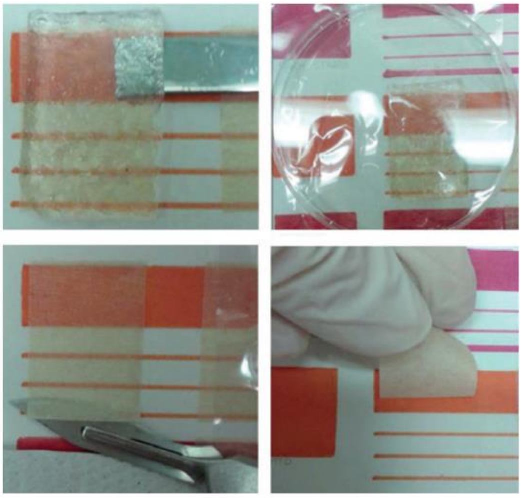
I disegni di Federico Fellini, oggetto dello studio, sono realizzati su differenti tipologie di carta, con le tecniche del pennarello e della penna a sfera. Qui di seguito una breve descrizione dello stato di conservazione e dei trattamenti effettuati.

Federico Fellini, *Autoritratto con Oscar. "A Rinaldo, l'amico di sempre"*, 1993, 302x215 mm, pennarelli su carta. Rimini, Cineteca Fondo Giuliano Geleng (2°)

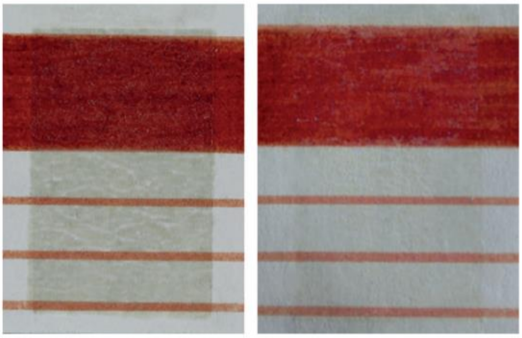
Il *verso* del disegno risulta adeso ai quattro angoli con segmenti di PSTs a un supporto secondario in cartone, applicato posteriormente alla realizzazione dell'opera (fig. 6).

Sul *recto* si notano, in corrispondenza dei quattro angoli, macchie rettangolari marrone scuro, che indicano uno stato di ossidazione dell'adesivo dei PSTs, penetrato all'interno della carta. Dopo il distacco meccanico del disegno dal supporto secondario, si rileva sul *verso* l'adesivo del PST ancora attivo e appiccicoso e questo conferma l'uso dei *Double Sided PSTs.*[7]

Dalle analisi in spettroscopia IR (ATR-FT-IR) condotte su un frammento di PST (Camp. G.R._13461/1(1)), si è riscontrato che l'adesivo risulta compatibile con una gomma sintetica Stirene-Butadiene-Stirene (SBS) segmento butadiene: 1449, 964, 2916, 2844 cm-1; segmento stirene: 697, 1601 cm-1 (fig. 7).



4. Applicazione degli *organogels* su campioni in laboratorio.



5. Applicazione degli *organogels* su campioni in laboratorio.

Federico Fellini, *Anniversario: "14 maggio 1957-14 maggio 1987,* 1987, 220x280 mm, pennarelli, penna a sfera blu e matita su carta. Rimini, Cineteca, Fondo Anna Giovannini

L'opera presenta dei PSTs della stessa tipologia, alcuni in corrispondenza della tecnica artistica e altri sul solo supporto cartaceo (fig. 8). Sul recto sono visibili tre PSTs: uno sul margine destro superiore in corrispondenza della tecnica artistica, il numero sette rosso e parte dei tratti di sfumatura celeste della vignetta; l'altro, posto nella zona centrale dello stesso margine, ricopre i punti esclamativi rossi della scritta e si ripiega sul *verso* del disegno. Il terzo è posto sul margine inferiore a sinistra, ricopre segni di matita e si ripiega sul *verso.*

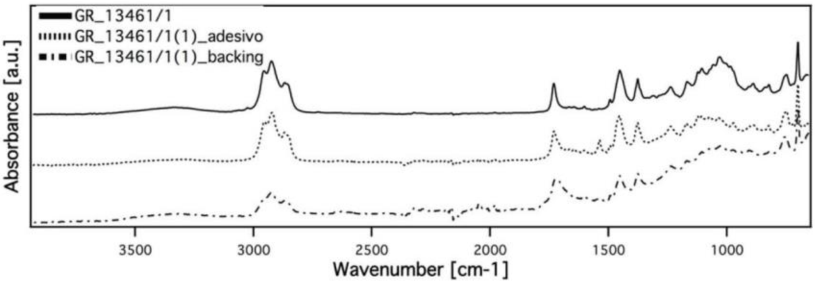
Dalle analisi in spettroscopia IR condotte su un frammento di PST (Camp. G.R._13461/6) si è riscontrato che l'adesivo è compatibile con un adesivo di natura acrilica (ca. 1730 cm-1, 1160 con spalla a 1240 cm-1) e il *backing* con un composto di natura cellulosica (fig. 9).

Federico Fellini, *Titta e Federico davanti ai resti degli affreschi nella chiesa di S. Agostino di Rimini*, 399x215 mm, penna a sfera nera su carta bianca. Rimini, Cineteca, Fondo Luigi Benzi

Sul *verso* del disegno, in corrispondenza del supporto cartaceo e della tecnica artistica, sono presenti due PSTs, il cui adesivo risulta penetrato nella matrice cartacea (fig. 10).

Le analisi in spettroscopia IR condotte su un frammento di PST (Camp. G.R._13461/9) rivelano che il *backing* è costituito da polipropilene (2950, 2916, 2865, 2838 cm-1; 1450 e 1375 cm-1) mentre l'adesivo è una gomma sintetica SBS (fig. 11).

6. Federico Fellini, *Autoritratto con Oscar. "A Rinaldo, l'amico di sempre"*, disegno a pennarelli su carta bianca, Rimini, Cineteca.



7. Spettro in ATR-FT-IR di un frammento di PST prelevato dal *verso* del disegno di Federico Fellini, *Autoritratto con Oscar. "A Rinaldo, l'amico di sempre"*.

Intervento di rimozione dei PSTs tramite organogels *in DEC*

In seguito ai risultati positivi della sperimentazione sui campioni si è proceduto alla rimozione dei PSTs dalle opere d'arte di Federico Fellini.

Prima di procedere alla rimozione dei PSTs, si sono rese necessarie alcune operazioni preliminari all'intervento: distacco dell'opera dal supporto secondario, pulitura a secco, test di stabilità del supporto cartaceo e test di solubilità delle tecniche artistiche (fig. 12).

I test sono stati eseguiti per verificare le interazioni tra supporti cartacei, tecniche artistiche e metodi di rimozione scelti.

L'intervento di rimozione dei PSTs si è articolato in due fasi: 1) rimozione del *backing*; 2) rimozione dell'adesivo penetrato nel supporto cartaceo.

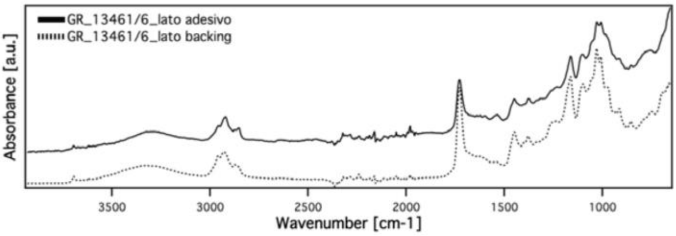
La prima fase ha previsto la rimozione del *backing* con gli *organogels* in DEC (fig. 13).

Sono stati selezionati i due *organogels* più ritentivi che hanno dato i risultati migliori in termini di rimozione, stabilità delle tecniche artistiche e dei supporti cartacei: PMMA E3 e l'ED50.

Il primo, leggermente più ritentivo, è stato utilizzato nei casi in cui i PSTs erano posti in corrispondenza della tecnica artistica, in modo da avere un rilascio di solvente più controllato e graduale; il secondo invece, meno ritentivo, nei casi di PSTs posti in corrispondenza del solo supporto cartaceo. Entrambi sono stati applicati per un tempo massimo di 10 minuti, come stabilito durante le prove sperimentali sui campioni. La rimozione meccanica dei residui superficiali di adesivo è avvenuta mediante tampone di cotone idrofilo imbibito di solvente DEC con l'ausilio di una stecca di teflon.

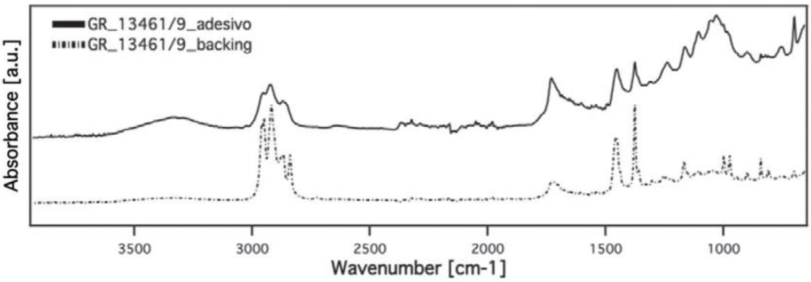
La seconda fase ha previsto la rimozione dell'adesivo penetrato all'interno della matrice cartacea con il tavolo a bassa pressione e l'utilizzo dei solventi DEC ed etilacetato (EA) puri.

8. Federico Fellini, *Anniversario 14 maggio 1957-14 maggio 1987*, disegno a pennarelli, penna a sfera blu e matita su carta bianca, Rimini, Cineteca.

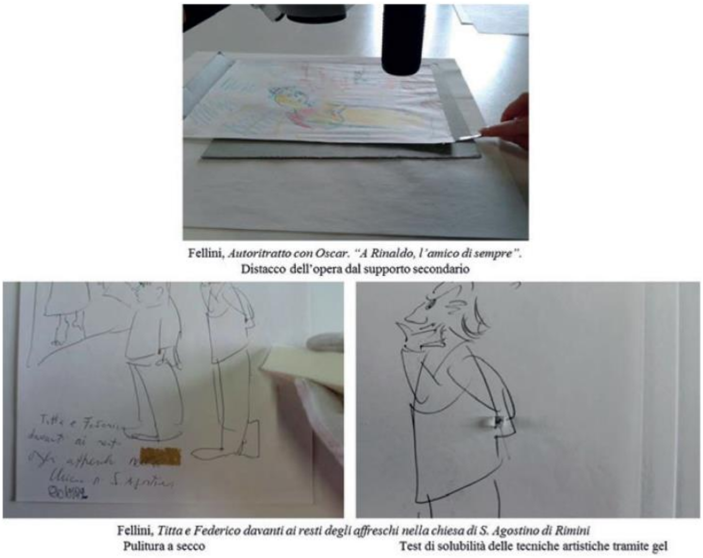


9. Spettro in ATR-FT-IR di un frammento di PST prelevato dal *verso* del disegno di Federico Fellini, *Anniversario 14 maggio 1957-14 maggio 1987*.

10. Federico Fellini, *Titta e Federico davanti ai resti degli affreschi nella chiesa di S. Agostino di Rimini*, disegno a penna a sfera nera su carta bianca Rimini, Cineteca.



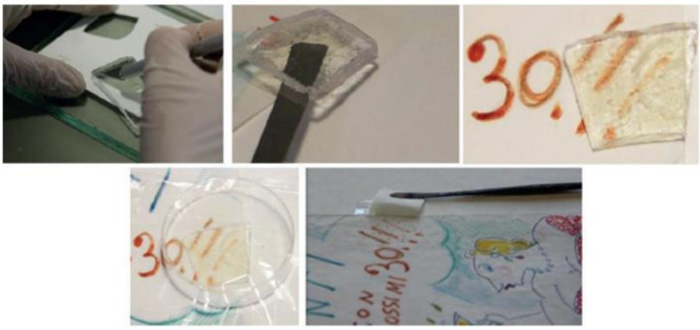
11. Spettro in ATR-FT-IR di un frammento di PST prelevato dal verso del disegno di Federico Fellini, *Titta e Federico davanti ai resti degli affreschi nella chiesa di S. Agostino di Rimini*.



Fellini, *Autoritratto con Oscar. "A Rinaldo, l'amico di sempre"*.
Distacco dell'opera dal supporto secondario

Fellini, *Titta e Federico davanti ai resti degli affreschi nella chiesa di S. Agostino di Rimini*
Pulitura a secco
Test di solubilità delle tecniche artistiche tramite gel

12. Distacco, pulitura, test.



13. Federico Fellini, *Anniversario: "14 maggio 1957-14 maggio 1987"*. Applicazione del PMMA E3 in DEC e rimozione del PST.

La rimozione dell'adesivo penetrato nel supporto cartaceo si è resa necessaria per i PSTs costituiti da adesivo a base di gomma sintetica SBS, a differenza degli adesivi acrilici dimostratisi più viscosi e meno tendenti a penetrare nel supporto cartaceo.

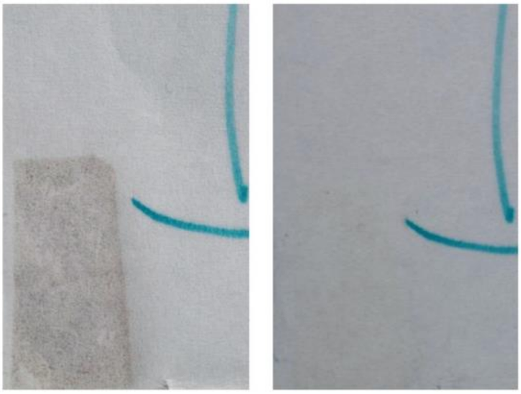
Federico Fellini, *Autoritratto con Oscar. "A Rinaldo, l'amico di sempre"*, 1993, 302x215 mm, pennarelli su carta bianca. Rimini, Cineteca, Fondo Giuliano Geleng (2°)
La prima fase di rimozione dei PSTs ha previsto l'utilizzo dell'*organogel* ED50 che ha comportato la rimozione del *backing* e una parziale rimozione dell'adesivo con un'attenuazione della macchia. La seconda fase ha mostrato una completa asportazione dell'adesivo penetrato nel supporto cartaceo con una notevole attenuazione della macchia (fig. 14).

Federico Fellini, *Anniversario: "14 maggio 1957-14 maggio 1987,* 1987, 220x280 mm, pennarelli, penna a sfera blu e matita su carta bianca. Rimini, Cineteca, Fondo Anna Giovannini
In questo caso studio, l'intervento di rimozione dei PST è risultato più delicato per la presenza di due PSTs sul *recto* del disegno in corrispondenza del tratto a pennarello, e quindi anche in questo caso si è utilizzato l'*organogel* più ritentivo, ottenendo l'asportazione del *backing* e dell'adesivo (fig. 15).

Federico Fellini, *Titta e Federico davanti ai resti degli affreschi nella chiesa di S. Agostino di Rimini*, 399x215 mm, penna a sfera nera su carta bianca. Rimini, Cineteca, Fondo Luigi Benzi
L'intervento è stato particolarmente delicato per il fatto che il PST è sopra i tratti grafici; per questo, si è intervenuti prima con l'*organogel* PMMA E3 in DEC e poi, una volta rimosso il *backing* e attenuata la macchia, si è completata la pulitura su tavolo aspirante con i solventi DEC ed EA puri (fig. 16).

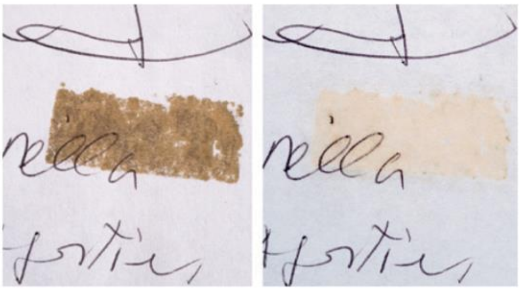
Conclusioni

Questo studio nasce dall'esigenza di trovare nuovi metodi per il trattamento di opere grafiche contemporanee, deteriorate da nastri autoadesivi di varia tipologia. La rimozione dei PSTs è uno degli interventi necessari nel restauro ma servono tecniche



14. Federico Fellini, *Autoritratto con Oscar. "A Rinaldo, l'amico di sempre"*. Particolare prima e dopo la rimozione del PST.

15. Federico Fellini, *Anniversario: "14 maggio 1957-14 maggio 1987"*. Particolare del tratto rosso della data 1987 prima e dopo la rimozione del PST.



16. Federico Fellini, *Titta e Federico davanti ai resti degli affreschi nella chiesa di S. Agostino di Rimini*. Particolare della scritta a penna a sfera prima e dopo la rimozione del PST.

meno invasive e nello stesso tempo, ugualmente efficaci, di quelle finora in uso.
L'utilizzo combinato degli organogels e del solvente atossico DEC rappresenta una via alternativa ai metodi tradizionali non solo di rimozione dei PSTs ma anche di attenuazione delle macchie da essi prodotte sulla carta.
I risultati ottenuti sui disegni di Federico Fellini, dimostrando l'efficacia di questo metodo in particolare su tecniche delicate e instabili come i pennarelli e gli inchiostri delle penne a sfera, incoraggiano a continuare la ricerca su altre tipologie di opere grafiche contemporanee.

Note
1) Il termine può essere tradotto con nastro sensibile alla pressione.
2) M.A. Smith, N.M.M. II Jones, S.L. Page, M. Peck Dirda, *Pressure-Sensitive Tape and Techniques for its Removal from Paper*, 'Journal of the American Institute for Conservation', 23, 1984.
3) P. Baglioni, N. Bonelli, D. Chelazzi, A. Chevalier, L. Dei, J. Domingues, E. Fratini, R. Giorgi, M. Martin, *Organogel Formulation for the Cleaning of Easel Paintings*, 'Applied Physics', 2015.
4) C. Cappello, U. Fischer, K. Hungerbühler, *What is a Green Solvent? A Comprehensive Framework for the Environmental Assessment of Solvents*, 'Green Chem.', 2007.
5) M. Trabace, *I nastri autoadesivi. Metodi sperimentali di rimozione da disegni contemporanei. I casi studio di Federico Fellini della Cineteca di Rimini*, diploma di laurea magistrale, Scuola di Alta Formazione, Opificio delle Pietre Dure, 2016. Si ringrazia per la collaborazione il dott. Nicola Bassano della Cineteca Comunale di Rimini per aver permesso questa ricerca sui disegni di Federico Fellini. Il restauro è stato eseguito nel Laboratorio di restauro dei Materiali Cartacei e Membranacei dell'OPD, diretto da Cecilia Frosinini (Direttore del settore) e Letizia Montalbano (Direttore tecnico del settore). Documentazione fotografica: Giuseppe Zicarelli; indagini scientifiche: Isetta Tosini. La sperimentazione è stata effettuata al CSGI, Dipartimento di Chimica, Università degli Studi di Firenze, diretto dal prof. Piero Baglioni, con il prof. Rodorico Giorgi, le dott.sse Nicole Bonelli, Maria Diletta Pianorsi, e Pamela Ferrari, in collaborazione con il restauratore Antonio Mirabile.
6) Roberto Mannoni è stato Direttore di produzione dei film di Fellini dal 1967. Alla morte del maestro, Giulietta Masina gli ha donato molti materiali dello studio.
7) Si tratta di nastri biadesivi.
8) M. Trabace, A. Mirabile, L. Montalbano, R. Giorgi, P. Ferrari, *An Innovative Method to Remove Pressure Sensitive Tape from Contemporary Felt-Tip Pen and Ball-Point Pen Drawings on Paper. The Case Studies of Federico Fellini from Rimini Film Library*, convegno internazionale (Bressanone, 27-30 giugno 2017).

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