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Original Citation:

Microemulsions, Micelles and Functional Gels. How Colloid and Soft Matter Preserve Works of Art / David Chelazzi, Rodorico Giorgi, Piero Baglioni. - In: ANGEWANDTE CHEMIE. INTERNATIONAL EDITION. - ISSN 1433-7851. - STAMPA. - (2018), pp. 1-7. [10.1002/ange.201710711]

Availability:

This version is available at: 2158/1114245 since: 2022-07-15T13:29:30Z

Published version:

DOI: 10.1002/ange.201710711

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Microemulsions, Micelles and Functional Gels. How Colloid and Soft Matter Preserve Works of Art

David Chelazzi^[b], Rodorico Giorgi^[b], Piero Baglioni^{*[a]}

Abstract: Colloid Science provides fundamental knowledge to fields such as pharmaceutical, detergency, paint and food industry. An exciting application is art conservation, which poses a challenge owing to the complex range of interfacial interactions involved in restoring artefacts. Currently, the majority of the most performing and environmentally safe cleaning and consolidation agents for artworks belong to soft matter and colloids. We report here on the development and application of increasingly complex systems, from microemulsions to semi-interpenetrating hydrogels containing such fluids. These systems have been used on diverse artefacts, from Renaissance frescos to works by Picasso and Pollock. Chemical design can be implemented to meet the requirements of curators, and knowledge of the colloids structure and dynamics can overcome serendipitous approaches of traditional conservation practice. Finally, we summarize future perspectives that soft matter and colloid science can disclose in the field of cultural heritage preservation.

1. The limits of classical approaches to cleaning artefacts

The conservation of mankind cultural heritage is a fundamental task, both from economic and societal perspectives. In the framework of artefacts' restoration, one of the main interventions carried out by conservators is the removal of unwanted layers from the surface of historical and artistic objects (easel paintings, murals, stone, paper, parchment, etc.) to recover readability and to prevent the degradation of the original substrates. Typically, layers to be removed include dirt, grease, and various natural or synthetic products used in the past and present conservation practice, e.g. siccativ oils (linseed oil), wax, triterpenoid resins, hydrocarbon or ketone resins, polyacrylates or acrylate-vinyl acetate copolymers (applied either in solution or dispersed in water using surfactants). All these products can undergo degradation, for instance through competitive cross-linking and scission of polymer chains (leading to change in molecular weight, solubility, and mechanical properties), or through photo-oxidation and successive thermal reactions (dehydration, condensation) that form extended conjugated structures producing yellowing.^[1-3] In several cases these layers develop detrimental compounds (e.g. acidic volatile organic compounds -

VOCs),^[4] or alter the physico-chemical properties of the artefacts. For instance, acrylate resins on the surface of murals modify the substrate's porosity and hinder permeability to water vapour, favouring the growth at the resin-mural interface of salts crystals, eventually resulting in strong mechanic stress in the pores and the disruption of the painting surface.^[5]

In the traditional conservation practice, the removal of unwanted layers is based on their solubilization either in pure solvents or solvent blends. Solubility is commonly predicted using parameters calculated according to different models. Hansen and Teas modified the Hildebrand solubility parameter (δ), defined as the square root of the cohesive energy density of a solvent, calculated from the enthalpy of vaporization and the molar volume of the liquid.^[6] Fractional parameters (f_d , f_p , f_h) derived by Teas are defined in such a way that $f_d + f_p + f_h = 100$. By plotting the fractional parameters in a triangular graph, it is possible to univocally identify each solvent by a point. Solvents that are close in a Teas chart have usually similar solvating properties, e.g. similar hydrophobicity or hydrophilicity, and solvent blends of known composition can also be placed on the graph. For complex materials, such as natural or synthetic resins, it is possible to define solubility areas by connecting all the points corresponding to the solvents in which such materials are soluble (see Figure 1).

This classic approach is still followed by conservators to solubilize grime and unwanted substances on the surface of works of art. However, there are important limitations to the use of solvents. Most artefacts have complex chemical composition, and the solubility of original components can be similar to that of unwanted layers. Therefore, the use of solvents can be risky and non-selective, leading to undesired swelling or solubilization of original materials. Moreover, most artistic substrates have pores in the micron size, thus whenever dirt or coatings are dissolved, they are quickly transported through the porous artefact's matrix, hindering effective removal. Finally, most solvents have toxicity issues.

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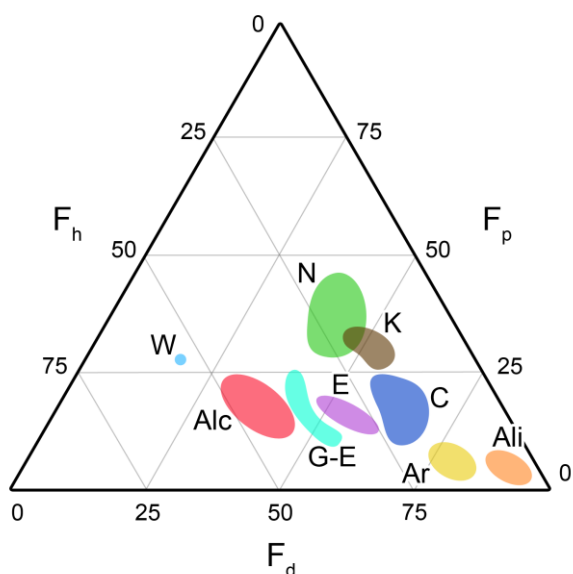


Figure 1. Teas solubility diagram indicating the solubility parameters of common families of solvents having similar properties. (W: water; N: nitrogen solvents; K: ketones; Alc: alcohols; G-E: glycol ethers and esters; E: esters; C: chlorine solvents; Ar: aromatics; Ali: aliphatics). Reproduced with permission from Ref 12, copyright 2013 The Royal Society of Chemistry.

Wolbers improved on the use of free solvents by including them in polymer dispersions, the so-called “solvent gels”.^[7] Namely, polyacrylic acid (PAA) was used to increase the viscosity of solvents. Tertiary amine ethoxylate surfactants (Ethomeen® C12 or C25), based on primary cocoamines, are used to deprotonate PAA, forming amine carboxylate salts. Having different hydrophilic-lipophilic balance (HLB) values, C12 and C25 can be used to thicken a wide range of liquids, from alcohols and ketones to aliphatic and aromatic hydrocarbons. The increased viscosity limits uncontrolled diffusion of the solvents through porous matrices, besides the surfactants contribute to the detergency process. These polymer dispersions proved effective and versatile, and are still considered a standard tool in the cleaning of works of art. However, a significant drawback relies in the need of a clearance step to remove both PAA and surfactant residues from the surface. This requires the use of free solvents, re-introducing the risk of solubilization, and swelling of original components.^[8] A recent update by Wolbers involves the use of modified silicone thickeners based on cyclopentasiloxane and dimethicone crosspolymers, such as Velvesil® Plus.^[9] These dispersions are less risky on water-sensitive surfaces such as acrylic paints (which are commonly unvarnished but can be polluted with surface dirt and dust), where the use of free aqueous fluids can lead to extraction of additives or surfactants originally included in the paint layer, causing the swelling or cracking of the surface. However, the necessity of a clearance step to remove polymer residues poses limitations to the use of these systems. The clearing solvents are the same cyclomethicones uploaded in the viscous dispersion.

While the health risks of silicone solvents are being partly assessed,^[10] the currently used solvent (decamethylcyclopentasiloxane, D5) has a fairly high boiling point (210 °C) that increases its permanence in the artefact's layers.

The use of solvents and thickeners has shown limitations that highlighted the need of advanced materials for the cleaning of works of art. In particular, three main aspects must be addressed: i) different mechanisms than classic solubilization need to be explored for the removal of dirt and coatings; ii) systems for the confinement of solvents must have ideal mechanic properties (so as to allow their easy removal from surfaces) and retentiveness of the fluids (to avoid uncontrolled interaction with the artefacts); iii) cleaning systems must employ “green” chemicals, and be safe both to the environment and operators.

These requirements can be met by systems borrowed from colloid and soft matter science, and specifically designed to selectively remove unwanted layers, as will be illustrated in the following sections.

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Rodorigo Giorgi got a BS in Chemistry and PhD in Science for Cultural Heritage Conservation at the University of Florence, where he is currently Associate Professor. Giorgi is also a member of CSGI. His research addresses the application of nanoscience to the conservation of cultural heritage, e.g. cleaning and consolidation of painted surfaces and stone, conservation of contemporary art materials, deacidification of manuscripts and archaeological wood. Giorgi is author of 110 publications in the field of nanoscience for cultural heritage conservation.



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2. Microemulsions and micelles

A significant improvement was represented by the development of nanostructured cleaning fluids, namely microemulsions and micelles, as opposed to classic solvent blends. A paper by De Gennes and Taupin in 1982 set a milestone, defining important parameters for the formation of thermodynamically stable oil-in-water (o/w) or water-in-oil (w/o) swollen micelles of nanometric size, or of bicontinuous phases.^[11]

The first microemulsion used in conservation was formulated in 1986 for the removal of wax contaminants from the surface of 15th century frescoes, during the restoration of the Brancacci Chapel in Santa Maria del Carmine Church (Florence).^[12] The wax had deposited throughout centuries owing to votive candles being blown in proximity of the murals, and the use of solvents was discouraged by the risk of simply moving the wax deeper into the wall. The microemulsion was constituted by ammonium dodecyl sulfate as surfactant, dodecane (ca. 10% w/w), and water (ca. 87%). These water-based systems were applied as loaded in hydrophilic sorbent matrices (cellulose poultices). The wax was removed from the wall substrate by the microemulsion and then absorbed in the sorbent. The use of aqueous microemulsions significantly reduced the impact on both the operator and the environment, as opposed to solvent blends.

The reported effectiveness of nanostructured fluids prompted studies both on their structure and reactivity when they are applied for the cleaning of artefacts. A relevant study provided fundamental information on two o/w systems, selected based on the following rationale:^[13] 1) One fluid, named XYL, contained a solvent insoluble in water (*p*-xylene), while the second, named EAPC, was a multi-component fluid containing two solvents partially soluble in water, i.e. ethyl acetate (EA) and propylene carbonate (PC); both fluids used SDS (sodium dodecyl sulfate) and 1-PeOH (1-Pentanol). 2) Both fluids, developed and assessed throughout the 2000-2012 decade, had proven effective in numerous case studies for the removal of synthetic polymers from artefacts, even though the EAPC fluid had shown effectiveness to a wider range of polymers. XYL and EAPC have different nano structure and behaviour as shown by Small-Angle Neutron Scattering (SANS) with contrast variation. XYL can be described as a classical o/w microemulsion, where xylene is confined exclusively within core-shell spherical micelles (i.e. the

partition coefficient of XYL, P_{XYL} , is 1, and $P_{\text{PeOH}} = 0.9$). In EAPC the solvents are partitioned between the continuous phase and the dispersed droplets ($P_{\text{EA}} = 0.7$; $P_{\text{PC}} = 0.3$; $P_{\text{PeOH}} = 0.9$). EAPC has faster removal kinetics than XYL towards the same acrylate copolymer (Paraloid® B72, ethyl methacrylate/methyl acrylate^[14]) and can be considered as one of the most performing systems, as it could remove a multi-layered coating of degraded polymers from the surface of wall paintings in the Annunciation Basilica in Nazareth, Israel (see Figure 2), where both traditional solvents and the XYL system had proven ineffective.



Figure 2. Application of the EAPC o/w nanostructured fluid on wall paintings from the Annunciation Basilica in Nazareth (Israel). Top: Before restoration. The alteration of the surface by aged coatings is evident. Bottom: After restoration. In the dashed box, an area is highlighted where the polymer coating has been left untreated as a reference for the evaluation of the cleaning result. Reproduced with permission from Ref 13. Copyright 2012 American Chemical Society.

Insights in the removal mechanisms have been provided along with structural studies, distinguishing between two different cases: 1) interaction of o/w fluids with low molecular weight compounds (fatty acids and triglycerides found in grime); 2) interaction with polymers, e.g. poly acrylate and vinyl acetate found in synthetic coatings.^[14,15]

The removal of wax from the Brancacci Chapel frescoes, falls in the first case, and occurred via a classical detergency mechanism, where the hydrophobic material (wax) is solubilized within the swollen micelles.^[12,15]

The removal mechanism for polymer coatings occurs through different mechanisms. Qualitative experiments carried out on films of Paraloid® B72 showed that the o/w nanostructured fluids do not dissolve the polymer; instead they cause swelling and

1 detachment of the film from the substrate (glass, mica). These
 2 observations were combined with analysis of both the fluids and
 3 the polymer film through Differential Thermogravimetry (DTG),
 4 Small-Angle X-ray Scattering (SAXS), Quasi-Elastic Light
 5 Scattering (QELS), SANS, and Atomic Force Microscopy
 6 (AFM).^[14,15]

7 It was shown that EAPC interacts with the polymer through a
 8 multi-step mechanism: 1) the swollen micelles act as reservoirs
 9 that exchange solvents with the polymer film; 2) the polymer
 10 selectively extracts an optimal solvent composition from the
 11 micelles; 3) the coating swells because of solvent diffusion into
 12 the polymer network (probably following case II diffusion^[16]) and
 13 detaches from the substrate, while the micelles get smaller and
 14 re-organize their structure after solvent exchange. The co-
 15 surfactant (1-PeOH) has a double role in XYL, as it builds the
 16 droplets and enhances the polymer removal.^[14,15]

17 Recent improvements involved the use of non-ionic surfactants,
 18 since their phase diagram is scarcely affected by salts present
 19 on murals also as degradation products or pollutants. Ethoxylated
 20 alcohols can be used to formulate cleaning fluids with water and
 21 2-butanone (methyl ethyl ketone, MEK), where MEK is present in
 22 the aqueous phase (24% solubility at 20°C).^[softmatter2014] These
 23 fluids proved more effective than correspondent formulations where
 24 SDS was used instead of the non-ionic surfactants. In particular,
 25 the effectiveness can be enhanced by working close to the cloud
 26 point of the system, which is tunable depending on the type of
 27 ethoxylated alcohol.

28 The removal of the coating might take place through dewetting,
 29 where the polymer on the surface rearranges into separated
 30 domains, and then detaches from the substrate. In fact, scarce
 31 attention has been so far dedicated to the role of surfactants in
 32 the process, which is central when it comes to thick (several
 33 microns) synthetic coatings. Quartz microbalance (QCM) and
 34 Confocal laser-scanning microscopy (CLSM) provided
 35 fundamental insight on the dewetting process by imaging the
 36 polymer at the interface with the substrate, following the
 37 application of different types of cleaning fluids.^[17,18] The
 38 removal of poly ethyl methacrylate/methyl acrylate (Paraloid®
 39 B72) was carried out using a ternary o/w system, ethoxylated
 40 alcohol surfactant, PC and water mixture, with PC being located
 41 mainly in the continuous aqueous phase.

42 According to thermodynamics a polymer should dewet from the
 43 glass surface when exposed to temperatures above its glass
 44 transition (T_g), simply with water or water/surfactant
 45 mixtures. In fact, raising the temperature above T_g increases
 46 the mobility of the chains, overcoming the activation energy for
 47 this process, which also depends on the polymer thickness. On
 48 the other hand, the ternary system (which is a non-solvent for
 49 the polymer) allows dewetting thick (e.g. 5 μm) films even at
 50 room temperature. Dewetting leads to the formation of new
 51 interfacial regions between the polymer and the non-solvent
 52 (disfavoured), and between the substrate and the aqueous phase
 53 (favoured). The detachment areas evolve following a nucleation
 54 and growth pathway, and coalesce until a critic value is
 55 reached, after which the polymer film is disrupted and
 56 detaches from the substrate as swollen droplets (see Figure 3).
 57 Future research should address substrates with high porosity
 58 and roughness, which are more

representative of real artistic surfaces. Furthermore, particularly
 relevant for the cleaning of contemporary art is the case of
 polymer films cast from emulsions rather than from solutions. In
 this case, the complex composition of the film (including
 additives such as fillers, plasticizers, stabilizers, etc.) is
 expected to consistently affect the removal mechanism.

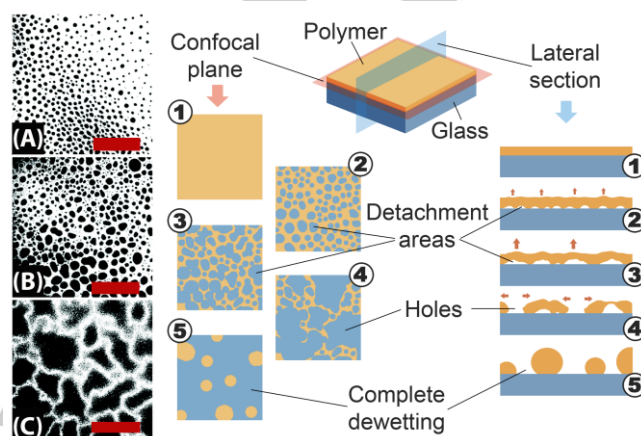


Figure 3. (Left) CLSM images of polymer–glass detachment regions corresponding to 5 mm thick Paraloid® B72 film after 300 s incubation with: (A) H₂O/PC, (B) H₂O/ethoxylated alcohol/PC (0.5% surfactant w/w), (C) H₂O/ethoxylated alcohol/PC (5% surfactant w/w); scale bars correspond to 50 mm length. (Right) The cartoon describes the dewetting process observed in CLSM experiments. On the left the confocal plane view is shown, while on the right, a view of the lateral section of the system is schematized. The drawing is not in scale, i.e., the thickness of the polymer film was enhanced for the sake of clarity. The dewetting process can be divided into the following steps: (1) the flat homogeneous polymer film is exposed to the liquid system; (2) at the glass/polymer interface, the film starts losing adhesion to the glass in small areas having a round shape; (3) the area of these detachment regions increases, and they tend to coalesce decreasing the contact points between the polymer and the glass; (4) when the detachment areas reach a critical size, the film breaks and actual holes are created, which tend to expand, minimizing the contact between polymer and glass; (5) finally, the polymer reorganizes in the form of globular droplets distributed over the glass surface. Polymer droplets have a diameter that is significantly higher than the thickness of the original polymer film. Reproduced from Ref. 18 with permission from the PCCP Owner Societies.

3. Gels

Substrates like canvas, paper, leather, parchment, or some painted layers encountered in the restoration practice, are sensitive to water that can cause swelling or leaching of original materials. This has prompted adequate confining systems to control the delivery of the aqueous complex fluids.

In the last decade, several classes of gels have been developed to avoid the limitations of traditional solvent thickeners. The most performing gels used in the cleaning of cultural heritage are chemical gels. For these systems the cohesive forces overcome the adhesion forces to the substrate (the artefact), favouring the easy removal of the gel from the surface, without leaving residues, after the cleaning intervention. Networks formed by a single type of crosslinked polymer and semi-interpenetrating

polymer networks (semi-IPNs) have been explored in order to obtain gels with optimal mechanical properties and retentiveness. Acrylamide was one selected monomer owing to its good water-loading properties, and the gel synthesis is a tunable process that can give a range of systems to adapt different case studies. The cobweb-like network of these gels has an interconnected porosity, with pore size distributions tunable from 1 to 100 μm .^[19] The meso/nano-porosity (measured via SAXS) can also be controlled varying the crosslinker/monomer ratio and the water amount in the synthetic route. Both the network's mesh size (actual distance between two consecutive cross-linking points) and the size of inhomogeneities (solid-like polymer domains) can be varied in the 6-10 nm and 12-18 nm range respectively. This reflects in different mechanical properties and water loading/release capacity of the gels. Two types of acrylamide gels were formulated and tested on canvas, where it was necessary to swell and remove aged and degraded acrylate-vinyl acetate adhesives (used as repairs or lining of paintings). The two gels had different equilibrium water content (EWC) and free water index (FWI, which indicates the amount of water confined in the gel that behaves as a bulk liquid). Lower values of EWC and FWI are indicative of more retentive networks, which is advantageous when treating water-sensitive substrates like canvas. The most retentive formulation, loaded with EAPC, allowed softening and swelling the adhesive, which can be removed without damaging the canvas fibres.^[19]

For cleaning purposes it is fundamental that the structure of the micelles is not significantly altered by confinement in the gels, which was confirmed by SAXS analysis.^[13,17,20]

Advanced semi-IPNs gels showed outperforming properties for highly sensitive substrates such as dyed paper and paintings with low amounts of binders (e.g. Tang-ka paintings, see Figure 4). These gels are made by embedding a linear or branched polymer into the network of another polymer with different properties, without chemical crosslinks between the two. In particular, a semi-IPN of poly(2-hydroxyethyl methacrylate), p(HEMA) and poly(vinylpyrrolidone), PVP, showed higher retentiveness than acrylamide gels, maintaining optimal mechanical properties and biocompatibility, allowing cleaning efficacy not achievable with conventional methods.^[21,22]

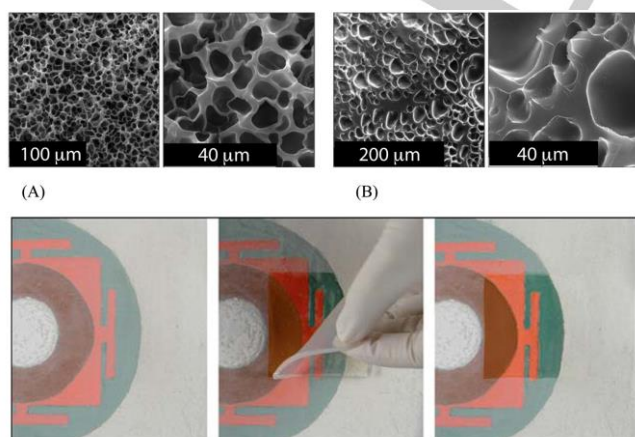


Figure 4. (Top) SEM images of p(HEMA)/PVP semi-IPN hydrogels. (A) Gel with higher HEMA and lower water content; (B) Gel with lower HEMA and higher water content. (Bottom) Removal of surface dirt from a highly water-sensitive, weakly cohered painted layer, using a hydrogel loaded with water. Reproduced with permission from Ref. 21, copyright 2013 American Chemical Society.

From a rheological point of view, Semi-IPNs behave as solid-like systems with infinite relaxation time. Similarly to sponges, they are able to absorb various fluids and solvents without dramatic changes in their characteristics, and can be easily handled and removed from the artefacts' surface as opposed to traditional thickeners. Recently, poly(vinyl alcohol) (PVA)-based gels with ideal characteristics for cleaning artefacts were obtained via freeze-thaw gelation of PVA solutions.^[23] The gelation process can be tuned varying the PVA concentration and the number of freezing cycles. Macroporous structures can be obtained, with high EWC (90-96) and FWI (0.96-0.98) values, and a solid-like behaviour, meaning that at most of the operational conditions they behave as chemical gels.

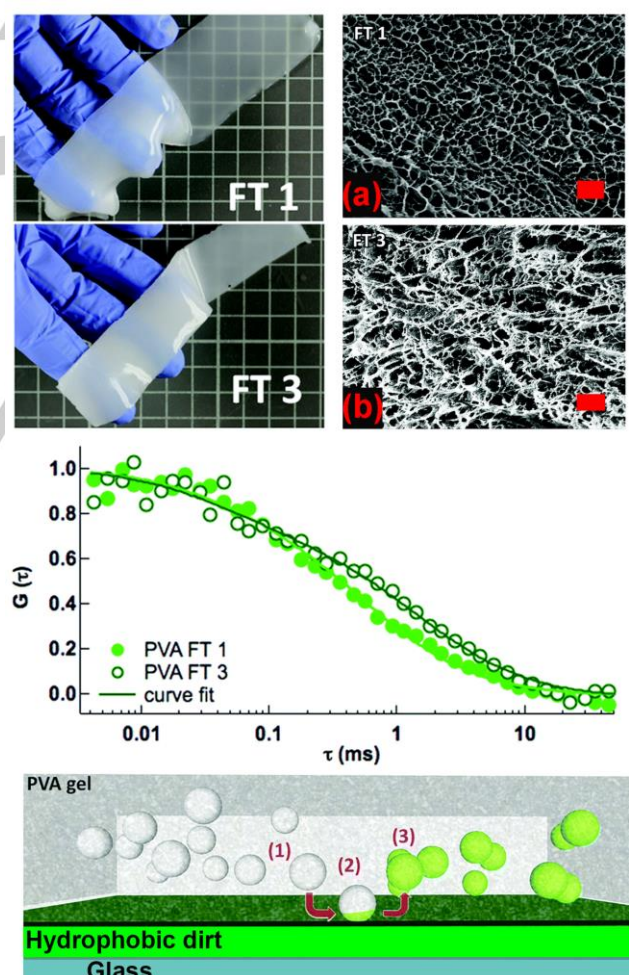


Figure 5. PVA-based gels, obtained with one (FT 1) or three (FT 3) freeze-thaw cycles. The SEM images show the macroporous structure (bar is 1 micron). The centre panel shows the representative FCS curves acquired

inside PVA FT1 (filled circles) and PVA FT3 (empty circles) gels loaded with unlabelled microemulsion after ten minutes interaction with a coumarin-labelled sebum soil-covered coverglass; curve fitting according to a two-component diffusion model (continuous lines). The bottom panel shows a scheme representing the interaction of the microemulsion-loaded PVA gels with the labelled hydrophobic dirt: the unlabelled droplets (1) interact with the labelled dirt (2) and encapsulate the low-molecular weight labelled dirt (3). Reproduced with permission from Ref. 23, copyright 2017 The Royal Society of Chemistry.

PVA-based networks show optimal adhesion to surfaces with roughness in the millimetre and sub-millimetre scale, frequently found in modern/contemporary art, as for instance works from Jackson Pollock.

PVA-based gels loaded with a toluene-in-water microemulsion were studied for the first time via Fluorescence Correlation Spectroscopy (FCS). The confined microemulsion droplets maintain their hydrodynamic behaviour, freely diffusing in the PVA network. FCS permits labelling different phases of the system, i.e. the gel, micelles, surfactants and soil. This allows monitoring the removal process and its kinetics. Upon soil solubilisation, FCS shows an increase of the droplets' size, and the soil-loaded droplets diffuse back into the gel, promoting the one-step removal of the layer (see Figure 5) without leaving gel residues as verified by 2D FTIR imaging. The presence of gel residues can be excluded on the treated areas down to a detection limit $<1 \text{ pg per } 30 \mu\text{m}^2$.

The aforementioned PVA-based gels, developed within the EU NANORESTART project,^[24] have been recently used to remove surface dirt and aged coatings from the surface of paintings by Jackson Pollock and Pablo Picasso.^[25] In these case studies, the gels were used as loaded with either water or nanostructured o/w fluids, and their mechanical and retention properties allowed the selective removal of unwanted layers, without damaging the original components of the masterpieces. While practical guidelines have been written on the use of the most consolidated soft matter and colloid systems developed so far for the cleaning of artefacts,^[26] open challenges remain to be addressed by future research work.

4. Perspectives and challenges

Because the composition and reactivity of works of art vary greatly, there is room for continuous improvements in developing gels and nanostructured fluids.

Firstly, there is the need to formulate microemulsions using environmentally friendly and low-toxicity solvents and surfactants. Surfactants should also decompose into volatile or inert compounds. Recently, a diethyl carbonate (DEC)-in-water fluid was formulated for cleaning murals, using N,N-Dimethyldodecan-1-amine oxide, DDAO as surfactant.^[27] Amine-oxides are benign and biodegradable, and alkyl carbonates are generally non-toxic and low-impact solvents, which opens to future applications.

Possible improvements also concern water-in-oil (w/o) microemulsions, which might prove beneficial on highly water-sensitive substrates, e.g. modern paint layers rich in water-

soluble additives. While some w/o systems have already been formulated for cleaning artefacts,^[28] future implementation should involve minimizing the amount of surfactants used.

Organogels (i.e. able to confine medium- or low-polarity fluids) are complementary to hydrogels, whenever working with solvents is still preferred to aqueous fluids. In this case, the use of "green" chemicals is a fundamental requirement. Recently, gels based on the crosslinking of methyl methacrylate (MMA) were loaded with ethyl acetate, butyl acetate or ketones, and used for the cleaning of canvas paintings and inked paper.^[29,30]

Another appealing application is the confinement of enzyme solutions in hydrogels. Enzymes can remove animal (protein-based) or vegetal (starch) glues, biofilms, and patinas, however it is fundamental to control their action on artefacts.

Regardless the physical state of the cleaning system (fluid, gel), a relevant task in current and future research is the development of systems able to respond to external stimuli that trigger their reactivity. Few years ago, positively charged cobaltferrite (CoFe_2O_4) nanoparticles were embedded in an acrylamide network.^[31] The resulting magnetic gel (see Figure 6) can be loaded with o/w microemulsions, and can be moved (and removed) applying a magnetic field, with virtually no mechanical stress on the surface.

Other responsive systems include self-healing or self-cleaning materials. Currently, hybrid coatings (e.g. combining organic polymers and inorganic nanoparticles) are being explored to provide works of art with improved resistance to soiling, pollution and degradation.^[32]

Implementing these perspectives in the framework of colloid and materials science, will enable the conservation of contemporary artefacts that exhibit highly complex composition and are affected by fast degradation processes, an issue still unsolved by traditional restoration methodologies.

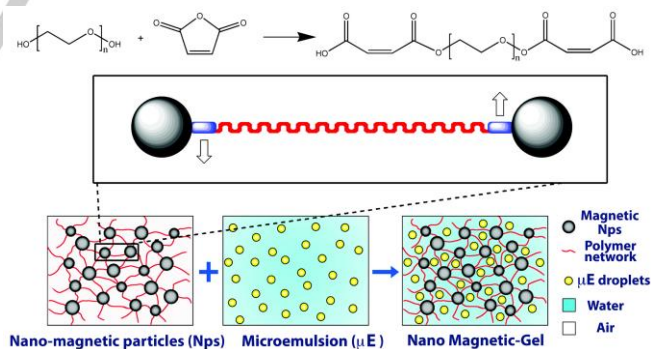


Figure 6. Example of functionalized responsive gel. The reaction scheme shows the esterification of PEG with maleic anhydride (MA), to form a MA-PEG polymer. The centre colour image shows the binding of cobaltferrite nanoparticles (black spheres) to the MA-PEG polymer (blue rectangles = MA residues; red lines: PEG chain). The colour bottom images show the network formed by the polymer with acrylamide chains, and the loading of an o/w microemulsion into the nanomagnetic sponge structure. Reproduced with permission from Ref. 31, copyright 2013 American Chemical Society.

Acknowledgements

1 CSGI and the European Union (NANORESTART project,
2 Horizon 2020 research and innovation programme under grant
3 agreement No 646063) are gratefully acknowledged for financial
4 support.

5
6 **Keywords:** art conservation • cleaning • colloids • detergency •
7 dewetting • functional gels • micelles • microemulsions • soft
8 matter
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- 10 [1] M. Favaro, R. Mendichi, F. Ossola, U. Russo, S. Simon, P. Tomasin,
11 P.A. Vigato, *Polym. Degrad. Stabil.* **2006**, *91*, 3083-3096.
- 12 [2] O. Chiantore, M. Lazzari, *Polymer* **2001**, *42*, 17-27.
- 13 [3] P. Dietemann, C. Higgit, M. Kälin, M.J. Edelmann, R. Knochenmuss, R.
14 Zenobi, *J. Cult. Herit.* **2009**, *10*, 30-40.
- 15 [4] D. Chelazzi, A. Chevalier, G. Pizzorusso, R. giorgi, M. Menu, P.
16 Baglioni, *Polym. Degrad. Stabil.* **2014**, *107*, 314-320.
- 17 [5] E. Carretti, D. Chelazzi, G. Rocchigiani, P. Baglioni, G. Poggi, L. Dei,
18 *Langmuir* **2013**, *29*, 9881-9890.
- 19 [6] H. Mollet, A. Grubermann. *Formulation Technology: Emulsions,*
20 *Suspensions, Solid Forms*, Wiley-VCH, Weinheim, **2008**.
- 21 [7] R.C. Wolbers in *Workshop on New Methods in the Cleaning of*
22 *Paintings and other Decorative Surfaces*, 1988 Marina del Rey, CA.
23 Canadian Conservation Institute, Ottawa, Canada, **1990**, p. 188.
- 24 [8] A. Casoli, Z. Di Diego, C. Isca, *Environ. Sci. Pollut. Res.* **2014**, *21*,
25 13252-13263.
- 26 [9] L. Angelova, R. Gridley, A. Hughes, L. Mina, K. Rayner, E. Schmitt, S.
27 Skelton, M. Sullivan, J. Walthew in *Gels, Thickeners, and Viscosity*
28 *Modifiers*. AIC Wiki, American Institute for Conservation of Art and
29 Historic Works, **2017**, [http://www.conservation-](http://www.conservation-wiki.com/wiki/Gels#Introduction:_Gels.2C_Thickeners_.26_Viscosity_Modifiers)
30 [wiki.com/wiki/Gels#Introduction: Gels.2C. Thickeners .26 Viscosity M](http://www.conservation-wiki.com/wiki/Gels#Introduction:_Gels.2C_Thickeners_.26_Viscosity_Modifiers)
31 [odifiers](http://www.conservation-wiki.com/wiki/Gels#Introduction:_Gels.2C_Thickeners_.26_Viscosity_Modifiers). Accessed 10 July 2017.
- 32 [10] W. Dekant, J.E. Klaunig, *Regul. Toxicol. Pharmacol.* **2016**, *74*, S67-S76.
- 33 [11] P.G. De Gennes, C. Taupin, *J. Phys. Chem.* **1982**, *86*, 2294-2304.
- 34 [12] R. Giorgi, E. Carretti in *Nanoscience for the Conservation of Works of*
35 *Art* (Eds.: P. Baglioni and D. Chelazzi), The Royal Society of Chemistry,
36 **2013**, p. 231.
- 37 [13] M. Baglioni, D. Berti, J. Teixeira, R. Giorgi, P. Baglioni, *Langmuir* **2012**,
38 *28*, 15193-15202.
- 39 [14] M. Baglioni, R. Giorgi, D. Berti, P. Baglioni, *Nanoscale* **2012**, *4*, 42-53.
- 40 [15] M. Baglioni, D. Rengstl, D. Berti, M. Bonini, R. Giorgi, P. Baglioni,
41 *Nanoscale* **2010**, *2*, 1723-1732.
- 42 [16] D.F. Stamatialis, M. Sanapoulou, J.H. Petropoulos, *Macromolecules*
43 **2002**, *35*, 1021-1027.
- 44 [21] M. Raudino, N. Giambianco, C. Montis, D. Berti, G. Marletta, P.
45 Baglioni, *Langmuir* **2017**, *33*, 5675-5684.
- 46 [18] M. Baglioni, C. Montis, F. Brandi, T. Guaragnone, I. Meazzini, P.
47 Baglioni, D. Berti, *Phys. Chem. Chem. Phys.* **2017**, DOI:
48 10.1039/c7cp02608k.
- 49 [19] G. Pizzorusso, E. Fratini, J. Eiblmeier, R. Giorgi, D. Chelazzi, A.
50 Chevalier, P. Baglioni, *Langmuir* **2012**, *28*, 3952-3961.
- 51 [20] E. Carretti, E. Fratini, D. Berti, L. Dei, P. Baglioni, *Angew. Chem. Int. Ed.*
52 **2009**, *48*, 8966-8969.
- 53 [21] J. Domingues, N. Bonelli, R. Giorgi, E. Fratini, F. Gorel, P. Baglioni,
54 *Langmuir* **2013**, *29*, 2746-2755.
- 55 [22] J. Domingues, N. Bonelli, R. Giorgi, P. Baglioni, *Appl. Phys. A* **2014**,
56 *114*, 705-710.
- 57 [23] R. Mastrangelo, C. Montis, N. Bonelli, P. Tempesti, P. Baglioni, *Phys.*
58 *Chem. Chem. Phys.* **2017**, DOI: 10.1039/C7CP02662E.
- 59 [24] www.nanorestart.eu; Accessed on October 16, 2017.
- 60 [25] <http://www.guggenheim-venice.it/inglese/conservation/pollock-project.html>
61 [http://www.nanorestart.eu/index.php?option=com_content&view=article](http://www.nanorestart.eu/index.php?option=com_content&view=article&id=397:studio-news&catid=110&Itemid=832)
62 [&id=397:studio-news&catid=110&Itemid=832](http://www.nanorestart.eu/index.php?option=com_content&view=article&id=397:studio-news&catid=110&Itemid=832); Accessed on August 1,
63 2017.
- 64 [26] P. Baglioni, D. Chelazzi, R. Giorgi, *Nanotechnologies in the*
65 *Conservation of Cultural Heritage*, Springer Dordrecht Heidelberg, New
York London, **2015**.
- [27] M. Baglioni, Y. Jaidar Benavides, D. Berti, R. Giorgi, U. Keiderling, P.
Baglioni, *J. Colloid Interface Sci.* **2015**, *440*, 204-210.
- [28] B. Ormsby, M. Keefe, A. Phenix, E. von Aderkas, T. Learner, C. Tucker,
C. Kozak, *JAIC* **2016**, *55*, 1-20.
- [29] P. Baglioni, N. Bonelli, D. Chelazzi, A. Chevalier, L. Dei, J. Domingues,
E. Fratini, R. Giorgi, M. Martin, *Appl. Phys. A* **2015**, *121*, 857-868.
- [30] M.D. Pianorsi, M. Raudino, N. Bonelli, D. Chelazzi, R. Giorgi, E. Fratini,
P. Baglioni, *Pure Appl. Chem.* **2017**, DOI: 10.1515/pac-2016-0908
- [31] M. Bonini, S. Lenz, R. Giorgi, P. Baglioni, *Langmuir* **2007**, *23*, 8681-
8685.
- [32] A. Pedna, L. Pinho, P. Frediani, M. Mosquera, *Prog. Org. Coat.* **2016**,
90, 91-100.

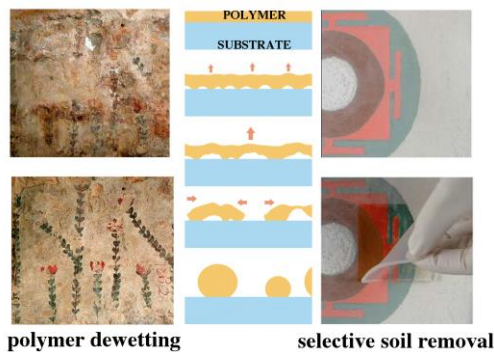
1 **Entry for the Table of Contents** (Please choose one layout)
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4 Layout 1:
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7 **MINIREVIEW**
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 10 Colloid and soft matter provide
 11 systems that enable the selective
 12 removal of soil and aged coatings
 13 from works of art.

14 Microemulsions and micelles
 15 favour the dewetting and
 16 detachment of polymer films from
 17 artistic surfaces; the detached
 18 films can be easily removed,
 19 recovering the artefact's
 20 aesthetic appearance. Gels can
 21 confine the cleaning fluids and
 22 release them gradually, avoiding
 23 overcleaning and leaching of
 24 original components.
 25
 26



*David Chelazzi, Rodorico Giorgi,
 Piero Baglioni**

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**Microemulsions, Micelles and
 Functional Gels. How Colloid and
 Soft Matter Preserve Works of
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27 Layout 2:
 28
 29

30 **MINIREVIEW**
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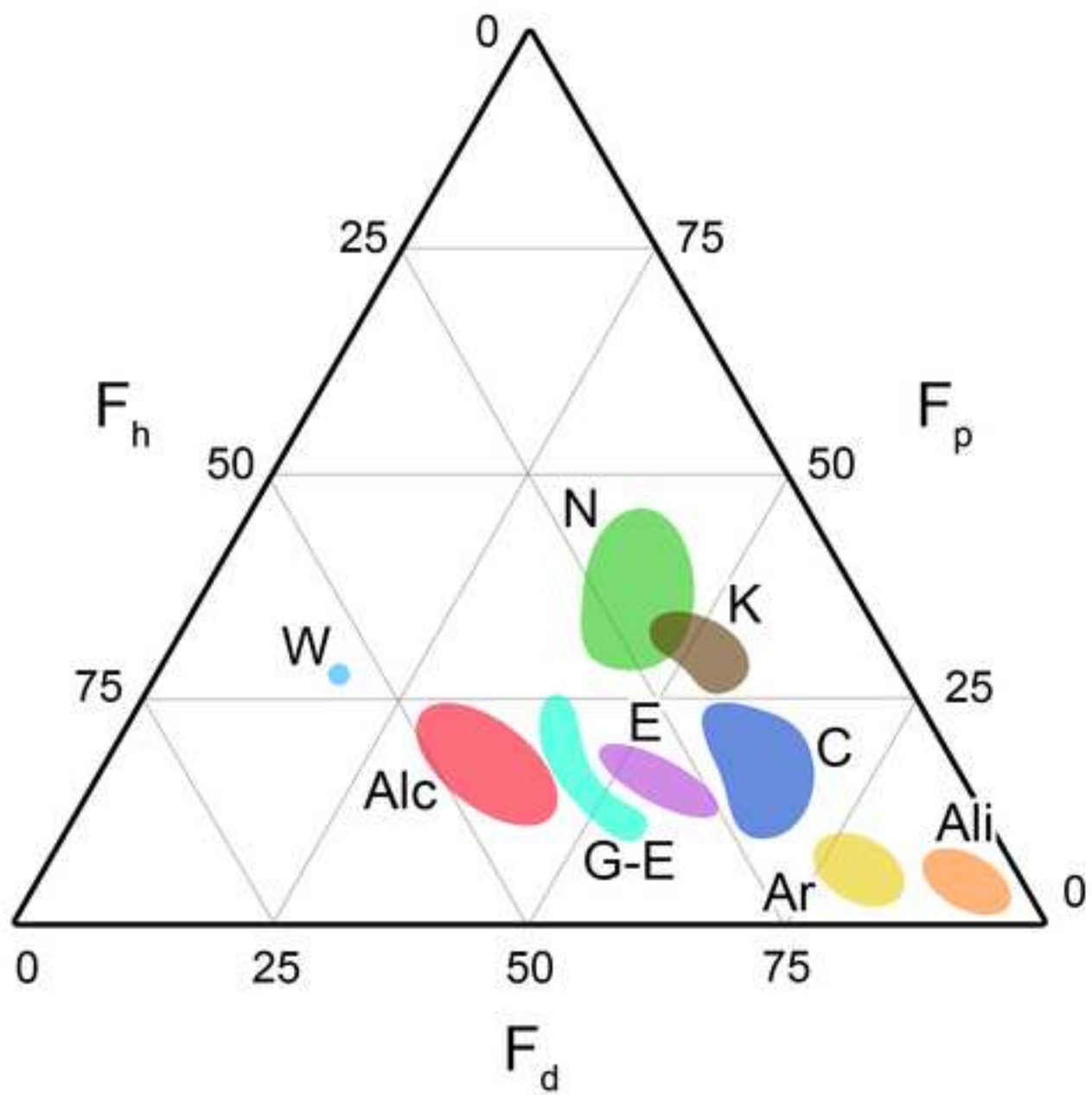
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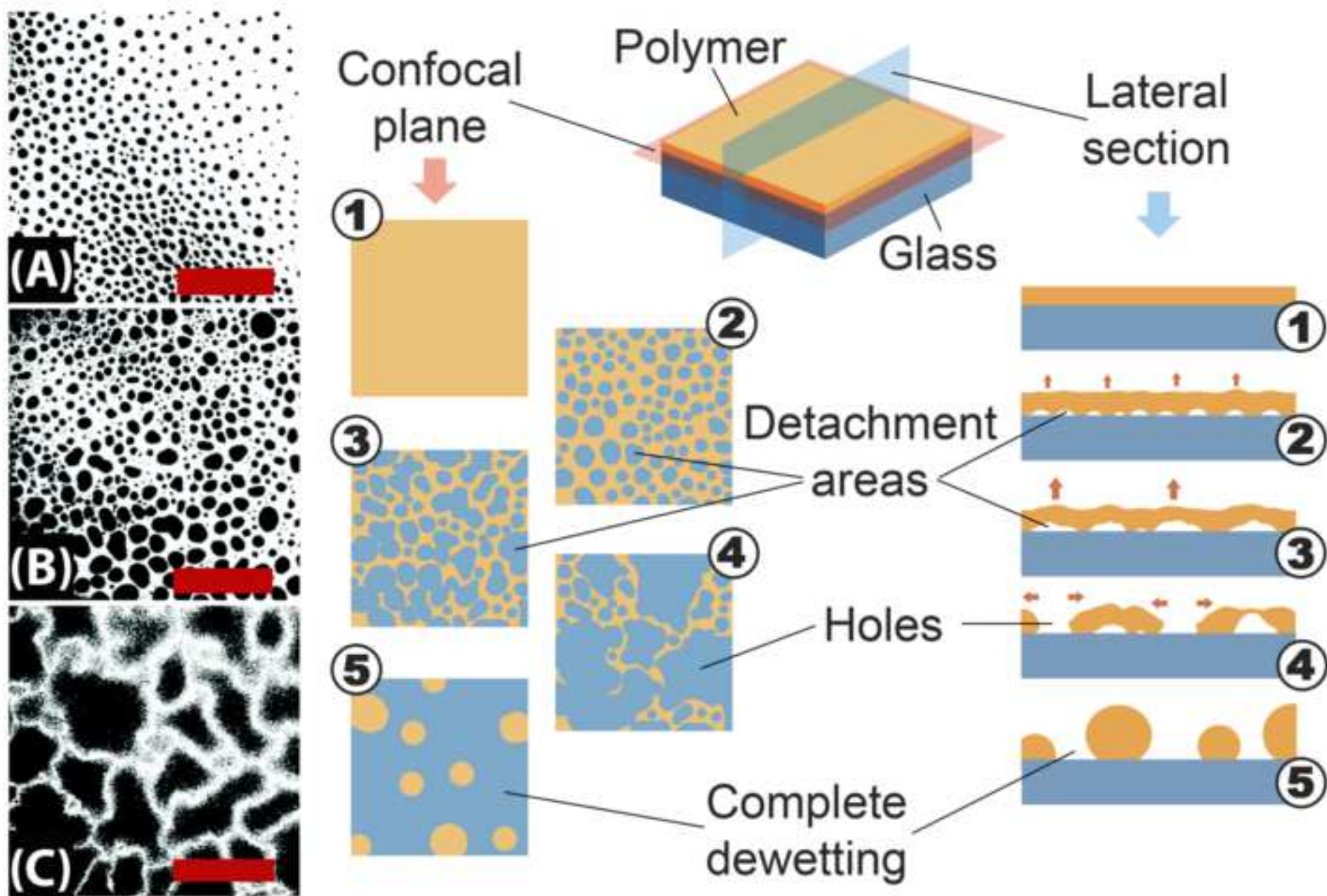
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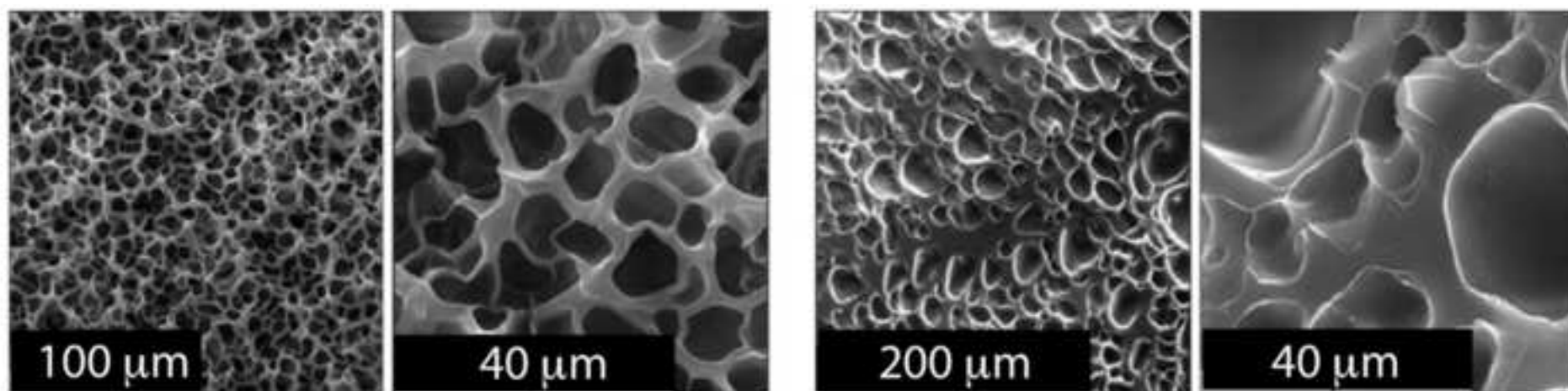
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