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Innovative Gels for the Removal of Unwanted Layers from Painted Artifacts

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Abstract

Water-based detergent systems, such as nanostructured fluids, offer several advantages, over organic solvents, for the cleaning of Cultural Heritage artifacts in terms of selectivity and gentle removal of grime materials or aged polymers, which are known to alter the readability of the painting. Unfortunately, most of the painted artifacts are water-sensitive, so using water-based systems might favor mechanical stresses between substrate and paint layers, which could lead to the detachment of pictorial layers. In order to avoid artifacts damage and to ensure a fine liquid diffusion control (layer by layer) for the removal of unwanted layers, water-based cleaning systems have been confined into innovative chemical hydrogels, specifically designed for cleaning water-sensitive Cultural Heritage artifacts. The synthesized hydrogels are based on semi-interpenetrating chemical poly(2-hydroxyethyl methacrylate)/poly(vinylpyrrolidone) networks with suitable hydrophilicity, water retention properties, and required mechanical strength to avoid gel residues after the cleaning treatment. Three selected hydrogel systems were investigated when loaded with water and with nanostructured fluids. Water retention and release properties were studied by quantifying the amount of free and bound water through Thermoanalysis; microporosity was obtained from Scanning Electron Microscopy; hydrogel's mechanical properties from Dynamic Mechanical Analysis; gel network's structure from Small Angle X-ray Scattering. To demonstrate both the efficiency and versatility of the selected hydrogels in confining and modulating the cleaning agent's action, several mock-ups were tested and two important case-studies were addressed: the removal of overpaintings from the contemporary mural painting of modern artist *Giuseppe Capogrossi* and the removal of grime and aged adhesives from an important *Vincenzo Coronelli*'s Terrestrial Globe.

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INTRODUCTION

INTRODUCTION

Conservation issues are continuously demanding innovative materials and techniques capable of providing efficient long-term preservation of Cultural Heritage artifacts. Conventional methods for the removal of unwanted layers from painted artifacts may be, therefore, potentially aggressive and cause irreparable damage to the work-of-art. Looking at the material's chemical nature, it is possible to divide these unwanted layers into two distinct classes, according to their water-affinity: hydrophilic and hydrophobic materials. While the firsts are removed with aqueous methods, hydrophobic materials, such as aged adhesives and brownish varnishes, are generally solubilized by solvent technology. Nevertheless, it is worldwide accepted the inconvenience of using neat solvents, since they inflict painting leaching and are rather toxic to the user.

The development in the last decades of nanostructured fluids (shortly nanofluids) has given the opportunity to discontinue the use of neat solvents. Some of these nanostructured fluids, such as microemulsions and micellar solutions, are water-based systems efficient in the swelling, solubilization and removal of hydrophobic coatings. Moreover, they guarantee the decrease of the amount of used solvent, while improving cleaning efficiency.

Water-based systems are straightforward and optimal for several applications yet, in some cases, limitations can still persist. Wherever the painted artifact is composed of *water-sensitive* materials (e.g. canvas, paper and some organic binders), then water-based systems, even though with major advantages over neat solvents, can become potential stressing agents to the painting's physico-chemical stability. The interaction of water with the hydrophilic materials of the painted artifact may cause mechanical stresses by swelling processes, which, can lead to detachment of the paint layers.

A remark should be made to the particular case of modern paintings that are composed of resin-based synthetic paints that are somewhat sensitive to cleaning procedures. Furthermore, the overpaintings present in these works-of-art are usually chemically similar to the original materials, so their removal through the conventional solvent selectivity method is non-appropriate.

The solution to these problems has been the use of confining systems, able to restrict the cleaning agent's penetration into the artifact's surface, which offers an increased control of the cleaning action. Over the last decades, attempts were made among restorers, based on the gel technology, to develop such systems. Examples are the use of thickeners (e.g. cellulose ethers and polyacrylic acids), *solvent gels* and polysaccharide gels (e.g. agar-agar and gellan gum). Yet, in most cases gel residues remain after treatment and evident spreading of the confined liquid is still observed, even if minimized with respect to the free system. Hence, the *Center for Colloid and Surface Science* research group (CSGI) has been recently developing some new confining systems to address these problems. Examples are the highly viscous polymer dispersions (e.g., rheoreversible polyallylamine based organogels, viscoelastic polyvinyl alcohol-borate based gels), and the chemical gels based on polyacrylamide networks. The main difference between chemical and physical gels is that the firsts have a polymeric network built by covalent bonds, i.e. permanent topological sites that account for an improvement of the elasticity of the hydrogel, and to the possibility of loading high amounts of liquid medium without undergoing solubilization.

For the above reasons, the aim of this thesis is to develop and study a highly retentive chemical gel for the controlled removal of unwanted layers from water-sensitive artifacts and whereas the cleaning procedure demands a layer-by-layer removal. This was accomplished by the synthesis of a chemical hydrogel based on semi-interpenetrating polymer networks (SIPNs), where the polymer network is built by poly(2-hydroxyethyl methacrylate) (pHEMA) and the crosslinking agent *N*,*N*'-methylenebisacrylamide, while the interpenetrated linear polymer in the network is poly(vinylpyrrolidone).

This dissertation is divided in two parts: Fundamentals and Experimental.

In the Fundamentals part, the theoretical background is described based on an in-depth investigation of the relevant literature.

In Chapter 1 the materials constituting Cultural Heritage artifacts are generally described, accounting for the chemical nature of original and unwanted materials. A general overview is as well presented on the traditional materials and methods used in restoration. For what concerns the cleaning process, the physico-chemical interfacial energies are briefly addressed, to explain the solvents permeation by capillary phenomena. Finally, the materials considered to be *water-sensitive* are explained.

The Chapter 2 is dedicated to the binders composing modern paints used in contemporary art, which are here presented separately due to their particularity and complexity. Synthetic resins are first described historically, accounting for the paints and coatings industrial development and their presence in the artist market. An insight on the chemical composition of acrylic, vinyl and alkyd resins are presented. Particularly, a detailed description is given to emulsion-kind paints. Concerns on the effects that ageing has on these materials are presented, as well as the actual cleaning issues, with particular interest in overpaintings removal.

In Chapter 3, the nanostructured fluids are described and their potential as advanced tools for the cleaning of Cultural Heritage artifacts is highlighted. First of all, to account for the cleaning subject, the solubilization process is generally explained. Nanofluids are composed of surfactants, whose classification and properties are described here, that build aggregates known as micelles. The factors influencing micelle formation are enlightened and the detergency phenomena produced by them are addressed. A remark is made to microemulsions, considering their interesting features as cleaning agents. Last, an overview of the actual use of nanofluids in conservation and restoration is presented.

In Chapter 4, gels are explained throughout their physico-chemical features. Due to the variety of gel systems, which are the physico-mechanical condition in-between liquids and solids, a detailed overview on the gel definition, is presented, as well as the types of classification. A remark is made to the definition of interpenetrating polymer networks (IPNs). A summary of the statistical approaches and the rheological behavior, accounting for the gelation process is presented. Hydrogel physico-chemical characteristics are detailed considering their structural and mechanical properties and the fundamentals of the main characterization techniques are briefly explained. Last, examples of gels used as retentive tools for the cleaning of Cultural Heritage artifacts are mentioned.

In the Experimental part, the research work is presented in four chapters, whereas the first two concern the synthesis and the physico-chemical characterization of the developed gel systems, while the last two concern the evaluation of the application features accounting for cleaning tests on mock-ups and on two important case studies.

In Chapter 5, the development of the synthesis method is detailed and the compounds used are explained with reference to the literature. Several gel series are shown to qualitatively evaluate the influence that each compound has on the final characteristics of the gel. The possibility to tune the gel’s application features is therefore highlighted. Three representative gel formulations are selected to conduct the physico-chemical characterization and the cleaning tests. Comparison with polysaccharide gels (agar-agar and gellan gum) on controlled water release is reported.

The Chapter 6 is dedicated to the physico-chemical characterization of the selected hydrogel system, here named *H50*, *H58* and *H65*. Hydrogel chemical composition is assessed by the gel content parameter and by pHEMA/PVP ratios obtained from spectra from Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance (ATR-FTIR). The interaction with the liquid fraction of the gel is evaluated with hydration/rehydration cycles and Thermoanalysis, which permitted to obtain relevant information such as the Equilibrium Solvent Content parameter, the diffusion mechanism, and the fraction of free and bound water inside gels. The loading of organic solvents and nanofluids is also considered. Mechanical analysis is presented based on rheological measurements. Influence on the hydrogel's mechanical features regarding the increasing of the amounts of cross-linker and HEMA in the composition is evaluated. Mechanical features of water-loaded and nanofluid-loaded hydrogels are compared. The hydrogel's microporosity was observed with Scanning Electron Microscope (SEM), which allowed graphing a pore size distribution for the selected hydrogels. Hydrogel's network was investigated with Small Angle X-ray Scattering (SAXS), accounting for average mesh size and inhomogeneities domains. Water-loaded and nanofluid-loaded hydrogels were compared with SAXS, to inspect on possible changes in the gel's network and in the nanostructured fluid system when they are combined in the same system.

In Chapter 7, the highly retentive features of the selected SIPN hydrogels are illustrated by the several cleaning tests carried out on different mock-ups. Two different cleaning agent systems are presented: neat water and nanofluids, to address the removal of hydrophilic and hydrophobic materials, respectively. The examples shown represent two conservation issues: the cleaning of water-sensitive artifacts using water-based systems and the layer-by-layer removal of materials that are chemically similar to the artifacts constituent materials.

Conclusively, the Chapter 8 demonstrates the application features of the SIPN hydrogels in two relevant case studies: the removal of overpaintings from a contemporary art mural painting of *Capogrossi*, using a selected nanofluid-loaded hydrogel; and the removal of superficial grime and an aged adhesive from a Terrestrial Globe of *Coronelli*, using both water-loaded and nanofluid-loaded hydrogels.

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PART I

Fundamentals

CHAPTER 1

Painted Works-of-Art: Definition and Cleaning Issues

1.1. Introduction

Painted works-of-art represent a vast range of art pieces or unmovable art, made of various types of materials. The meaning of work-of-art, or artifact, in this context, is defined as a man-constructed structure with artistic and/or historic value. In the conservation and restoration field, delicate cleaning procedures are usually necessary when facing painted artifacts, due to their complexity. Moreover, not all painted artifacts have the same elements, as there are so many painting techniques worldwide. In this chapter, a general description of the layers that mostly constitute the structure of a painted artifact is presented without being fully exhaustive. It should be noticed that this description is not intended to cover every painting technique, but only the most representative cases, in a European context.

The last layers of an aged painted artifact are, in general, composed by a varnish or coating and by superficial grime. The first, if exists, had been applied in order to protect the painting from environmental exposure, so its ageing is noticeable. Both these layers lead in time to the accelerated ageing of the artifact and, since they have no artistic or historic value, their removal becomes a valid option. These unwanted layers can be from different chemical natures: varnishes and adhesives are hydrophobic layers, while grime is usually solubilized by water. Furthermore, for what concerns the removal of hydrophobic materials, the use of organic solvents is still a standard conservation procedure. However, it is presently known that their use can cause paints swelling or leaching of pigments, as well as the irreversible deposition of the recrystallized unwanted compounds within painting pores. In fact, materials constituting artifacts have an intrinsic porosity, which is an important factor to take into account, ascribed to the capillarity phenomenon, during cleaning procedures.

Water-based systems are, therefore, the more efficient, green and safe cleaning tools to use, and they have been applied with success in the removal of polymers from wall paintings. In particular, they can avoid the spreading of the solubilized polymer into inner layers. However, some issues arise in cases where both pictorial layers and support are from organic base and, thus, may prone to swell or be solubilized when in contact with water. Due to these complexities, painted artifacts, as mostly delicate objects, must receive special care in order to remain in optimum conservative condition. For this reason it is important to characterize the materials constituting the painted artifact and understand its demands when facing a cleaning treatment.

1.2. Structure of painted artifacts: overview

Painted artifacts are complex composite structures. In fact, the characterization of their materials has been subject of research for several years and even in present days new findings come out about new painting materials and unusual techniques. Considering the importance to know about the materials involved during a cleaning process and the chemical and physical processes related to it, the materials that can usually be found in painted artifacts are described in summary further on.

Painted artifacts can be simply schematized by a support, which is the base that underlies a series of layers constituted, from bottom upward, by a preparation layer, or ground, the painting layers and, likely, a varnish (see figure 1.1).

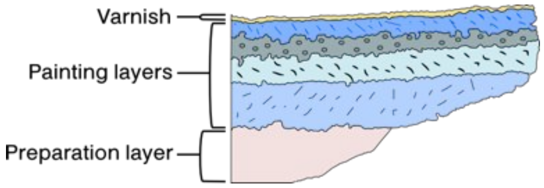

Figure 1.1. Schematic cross-section of the layers that generally compose a painted artifact, lying over a support.

From the conservation point of view, supports constitute the most important physical fraction of the painted artifact since they provide physico-mechanical stability to the painting layers. The material nature of the support may be a way to define the painting technique. Furthermore, the support's material nature can be divided into organic and inorganic. Examples of artifacts made of organic supports are canvas paintings, panel paintings, watercolors on paper, etc. Examples of artifacts made of inorganic based supports are *fresco* paintings, ceramics, stone sculptures, etc. In order to simplify this subject, while still covering a wide range of painted artifacts, only some painting techniques will be addressed further on: panel painting; canvas painting; paper manuscripts; watercolors; and wall paintings.

1.2.1. Panel and canvas paintings

Panel and canvas paintings cover a wide range of painted artifacts for indoor display, and are usually defined as easel paintings, because, unlike other painting techniques, these are painted in vertical by use of an easel.

1.2.1.1. Support

Panel supports are made of wood panels and are perhaps one the most ancient supports used for painting. Generally, wood is characterized mostly by its growth rings surrounding the central pith of the tree. There are two types of wood plants: *softwood* and *hardwood*. The main characteristic to distinguish them is the presence of vessels in *hardwoods*. Oak tree (*hardwood*) is the most common support for European panel paintings, while less common are panels made of beech, poplar and linden for *hardwoods* and fir, pine, spruce for *softwoods*. The growth rings are caused by the formation of new wood cells during the seasonal growth, the *earlywood* (large cells) during spring and the *latewood* in the summer, which are gradually reduced in cell diameter and increased in cell wall thickness. A wood cell has a longitudinal shape, reflected in tracheid cells or ray cells, and is constituted by a wall cell and an inner cell. The wall cell is composed mostly by cellulose, hemicellulose and lignin that are responsible for the wood's mechanical strength.[1–3] The cut type of the wood plane reflects the swelling behavior of the plane and its mechanical stability. There are three kinds of cut type in a wood trunk: radial, the perpendicular cut to the rings; tangential, the parallel cut to the rings; and the cut along a cross or longitudinal section. Obviously, only radial or tangential cut planes may be used as painting supports. Moreover, the radial cut plane is the most stable, since, when exposed to different ambient conditions, its dimensional change is half of the one in tangential cut plane.[1] Certain panel paintings have a *cradle*, an auxiliary support, which is a structure of wooden bars placed along a grid pattern in the panel's back. It adds additional support and may prevent the panel from deforming. However, when exposed to considerable changes in relative humidity, the *cradle* itself causes deformation to the panel since it restrains its natural movement.[2]

Canvas paintings, on the other hand, might be the most diffuse painting technique after the 16th century, since, unlike panel paintings, the support does not have dimensions' constraints.[4] Canvases are textile-based supports, which are sized with a diluted glue, usually starch or animal glue, to cover every gap between threads and to make the textile impermeable in order to support the painting. The most common textiles used are from vegetal (e.g. linen, cotton, and hemp) or animal source (e.g. silk). More recently, also synthetic fibers constitute canvases, like polyester. As for the firsts, the main component is cellulose, while fibers of animal nature are protein based.[5] Canvases are composed by the weaving of warp and weft fiber-threads, which is usually plain, that is, following a 1:1 matrix. From a conservation point of view, the weight of a canvas is an important factor, and it refers to the thread count, which is related to the tightness of the canvas. More open is the weave of the canvas less is physically stable when facing oscillations in temperature and humidity conditions. Moreover, canvases are usually stretched in a wooden frame, named *stretcher*, so tensile forces in the corners of the canvas are expected to be the highest.[4]

1.2.1.2. Painting layers

In both panel and canvas paintings, a preparation layer (ground layer) covers the support, and is made of a binder (usually animal glue) and a filler (e.g. chalk, yellow ochre). Its function is to flatten and prepare the surface to receive the painting layers, which are composed, mainly by pigments (usually inorganic compounds) and binders.[4,6] The latter normally identifies the painting technique, which can be in general classified as: tempera painting, oil painting, or modern painting.

Tempera painting technique, which is particularly diffused during medieval ages on panel paintings, is made of a water-miscible medium mixed with pigments. Egg yolk, constituted mostly by proteins, fatty acid esters and lecithin, is the most used binding material in tempera. When it dries it forms a high-cohesive film that, over time, reduces in water-solubility, due to the denaturation of the proteins. In fact, the ageing of dry films of egg yolk, induced mostly by light radiation, results in the degradation of the amino acids leading to crosslinking between them and to the oxidation of the triglycerides.[7–9]

Oil paintings, on the other hand, are based only on siccative oils, so they constitute hydrophobic layers. These are made of three kinds of unsaturated fatty acids: oleic acid, linoleic acid and linolenic acid that can polymerize and form a dry film. In particular, the drying of siccative oils is a complex process and involves the readily oxidation of the triglycerides, and, consequently, the presence of peroxides that induce oil polymerization, resulting in a cohesive solid film. In the presence of certain pigments, such as lead white, this process can be increased in speed.[8,9] Linseed oil is the most used for painting, since it is faster drying due to the higher amounts of linolenic acid, if compared with other drying oils, such as poppy seed and walnut oils.[10] In some cases there is a mixed method made by the combination of oils with other water-based binders, such as egg, glues, casein, etc., named *tempera grassa*. In other cases, oils are mixed with natural resins. In particular cases, only natural resins are used as binding source.[8]

In modern painting, it is possible to divide the materials employed in two kinds. While there is a group of contemporary artists that continues to use drying oils from natural source, the majority of them use modern paints from synthetic source, from a wide range of polymeric resins. Hereinafter, only binders and its materials from natural source will be discussed, while the definition of synthetic resins will be addressed in chapter 2.

1.2.1.3. Varnish

In easel painting, a last protective layer is expected. It is in general composed by natural resins applied with an organic solvent. After the solvent totally evaporates, it acts as an hydrophobic layer, while saturates the painting colors by reducing the diffuse light and protects the underneath binder from direct light. Dammar and mastic are the most common used resins.[6,8]

1.2.2. Paper manuscripts and watercolors

Supports made of paper for painting or printing come from ancient Chinese tradition. In Europe, only in 15th century did the paper replace parchment and started to be used in a large scale, mainly because of the introduction of book-printing[11]. The main component of paper is cellulose, featured as short fibers (from 10 to 50 μm), which are deposed during paper production by an aqueous suspension, in a random manner. Once dry, cellulose fibers form hydrogen bonds with other neighborhood fibers, which are the main responsible for the mechanical strength of paper sheets. Cellulose fibers derive from various sources of plants. Until the 20th century the main source for papermaking was the rags made of cotton, while nowadays cellulose fibers are extracted from wood pulp.[12]

The most common processes of papermaking are: dispersion of fibers; refining; bleaching; sizing (e.g. rosin-alum system); addition of fillers (e.g. kaolin, chalk); sheet-forming.[12] Depending on paper applications purposes, different treatments are done to paper in order to change its final characteristics. Naturally, paper used for watercolor is less sized than a paper used for printing, and, at the same time, is only slightly pressed, because a rougher surface is necessary.[11] The pH of paper is an important condition to monitor with the ageing of paper artifacts, since cellulose fibers are anionic, due to the presence of acidic groups, introduced during the papermaking process.[12]

Paper can be, therefore, a support for different painting techniques. The most representative are miniatures in illuminated manuscripts and watercolors. The first is based on tempera painting, commonly made of vegetal gums, egg white, or animal glues. Inks are preferred for writing, since they are usually permanent and resistant to water. Iron gall ink is the most used, which comprises iron salts and tannic acids, in a combination with gum arabic as binding media.[13] Watercolors, are based on vegetal gums, such as gum arabic, or on synthetic polymer emulsions in modern artworks.[8] Vegetal gums are extracted from certain plants and contain branched polysaccharides. Gum arabic is the most common gum used in watercolors and gouache techniques, since it is transparent and soluble in water. To form permanent films, it can undergo crosslinking in association with metal ions and gelatin.[6]

1.2.3. Wall paintings

Wall paintings are from inorganic based support and, commonly, also the painting layers are from inorganic source, with an exception for the modern painting on walls, where the painting layers are based on synthetic polymers. Wall paintings also cover paintings done on ceilings and other stone or brick surfaces.

The most representative technique of this kind is the *fresco*. In *fresco* painting a structural support is prepared with a mortar layer (*arriccio*), which is the base for fixing the painting. It has about 1 to 2 cm thick and is typically comprised of one part lime to two parts sand.[14] The drying of a lime-based layer of this kind has chemical and physical processes going simultaneously: water absorption through the wall; evaporation of water from the surface of lime; and carbonation of the calcium hydroxide:[8]

$$\mathrm{Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)} \qquad (1.1)$$

Over this layer there is the *intonaco* layer, the basis of the painting, which is composed by a lime-rich mortar with fine particle size. Pigments diluted with limewater are applied over this wet layer to produce the *fresco* painting. The pigments are cemented in the painting due to carbonation of the calcium hydroxide of the *intonaco*.[6] Once this layer is dry some painting can be done by *secco* painting, which consists on applying paints with different media source, such as temperas, directly on the dried surface.[14]

1.3. Hydrophilic and hydrophobic unwanted layers

As well as all materials, also painted artifacts are subject to degradation over time. The rate at which it occurs depends mostly on the conditions of which they are stored. The most evident effects due to ageing are the formation of superficial layers that are not original to the painting, such as dust accumulation from atmospheric deposition, or the lost of the protective function of the applied varnishes. From a conservative point of view, in most cases, the removal of these layers is ethically well accepted, since their presence in contact with the original painted layers can induce further degradation. In the particular case of varnishes, it is a common procedure to remove the old varnish and replace it for a new one, thus compatibility and reversibility are important factors to consider.

For what concerns the subject of this thesis, it is important to define the composition of these materials, since it concerns the choice of the cleaning system used for their removal. In this context, unwanted layers can be divided into hydrophilic and hydrophobic materials. The definition of hydrophilic and hydrophobic is due to the contact angle between a water liquid drop and the solid surface (see under 1.5 heading). If the angle is less than 90º, then it is an hydrophilic surface, otherwise it is hydrophobic.

Synthetic resins are used extensively in restoration treatments, since they can act as adhesives, varnishes, consolidants and binders for overpaints. Under ageing, these films undergo cross-linking, so their solubility is reduced, and may change color. Their removal is yet not a standard method as it is for traditional materials, due to their chemical nature's high variety (see chapter 2). Some of the restoration synthetic resins are summarized in table 1.1.

Table 1.1. Commercial product, chemical composition, supplier and main application in the field of conservation of cultural heritage.[15,16]

Resin	Composition	Supplier	Application
Butyl methacrylate (BMA)			
Elvacite 2044	*n*BMA	Du Pont	Consolidant
Elvacite 2046	*n*BMA-*i*BMA	Du Pont	Consolidant
Paraloid B-67	*i*BMA	Röhm & Haas	Varnish
Plexisol P 550	*n*BMA	Röhm	Binding medium, consolidant
Butyl methacrylate–2-ethylhexyl methacrylate (BMA-2-EHMA)			
Plexigum PQ 611	*i*BMA-2-EHMA	Kremer	Wall painting binding medium
Butyl acrylate-methyl methacrylate (BA-MMA)			
Plextol D-498	*n*BA-MMA	Röhm & Haas	Binding medium
Primal AC-35	*n*BA-MMA	Röhm & Haas	Binding medium
Butyl acrylate–butyl methacrylate–methyl methacrylate (BA-BMA-MMA)			
Primal E-330-S	*n*BA-*n*BMA-MMA	Röhm & Haas	Mortar consolidant
Ethyl acrylate-methyl methacrylate (EA-MMA)			
Paraloid B-82	EA-MMA	Röhm & Haas	Varnish
Plextol B-500	EA-MMA	Röhm & Haas	Binding medium, adhesive
Primal AC-33	EA-MMA	Röhm & Haas	Binding medium
Primal B-60	EA-MMA	Röhm & Haas	Consolidant
Methyl acrylate–ethyl methacrylate (MA-EMA)			
Paraloid B-72	MA-EMA	Röhm & Haas	Consolidant, varnish
Polyvinyl acetate-butyl acrylate (PVAc-BA)			
Mowilith DM5	PVAc-*n*BA	Hoechst/Clariant	Binding medium, adhesive
Ketone			
Laropal K80	Mix of cyclohexanone molecules	BASF	Varnish
Hydrocarbon copolymer			
Regalrez 1094		Eastman	Varnish

1.3.1. Air-born soil

Air-born soil deposits rather quickly in all surfaces. Over time, and in combination with greaser materials, it can be ingrained to a more firmly fixed layer, giving rise to a grime layer. This layer may contribute to the further deterioration of the organic materials composing the surface of the painted artifact.

Soil filtered from urban air contains salts, solid materials, oils, waxes, clay and soot. Solid materials can cause damage to the surface's morphology by friction, especially due the sharp edges of the crystalline materials. Furthermore, dust may cause color alteration (mainly yellowing), due to the presence of metal ions that may form light-absorbing compounds. Surface grime can attract acid or alkaline compounds, from the atmosphere (e.g. sulphur dioxide, nitrogen dioxide, hydrogen sulphide and formaldehyde) that may lead to the formation of acid solutions with moisture and promote hydrolysis of the organic compounds. Fat, oils and other greaser materials contain free acids and can easily embed further soil.[5] These layers are therefore composed by both organic and inorganic materials. However, water alone can act as a good solvent also for soil particulate due to its high dielectric moment.[17] In this context, grime is considered to be a hydrophilic layer since its removal can be done mostly by pure water.

1.3.2. Adhesives

Adhesives are organic substances and by definition they can hold objects together due to their high cohesion and adhesion forces. Many compounds can act as adhesives and their choice depends on the kind of material to be glued. In general terms, adhesives are in most cases already products from previous restoration interventions, and like all organic materials, they are prone to degrade over time. Examples of adhesives used in such interventions are based on casein, starch, collagen and paraffin, for natural source adhesives, while for synthetic source adhesives they are based on polyvinyl acetate (PVAc) (e.g. Mowilith DM5), acrylic resins (e.g. Plextol B500) and on microcrystalline paraffin with synthetic resins, such as Lascaux 443-95.[2] Lining procedure is a good example where adhesives are applied in an extensive way in paintings. A lining consists of a structural treatment where a new canvas is attached with an adhesive to the backside of the original canvas support for the purposes of stabilization.

In general the degradation of adhesives result in a more rigid and brittle film, and if exposed to light, it may be presented as a yellowed layer. Moreover, adhesives may become sticky, so they can attract and ingrain particulate dust. Adhesives are usually made from animal or vegetable glues and from natural or synthetic resins. The pH of adhesives may decrease upon ageing which may induce hydrolysis in the presence of water.[5] Some of these adhesives (such as animal glues) are hydrophilic in nature, but with ageing the water affinity is reduced (water can only slightly swell these layers), so their removal is usually done with organic solvent systems.

1.3.3. Varnishes

Varnishes constitute the final layer of a painting, giving rise to a glossy or matt appearance of it. Its degradation is reflected by discoloration and fine cracks along the flat surface. The type of varnish may be oil varnish, which are basically constituted by drying oils; oleoresinous varnish, a mixture of drying oils and resins; albumen varnish, that is, egg-white applied in water solution (manly used for varnishing tempera paintings); resin essence varnishes, which are natural resins applied in solution with petroleum distillates; wax varnishes that may be dissolved in petroleum distillates or in resin varnishes; and synthetic resin varnishes, usually dissolved in polar solvents. The most commonly found in paintings nowadays are the resin-based varnishes. Natural resins are secretions made by trees to seal their wounds. Their chemical composition is a mixture of resin alcohols, resin acids, resin ethers, hydrocarbons, etc. Since 12nd century, resins, such as sandarac, amber or mastic, had been applied as oleoresinous varnishes. Over the 16th century, resins replaced oil in varnishes all over Europe. Dammar resin, extracted from an Asiatic source tree, did only enter in the European context after the 19th century. Synthetic resins are mainly based on PVAc; polyacrylates (such as Paraloid B-72 and B-67); ketones, such as the polycyclohexanone Laropal K80; and hydrocarbons, such as Relgalrez 1094.[2]

When removal of this layer is necessary, the more polar solvents may no longer be used, due to the grade of cross-linking that underwent the varnish. Synthetic resins varnishes have further disadvantages other than discoloration and cross-linking over time, since they also loose elasticity and become brittle, and, due to their low T_g (glass transition temperature), at ambient temperature they may be sticky and ingrain the deposited dust.[2]

1.3.4. Consolidants

Even if it may be made of the same compounds, consolidants should not be confounded with adhesives, since the function of the firsts is to assist the recovery of a lost cohesion along the microstructure, so they should be able to penetrate into the most inner layers of the friable material. Due to this demand, consolidants may not be prone to removal. For the natural source materials, an example is the use of animal glue in a diluted form, mainly to consolidate the paint layers of easel paintings.[8] Although, for wall paintings, inorganic source consolidants are usually preferred, due to similar chemical nature, it is yet possible to find consolidations carried out with synthetic organic adhesives.[18] In fact, synthetic resins are nowadays the most used consolidants, which are mainly based on acrylic and vinyl polymers, such as Paraloid B72, and Primal AC33.[19,20] The degradation of organic consolidants can endue, in one hand, the loose of its function, with consequently loss of substrate cohesion, and, on the other hand, induce mechanical damage due to the different physical behavior with respect to the original materials.

The particular case of polymer consolidants in wall paintings it is worth referring, since their removal is, at present, one of the main concerns of conservators. When a wall painting is coated with a polymer film the permeability to water vapor is highly decreased, so the crystallization of salts may take place within the pores of the painted layers, which can eventually lead to the detachment of the wall painting from the support.[21]

1.4. Traditional cleaning in restoration: materials and methods

Cleaning is a restoration procedure that aims to bring the surface to a state that resembles as close to the original appearance of the painted work-of-art, as the original materials can allow. This, in practice, reflects in the most potentially aggressive interventions that a painted artifact may pass through. In fact, none of the present cleaning techniques can assure a complete removal of the unwanted layers without causing risk to the original layers, either by solvents permeation, or by mechanical stresses caused by dry methods. Here below, a brief description of actual methods and materials used by conservators is presented.

For what concerns grime removal, using water-based systems is still the most effective method used. In some cases a wetting agent may be added, such as a surfactant, to aid dirt and greaser materials trapping into the cleaning system. While the traditional use of potatoes and onions has been abandoned, saliva is still used by conservators in their cleaning procedures.[17,22] When facing unvarnished paintings, the procedure of using water is more complicated, due to the contact of water-based systems with water-sensitive original layers, so dry methods are usually applied. Among the most common materials there are erasers, fabrics, sponges (usually rubbers) and gum powders. However, these methods may also cause damage, since the mechanical action produced may involve abrasion, gloss changes and pigment removal from low-cohesive paint films. Moreover, dry methods usually leave micro-deposit residues over the surface, which with time undergo degradation.[23,24]

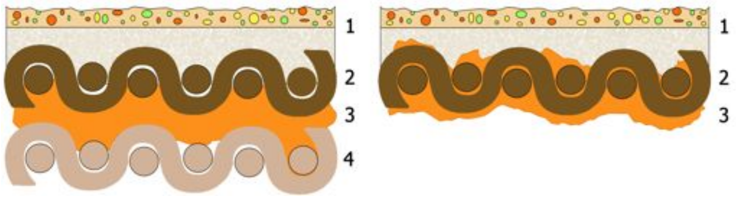

Figure 1.2. Schematic cross-section of a painting with a lining (left) and after its removal using solvent technology (right). 1 Preparation and painted layers; 2 original canvas; 3 adhesive; 4 canvas used for lining.

In traditional methods, the removal of well-oxidized varnishes from oil paintings was done usually with spirits of wine or turpentine.[22] Conversely, painted artifacts can be much more complex than this, so other solvent mixtures were used depending on the materials involved for each particular case. Nowadays, there is such a wide range of organic solvents available to conservators that they are still their first choice for removing varnishes, even if it has been demonstrated the swelling of paint films caused by the use of organic solvents.[25,26] Some of the most used solvents in conservation among with their surface tension value are summarized in table 1.2. An example of a delicate intervention over an unwanted layer with risk of solvent permeation is the case of lining removal (see figure 1.2). While in traditional lining the adhesive used is a wax resin, so the detachment of the lining canvas from the original support is done with relative easiness, in the case of lining where synthetic resins are used, the adhesive must be softened with a solvent before the fabric can be removed.[2] Solvents, in this situation, may easily penetrate into canvas fibers and go through the painting layers, and, in the worst case, transport the solubilized adhesive within, as illustrated in figure 1.2 (right).

In order to reduce the solvent permeation into the paint film, some intent on increasing solvent viscosity has been tested, for example, with the use of cellulose ethers (e.g. Klucel) and polyacrylic acids (e.g. Carbopol). However, only some solvents can be mixed with these polymers, usually the most polar ones. In addition, the high evaporation rates of the solvents interested, can lead to the formation of dry films of solid material on the treated surface, which is difficult to remove due to the adhesiveness of the gelling material.[27] To face this problem, in 1988 Wolbers introduced a new system based on solvents in their thickened state, with higher viscosity with respect to the previous ones and in combination with surfactants and water.[17,28] They are known in the restoration field as “solvent gels” (for the gel definition see chapter 4). The problem with solvent gels persists with the residues left on the surface after the cleaning.[29] However, it was thanks to the introduction of these water-based systems and their systematic application in various case-studies, that nowadays the use of aqueous systems is a well-established method as a preferred alternative to the use of solvents.[30]

1.5. The role of porosity in the cleaning process

Wet cleaning on artifacts always involves the interaction of a liquid with a solid. To understand this complex process, it is important to generally describe spreading processes and the forces present in the interfacial region. For what concerns the ideal cleaning process in the conservation field, the forces of interaction between the surface (solid) and the liquid (cleaning agent) should be high enough to just slightly wet the surface in order to remove the unwanted layers by solubilization or other chemical processes, while avoiding the spreading of the liquid within the original layers. Moreover, it is worth noticing that every surface has an intrinsic porosity, so liquid permeation by capillary process is likely to be present. In this case, only solid surfaces that remain invariable in contact with liquids, i.e. that do not swell are assumed here.

Table 1.2. Surface tension (γ) and viscosity (η) at 25°C of some pure liquids.[31]

Name	**γ (mN·m^{-1})**	**η (mPa·s)**	**Name**	**γ (mN·m^{-1})**	**η (mPa·s)**
Hexane	17.89	0.300	Butyl acetate	24.88	0.685
Ethanol	21.97	1.074	1-Butanol	24.93	2.544
Methanol	22.07	0.544	1-Pentanol	25.36	3.619
Nonane	22.38	0.665	Trichloromethane	26.67	0.537
1-Propanol	23.32	1.945	Acetic Acid	27.10	1.056
Ethyl acetate	23.39	0.423	Toluene	27.93	0.560
Acetone	23.46	0.306	*p*-Xylene	28.01	0.603
Cyclohexane	24.65	0.894	Water	71.99	0.890

1.5.1. Surface tension and interfacial energy

The surface tension (γ), expressed by force per length unit (N·m^{-1}), is defined by the necessary work to increase the surface area of a liquid. It reflects in the contract of a liquid, due to the presence of intermolecular characteristic cohesive forces that allow resisting an external force, creating an interfacial tension (see table 1.2. for surface tensions of selected solvents).

For solids in contact with liquids, the interfacial tension formed (γ_{sl}) is given by their single surface tensions:

$$\gamma_{sl} = \gamma_s + \gamma_l - W_{sl} \tag{1.2}$$

where γ_s and γ_l are the surface tensions of solid and liquid, respectively, and W_{sl} is the work required to increase surface area between solid and liquid. In the case of an ideal smooth surface, this causes the formation of a spherical liquid drop over the surface. The adhesion forces solid-liquid compete with the cohesive forces liquid-liquid, causing the liquid to spread along the surface until it reaches an equilibrium state. When this occurs, a liquid droplet is formed with a specific contact angle (θ) with the surface (figure 1.3.).

If the liquid drop in contact with a solid surface is exposed to air, then the Young's equation applies:[12]

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \tag{1.3}$$

where γ_{sv}, γ_{sl} and γ_{lv} are respectively, the solid-vapor, solid-liquid and liquid-vapor interfacial tensions.

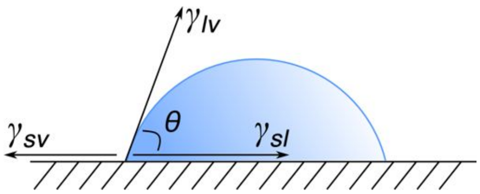

Figure 1.3. Contact angle (θ) between a liquid droplet and a solid surface.

1.5.2. Capillary pressure

From a practical point of view, the materials involved have porous surfaces, so considerations on capillary pressure are fundamental. In general, a porous solid is defined by a solid with cavities, channels or interstices, which are deeper than wide. Usually, for simplicity, pores are considered to have cylinder or sphere form, otherwise it would be complicated to define a real porous structure, due to the wide pore size and pore shape distribution, as well as to the existing connections between pores.

A liquid droplet in contact with a single pore becomes curved, and a meniscus is formed (see figure 1.4.). This is caused by the difference of pressures between liquid molecules in the interphase and the ones in the bulk. Following the Young-Laplace equation and assuming an uniform cylindrical-shaped pore with *a* radius, the pressure difference, *Δp*, may be expressed as follows:[12]

$$\Delta p = \frac{2\gamma_{lv}\cos\theta}{a} \tag{1.4}$$

If the angle between the solid pore wall and the liquid is greater than 90º, then *Δp* is negative so the liquid does not penetrate spontaneously by capillary action.

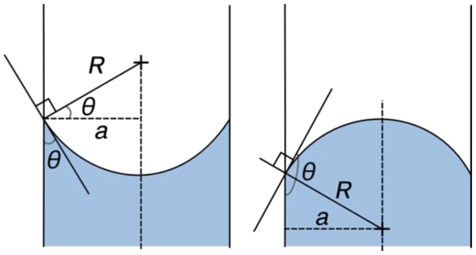

Figure 1.4. Contact angle (θ) of the formed liquid meniscus, with radius *R*, with the capillary tube with of radius *a*. If θ is less than 90° (left) a convex meniscus is formed, otherwise, if greater than 90° (right) a concave one is observed.

It is, then, possible to predict the penetration depth of the liquid within a pore of cylindrical shape, considering the model of Washburn about the rate of penetration of fluids into a single capillary:[32]

$$\frac{dl}{dt} = \frac{a}{\eta}\frac{\gamma}{4l}\cos\theta \tag{1.5}$$

where η is the viscosity of the liquid and *l* is the length of the distance travelled by the liquid in the capillary in function of time *t*. The rate of penetration of a liquid is, therefore, equal to the distance which the liquid penetrate a capillary tube of unit radius in unit time, when flowing under its own capillary pressure.[32]

According to this, and assuming the same solid surface, it is clear that a liquid with low surface tension will penetrate deeper with respect to water that has high surface tension.

1.5.3. Solvents permeation during cleaning

The phenomenon of liquid penetration within pores has been briefly explained so far. From a practical point of view in the cleaning of cultural artifacts, organic solvents will penetrate more within the pores of artifacts' surface, with respect to water-based systems. Furthermore, organic solvents, used for the solubilization of polymers and other hydrophobic materials, can penetrate within pores in solution with the dissolved material. After the solvent evaporates, the non-volatile components recrystallize inside surface porosity (figure 1.5.). These materials not only are difficult to remove, but also continue to age over time, which may induce further degradation to the painted artifact.

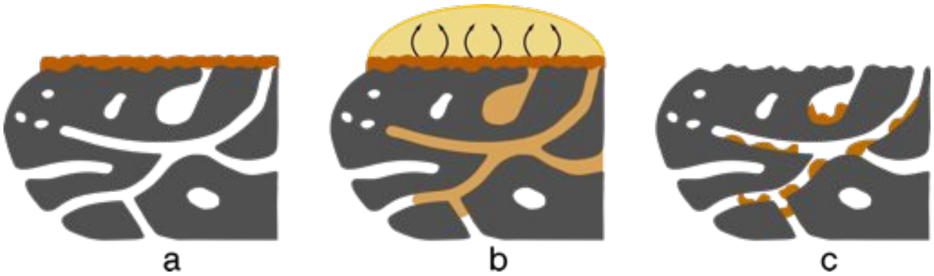

Figure 1.5. Schematization of the effects of solvent permeation within a porous surface. (b) Solvent system solubilizes the hydrophobic material while penetrating some layers into the painted surface; (c) the solvent evaporates leaving the non-volatile compounds recrystallize within inner pores.

For these reasons, the use of neat solvents is in most cases massively discouraged by scientific professionals interested in the conservation of painted artifacts. Moreover, conservation researchers have been pursuing new methods for reducing the solvents impact on cleaning procedures, and some innovative approaches have been outlined so far. Examples are the use of water-based systems able to remove polymers, such as micellar solutions and microemulsions,[21,33–36] and the use of gelatinous systems to decrease solvents penetration into the substrate, such as Klucel, Carbopol and solvent gels.[17]

1.6. The cleaning issue of water-sensitive artifacts

When it comes to cleaning by using water-based systems one must take into consideration the water-sensitivity of certain materials composing the painted artifacts. The water sensitivity of materials is mostly caused by the easily formation of hydrogen bonds between water molecules and the material. This may be reflected in swelling/deswelling behavior, or in materials dissolution.

1.6.1. Vegetal source materials - polysaccharides

This class of materials can be found in many materials composing painted artifacts. The most representative of this class are starch, vegetal gums and cellulose. Considerations on water sensitivity of these materials must take place, since the high number of hydroxyl groups makes them prone to form hydrogen bonds. For this reason, polysaccharides are extensively used as adhesives, painting binders, etc. However, in contact with water liquid or water vapor, the cohesive forces may compete with the water-material forces created by the hydrogen bonds created.

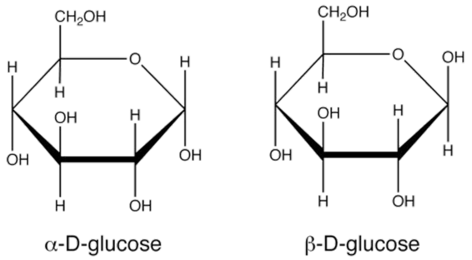

Figure 1.6. The two isomers of the D-glucose saccharide.

Starch is mainly composed by two polysaccharides built from α-D-glucose units: amylose and amylopectin (see figure 1.7). While amylose is a linear polymer with a helical structure, amylopectin is a random branched polymer, which confers the gel properties of starch. The sensitivity to water of starch is reflected by the different mechanical behaviors that undergo its polysaccharides: the helical structure of amylose tends to shrink, while the short branched chains of amylopectin tends to swell.[5]

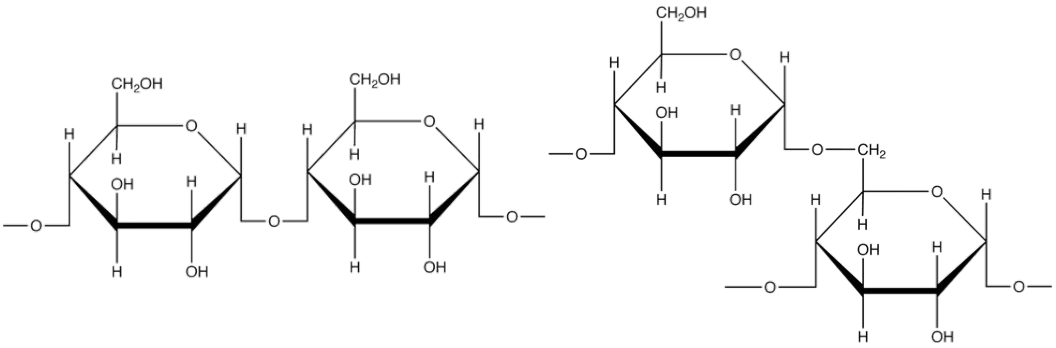

Figure 1.7. Amylose (left) ad amylopectin (right) of starch.

Gum arabic is composed by a variety of monosaccharides: arabinose, rhamnose, galactose, glucoronic acid and galacturonic acid. For what concerns the water sensitivity of this material, the last two acidic ones play an important role, since they readily dissolve in water. Moreover, the acidity of this binder may cause the acid hydrolyzation of cellulosic materials in the presence of water.[5]

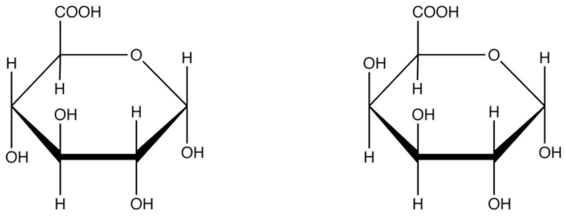

Figure 1.8. Glucuronic acid (left) and galacturonic acid (right) of gum arabic.

Cellulose is by far the most important polysaccharide to consider, since in many cases it acts as main component of the painting support (e.g. paper and wood). Cellulose is a natural polymer composed of units of β-D-glucose units and exhibits both crystalline and amorphous regions. The crystalline structure confers mechanical strength, while the amorphous part is responsible for the flexibility of cellulose and for the diffusion of liquids within the cell due to the presence of capillaries and pores.[5]

As illustrated in figure 1.9, the exceptionally good cohesion forces of cellulose in paper sheets and in wood are due to the ability to form hydrogen bonds between the fiber-fiber hydroxyl groups. In the presence of water vapor or water liquid, water can form new secondary bonds between the interchain bonds in the amorphous parts, so excess of water will cause swelling of cellulose cells.[3,5,12]

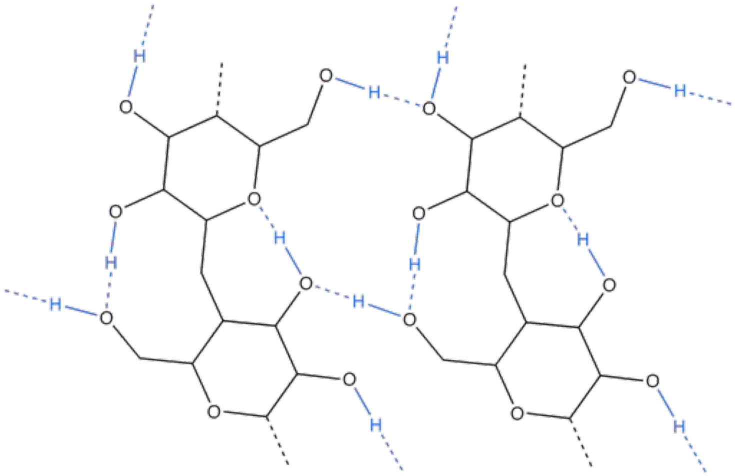

Figure 1.9. Two-dimensional view of unit cell of cellulose with intramolecular and intermolecular hydrogen bonds between hydroxyl groups.[12]

Cellulose based supports are, therefore, expected to be strongly hygroscopic. Paper, wood and vegetal source textiles (made of cotton, linen, etc.) are the most relevant to consider, since they may change considerably in presence of water molecules. In paper supports mechanical strength is reduced in contact with water, since it will compete with the hydrogen bonding between fibers, so the fiber-fiber interchain loose in cohesion, which can lead to a complete separation of the paper fibers with the subsequently loss of the painted support.[12] As for wood, panel supports have already an intrinsic moisture, which is in constant equilibrium with the ambient climate. Accordingly, the quite significant variations on the internal moisture of wood can induce noticeable dimensional change. Moreover, this change is determined by the anatomical direction in the wood panel (tangential, radial or longitudinal) and varies among tree species. Since painted layers do not have the same elasticity as wood panels have, damages in the painting layer will result.[1,2]

Textile supports show a completely different behavior with respect to wood panels. In contact with water, the cellulose-based fiber threads will swell, particularly transversely to the axis, and the canvas support will, in turn, shrink (see illustration on figure 1.10). This effect depends mostly on the fiber density and on canvas' weight: the less space fibers have to swell, the most noticeable the shrinkage will be. The contrary forces between painting layers and support may induce the firsts to become unattached from the support. Furthermore, since canvas are constituted by fiber threads in tension, the presence of water can induce serious strain effects, that may be responsible for the loss of fibers elasticity in the long therm.[2,5]

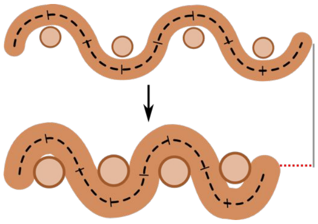

Figure 1.10. Swelling of canvas' threads, when in contact with water, leading to canvas shrinkage.

1.6.2. Animal source materials - proteins

Proteins have numerous sites able to form hydrogen bonds (peptide bonds, carboxylic and amine groups, etc.) so they are usually hydrophilic. With ageing and, more particularly, with light radiation, proteins undergo denaturation. Consequently proteins will decrease in water solubility. For this reason tempera paintings resist in time. Nevertheless, protein based materials are still water-sensitive since the peptide groups remain invariable with denaturation, and these may form hydrogen bonds.[8] From all materials original to painted artifact that are protein based, the most important to analyze are animal glue, casein and egg.

Animal glue is obtained from skin, bone or tendons and is composed mostly by gluten, a partially hydrolyzed collagen. Animal glues may swell in cold water or be solubilized in water under heating. In the presence of water, the gluten's hydrophobic side groups of the helical chains tend to arrange themselves in order to avoid water, so first, animal glue will swell under water absorption, then the material will shrink. This is important since animal glue composes most of the ground layers in painted artifacts. It must be, however, considered that the pigments in these layers may act as cementing compounds, so to prevent swelling/shrinkage.[5]

Casein contains proteins and milk contaminants, such as lactic acid and lactose. Casein is insoluble to water in normal pH conditions. It is, therefore, mixed with alkaline compounds, such as ammonium hydroxide or lime and plasticizers, in order to prepare an applicable water-solution of casein. Therefore, casein-based layers are sensitive to water, and will eventually shrink on absorption of moisture.[5]

Egg based materials must be divided into albumen and egg-yolk. The main difference in the composition of these is that in egg-yolk there are fats and oils, which confers elasticity to the painted layer, as well as, hydrophobicity. The presence of acidic and alkaline compounds causes accelerated ageing and the layer becomes more rigid and brittle. This material is prone to biological attack, mainly if exposed to water.[5]

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CHAPTER 2
Modern Paints Used in Contemporary Art

2.1. Introduction

At the beginning of the 20th century the first synthetic materials began to emerge as a result of the exponential growth in the paint and coatings industry. The first synthetic resins were produced and were introduced in paints as binding media. Not so long after, artists' interest started to be towards these new appealing materials. In fact, the use of these new materials by artists was in close relation with paint and coatings industry development, which continuously changed paint formulations to face different application demands. Thus, there is a wide range of compounds that may be found in a contemporary painting. Nonetheless, the most representative classes of synthetic resins used by artists can be distinguished into acrylic, vinyl and alkyd, being the far most used the acrylic kind.

There are two kinds of synthetic resin paint formulations: solvent-based and waterborne paints. Waterborne paints, or emulsion paints, are less toxic, easy to apply and dry faster than solvent-based paints. Adding to the fact that their brilliant colors were much more appealing than traditional paints, it is obvious that contemporary artists used extensively these new emulsion paints, which opened a new world of possibilities in art experimentation. All these paint materials are complex systems that have quite distinct physical properties and exhibit different sensitivities to organic solvents and water, so the identification of modern paint's components is fundamental before any cleaning procedure.

In the context of the thesis aim, these materials are here described in detail, along with their specific conservation issues. Particularly, there are two relevant problems in conservation of contemporary paintings: the cleaning of superficial grime using water-based systems and the removal of overpainting layers from painted surfaces. The first issue is related to emulsion paints, which are known to swell in the presence of water. On the other hand, the overpainting issue is focused here because these layers are usually made of materials that are chemically similar to the original painting layers, so their selective removal, only by solubility theory, is not straightforward. The challenging character of cleaning these painted artifacts was embraced within the thesis aim.

2.2. Synthetic resin-based binders in modern paints

A synthetic resin is a polymer from synthetic source that resembles in physical properties to natural-source resins but not in its chemical nature. In fact, the term “resin” is used because, like resins, they are soluble only in organic solvents and able to form a thin continuous film when the solvent evaporates, which is usually transparent or translucent. Its chemical nature is, however, quite different, since natural resins belong to the terpene family and synthetic resins are macromolecules, obtained from a polymerization process.

One of the most important uses of synthetic resins is in paint and coatings industry. They are nowadays the most used binders in a wide range of applications: construction; product finishes; automotive industry; traffic paints; etc. Paints of this kind can be waterborne or solvent-based paints. The firsts, refer to emulsion paints (in the US are designated as latex paints), i.e. the polymer is dispersed in water with surfactants and additives. Solvent-based paints, as the name suggests, are dissolved in an organic solvent.[1]

2.2.1. Historic overview of synthetic resins

The very first semi-synthetic resin produced in a laboratory was the nitrocellulose, discovered by Henri Braconnot in 1832. It was obtained by reacting cellulose fibers with nitric acid. It was widely used as enamel spray paint (solubilized in an organic solvent) for the automotive industry from DuPont Chemicals, trademarked Duco, after the First World War. Attempts were made to produce nitrocellulose’s brushing paint by the addition of an alkyd resin, i.e. a polyester resin, however, with poor application features, due to the high amounts of required organic solvent that evaporated too fast to brush out the paint homogeneuosly.[2] The polyester resins production dates 1847 with the reaction of glycerol and tartaric acid by J. Berzelius. In 1901, W. Smith synthetized an alkyd resin by the reaction of phthalic anhydride with glycerol. The resulting resin was insoluble and brittle due to the highly branched polymer. Nonetheless, it gained some interest by the industry that starting from 1910 to put efforts in improving this polyester resin. In 1927, R. Kienle, from General Electric, patented the addition of unsaturated fatty acids to the reaction, producing a flexible and soluble resin for surface coating applications.[3] Oil-modified alkyd synthetic resins, due to their high resistance and fast dryness, are still nowadays the dominant binder in brushing paint in industrial and household paints. The most representative example of this binder for decorative paints is composed of glycerol, phthalic anhydride and a drying oil (examples are Dux and Dulux, from DuPont Chemicals). After 1960 glycerol was substituted by pentaerythritol.[2,4]

At the same time, a new class of synthetic resins was being developed: acrylic resins. Almost all acrylic polymers are based on acrylic and/or methacrylic esters. The monomer acrylic acid was obtained in 1843 by air oxidation of acrolein from glycerol by Redtenbacher, while methacrylic acid in 1865. In 1901 O. Röhm described the liquid condensation products obtained from methyl and ethyl acrylate in the presence of sodium alkoxide. Later on, in 1927 Röhm introduced a new acrylate synthesis by heating ethylene cyanohydrin, sulfuric acid and alcohol. In the mid-1930 the first acrylic resin is casted, based on methyl methacrylate (MMA) monomer, obtained from the reaction of acetone cyanohydrin, sulfuric acid and methanol. This acrylic polymer, commercialized by Röhm and Haas under the trademark Plexiglas, was extensively used as a substitute for glass in aircrafts enclosures, since it was lightweight and shatterproof.[4,5] With the end of Second World War acrylic polymers began to be commercialized for civilian uses, mainly as acrylic emulsion paints, since they offered a non-toxic rapid-drying alternative to the alkyd-based paints, which dominated the market of household paints until the date. The first commercialized waterborne emulsion paint for household use was Kem-Tone paint (Sherwin-Williams, 1941), obtained from a linseed oil-lime rosin varnish suspended in casein. Afterwards, styrene-butadiene emulsions were commercialized (Dow Chemicals, 1946).[6,7] However, it was only in 1953 that an acrylic emulsion was commercialized: Rhoplex AC-33 (US) and Primal AC-33 (Europe) (Röhm and Haas), although acrylic emulsions had been already commercially available since 1925 for waterproof leather coating and textile finishes. Many improvements were done afterwards to acrylic emulsion paints by adding different polymers and copolymers (such as styrene-acrylic and vinyl-acrylic resins) and by the incorporation of additives.[4,5]

Vinyl resins consist of a smaller class of synthetic resins and refer only to polymers of vinyl chloride and vinyl acetate along with their copolymers, modified polymers and derivative products. Bauman discovered poly(vinyl chloride) (PVC) in 1872, while poly(vinyl acetate) (PVAc) was discovered by Klatte and Rollet in 1913.[4] There was not much commercial interest in vinyl resins since these homopolymers are far too brittle to be used alone, although PVAc was being developed for its potential adhesive properties. In 1928 Reid presented the copolymerization of vinyl acetate with vinyl chloride, resulting in a resin with improved properties, able to be used as lacquers and plastics.[8] At the same time, W. Semon at B. F. Goodrich Co. was doing progress in plasticizing these polymers. In particular, he discovered that tricresyl phosphate (TCP) and dibutyl phthalate (DBP) were effective plasticizers for PVC.[9] In the mid-1940, PVAc emulsions made its appearance as a commercial product for paint industry, available from DuPont Co. and others. Starting from the 1960s, the plasticization of PVAc is done with the copolymerization with highly branched vinyl esters (commercially known as VeoVa®).[4]

2.2.2. Modern artists' paints

Mexican muralist Siqueiros, after his leading workshop "A Laboratory of Modern Techniques in Art" in 1936 claimed:[1]

"*I am the first artist to lay claim to the use of painting materials with a synthetic resin base. And already at this moment there are at least some fifty American or America-based painters who are following my example. What will happen when all the painters in the world (...) grasp the convenience of using these modern materials?"*

Siqueiros was pioneer in using coating paints that were commercialized for domestic or industrial uses, for artistic purposes. In fact, other artists proceeded with this experimentation: Pablo Picasso and Jackson Pollock used alkyd resins for household in the mid-1950, and others used commercially available PVAc emulsion paints.[1,4,10]

In 1947, the first line of artists' acrylic paints in turpentine solution was introduced by the paint maker Leonard Bocour with Sam Golden, commercially known by Magna, used by important twentieth century artists, such as Roy Lichenstein. However, it was in 1956 that an acrylic emulsion line for artist's use was produced, trademarked Liquitex, by Henry Levison from Permanent Pigments Co., based on the copolymer poly(ethyl acrylate/methyl methacrylate). Only after its reformulation in 1963 to a thicker form, in order to be commercialized in tube paint, it was widely adopted by artists, due to its fast dryness, non-toxicity, intense colors and apparent durability. After this, manufacturers developed many other resin lines used for artists' acrylic paints, mostly after 1964, such as Primal (AC-22, AC-34, AC-234, AC-634) from Röhm and Haas and Plextol B-500 from Röhm. Acrylic emulsions' formulations have been modified since then. In the early 1960s styrene was copolymerized with acrylic esters as low-cost paint grades (e.g. Brera paint from Maimeri, a terpolymer of styrene, *n*-butyl methacrylate and 2-ethyl hexyl acrylate). In the late 1980s artists' acrylic emulsion paints were converted to p(*n*-butyl acrylate/methyl methacrylate) type (e.g. Primal AC-235, AC-2235 from Röhm and Haas).[11,1,10]

Table 2.1 General information about the three most important synthetic resin classes.[10]

Synthetic resin	Chemical composition	Date of first appearance	Name of grade/Paint maker	E.g. of early modern artists using it
Acrylic	**p*n*BMA** (solution)	1947	**Magna®** / Leonard Bocour and Sam Golden	Roy Lichenstein Morris Louis Kenneth Noland
	p(EA/MMA) (emulsion)	1956	**Liquitex®** / Henry Levison (Permanent Pigments Co.)	Patrick Caulfield Helen Frankenthaler David Hockney John Hoyland Robert Motherwell Bridget Riley Andy Warhol
PVAc	**PVAc** (emulsion)	1954	**Flashe®** / Lefranc & Bourgeois	Sydney Nolan Kenneth Noland Bridget Riley
Alkyd	**Polyol / polybasic acid / drying oil**	1970	**Griffin®** / Winsor & Newton	Gillian Ayres Peter Blake Patrick Caulfield Ben Nicholson Francis Picabia Pablo Picasso Jackson Pollock Pierre Soulages Frank Stella

Note: p*n*BMA=p(*n*-butyl methacrylate); p(EA/MMA)=p(ethyl acrylate/methyl methacrylate); PVAc=poly(vinyl acetate).

As for alkyd resins, artists used mainly the already available household paints. There is only one alkyd's grade of artist's quality, marked Griffin (Winsor & Newton, 1970), even though alkyds are also present in the commercialized oil artist's paints. PVAc emulsions, on the other hand, were not so embraced by artists, as were other acrylic emulsions. Only after the 1960s, when softer formulations of PVAc copolymerized with VeoVa® monomers were available, did these paints gain some interest by artists. Paint manufacturers introduced then artist's paint grades based on vinyl emulsions, such as Spectrum and Rowney and vinyl-acrylic copolymer emulsions, such as Reeves and New Masters. Nowadays, the only remaining PVAc emulsion paint is Flashe (Lefranc & Bourgeois, 1954).[10] Particular is the case of nitrocellulose that, even if its occurrence was limited in artists use, it was one of the main binders in enamel spray paints, which were also used by artists, for example, Richard Hamilton.[1,11]

In table 2.1 there is a summary of the most relevant artist's paints and their description, along with some examples of modern artists that used that synthetic resin classes (either artist or household grade).

2.3. Chemical nature

Due to the variety of synthetic resins used by modern artists, as well as their intense experimentation of the newly available products at the same time as their were being developed and improved by paint manufacturers, it is important to know the chemistry of these materials and how an synthetic resin-based paint is made of, in order to understand their behavior with ageing or with cleaning procedures. Pigments will not be described in this work, since their influence on the cleaning issues discussed in this thesis is minimal.

2.3.1. Acrylic resins

The term "acrylic" covers a wide range of high molecular weight polymers based on acrylates and methacrylates, which are, respectively, the esters of acrylic acid and methacrylic acid. Acrylic paints are thermoplastic products, meaning that they undergo film formation just by evaporation of the solvent, which is water, in the case of emulsion paint. Acrylic homopolymers vary much in their physical properties, mostly because of the chain length of the alcohol group. This is related to the glass transition temperature (T_g) of the polymer, which defines the temperature at which it passes from a glassy to a rubbery state. Moreover, considerably under the T_g, the polymer exhibits an excessive brittleness, while much over it is tacky and may incorporate dirt.

The most relevant homopolymers for making paints are presented in figure 2.1. The only homopolymers that have a T_g suitable for application purposes are the pBMAs. More specifically, the p*n*BMA resin is the polymer in solution of Magna paints.[1,12]

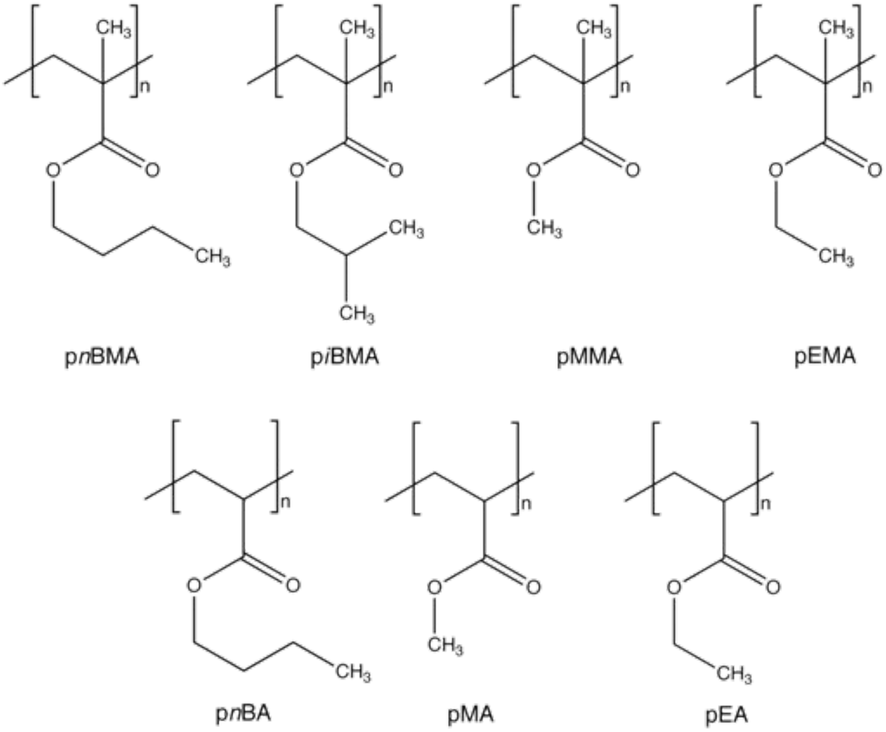

Figure 2.1. Molecular structures of some acrylic homopolymers of interest for artist's paints. In the first row the methacrylates: BMA=butyl methacrylate; MMA=methyl methacrylate; EMA=ethyl methacrylate. In the second row the acrylates: BA=butyl acrylate; MA=methyl acrylate; EA=ethyl acrylate.

On the other hand, acrylic emulsions are usually composed by copolymers and terpolymers. In fact, the combination of the single properties of other acrylates and methacrylates can be done by copolymerization (or terpolymerization. For example, the copolymerization of EA or *n*BA with MMA result in a copolymer with suitable properties for emulsion paints, with a T_g around 12ºC.[1] Changing the ratios of the two/three components, adjusts the T_g of the final paint. For example, acrylic media from Primal series combine the harder methyl methacrylate (MMA) with the softer ethyl acrylate (EA) to create the required working properties, such as flexibility and durability. Over the years p(EA/MMA) have been substituted by p(*n*BA/MMA) since the latter is more hydrophobic, which is specially important for outdoor paints.[11]

2.3.2. Vinyl resins

The vinyl resins classification do not refer to polymers containing the vinyl functional group (H2C=CH–), as the name suggests, but a simpler designation given in the plastics and coatings industries to refer to products derived from PVC and PVAc polymers. The most important vinyl resin to consider in artists' paint is the PVAc resin, whose structure is shown in figure 2.2.

PVAc homopolymer alone is too hard to form a continuous film from an emulsion, so normally the addition of plasticizers or the copolymerization with softer polymers has been proposed. An example was the addition of plasticizer dibutyl phthalate (DBP) in the range of 10-20% w/w.[13] However, this plasticizer tended to migrate to the surface.[14] Another more recent approach was the copolymerization of PVAc with the highly branched C_9 and C_{10} vinyl esters, commercially known as vinyl versatates, or VeoVa®. The carbonyl of the vinyl ester structure permits its copolymerization with vinyl acetate and the resulting copolymer is softer than the PVAc homopolymer.[11]

The PVAc emulsion paints, comparing to acrylics, are generally considered to be slightly inferior for what respects the toughness and binding power. On the other hand, they are less expensive and suitable for interior use.[1]

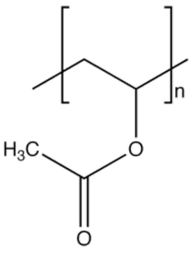

Figure 2.2. Molecular composition of poly(vinyl acetate).

2.3.3. Alkyd resins

Alkyds are composed by a polyhydric alcohol and a polybasic carboxylic acid to form a polyester backbone, which can be modified in order to obtain a more flexible polymer, by lowering its degree of cross-linking through the addition of a third component, a monobasic fatty acid that act as dangling chains. The resulting polymer is, then, an oil-modified alkyd (also referred as synthetic drying oils). The term "alkyd" is the combination of "al" of alcohol and "cid" of acid that was afterwards changed to "kyd" for euphony.[4]

The most important polyhydric alcohols used in alkyd resins are glycerol and pentaerythritol. As for the polybasic carboxylic acids the most common is dibasic acid phthalic anhydride. The monobasic fatty acid source may be a drying oil (e.g. linseed and soy oils). The oil/resin ratio, or "oil length" is an important feature to identify the alkyd type. In fact, it determines the solubility of the paint. Example of a representative alkyd resin is shown in figure 2.3, containing in its structure phthalic anhydride, glycerol and linoleic acid. Some modifications are made to alkyd paints to improve certain properties. The most common are the addition of styrene, vinyl toluene, isocyanates, acrylic, epoxy, or silicone compounds.[1]

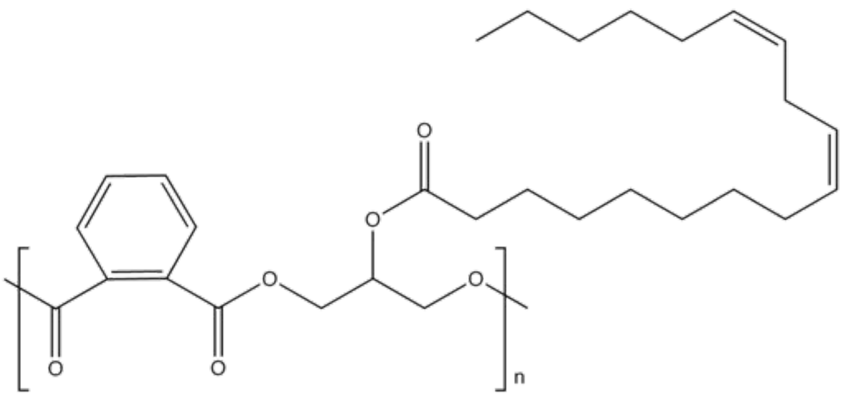

Figure 2.3. Example of a common alkyd molecular structure containing phthalic anhydride, glycerol and linoleic acid.

2.3.4. Other synthetic resins

A small remark should be addressed to other synthetic resins, since they may also be present in artworks. An example is nitrocellulose, which is the term applied to paints and lacquers that contain mixtures of cellulose nitrate polymer with a second resin, usually alkyd, to improve gloss, adhesion and hardness, and plasticizers, usually phthalates (e.g. dibutyl phthalate and dioctyl phthalate). Additionally, polyurethane, epoxy and silicone resins, may as well be bound as main binder in paint formulations, however, these kind of paints are usually too expensive to be used by artists, since their formulations are addressed for coating that require high durability and weather resistance.[11]

2.4. Paint formulation

2.4.1. Solvent-based paints

Solvent-based paints can be presented as varnishes, enamels or lacquers, and are based mainly by alkyds and nitrocellulose, but also by epoxy, acrylic and polyester resins. These paints are based on polymers dispersed or dissolved in an organic solvent, which content in the paint is usually high (>60wt%) to permit a low viscosity of paint. Examples of solvents are aliphatic hydrocarbons, aromatic hydrocarbons, esters, alcohols, ketones, and glycol ethers. The most widely used solvents are toluene, xylene, methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK). The solvent portion of the paint evaporates after it has been applied, letting the paint film to cure as the evaporation takes place. The curing of the paint film is normally a physical process, except for some binders, such as alkyds, where there is also a cross-linking effect by oxidation of the hydroxyl groups.[15]

2.4.2. Emulsion paints

Emulsion paints are the most used kind of paints in contemporary paintings and because of their extremely complex system they are explained here in detail. Emulsion paints are waterborne paints on which water acts as the dispersing agent of the polymer in the presence of an appropriate surfactant and additives for stabilizing the system. These paints are produced through an emulsion polymerization process, where the solid polymer fraction is high (50-60wt%).[15]

2.4.2.1. Emulsion polymerization process

The water dispersion in the early state of emulsion polymerization (see figure 2.4) contains an initiator, which forms free radicals, droplets of monomer, which are emulsified by a surfactant, and micelles containing monomer. Monomer molecules are expected to be also soluble in the water phase. The polymerization reaction is carried out under agitation, so when the polymerization is in the propagation phase it leads to formation of growing polymer particles stabilized by the surfactant. To readjust emulsion equilibrium, surfactant stabilizing monomer droplets is transferred to the growing polymer particles. Consequently, monomer molecules in the droplet are moved into the water-phase to react in propagation phase with the growing polymer particles or to form new ones. After polymerization the remaining surfactant becomes absorbed by the polymer particles in the polymer/water surface interface.[1]

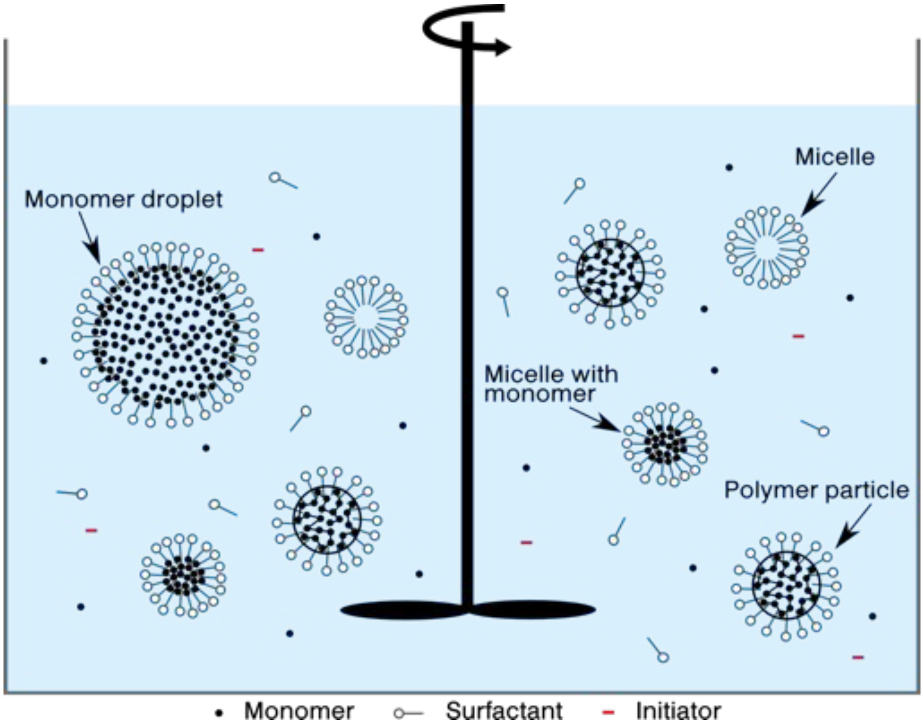

Figure 2.4. Schematic not to scale representation of an early state of emulsion polymerization (adapted from[1]).

2.4.2.2. Surfactants

Surfactants are an important additive in emulsion paints, since not only they reduce the surface tension of water, improving wetting of the paint, they also nucleate and stabilize the formed polymer particles in the water dispersion. Surfactants are normally added in 2-6wt%, and the most common are nonionic (e.g. nonyl phenol ethoxylates and alkyl phenol ethoxylates) and anionic, such as alkyl or aryl sulfates and phosphates of carboxylic acids. Mixed nonionic-anionic systems can also be found.[1]

In the past two decades surfactants with reactive groups are being used during polymerization as comonomers (also named surfmers), to improve paint characteristics.[17,18] This copolymerization is also intended to avoid migration of the surfactant, once the paint film is formed.[19] The physical-chemical characteristics of surfactants will be detailed further in chapter 3, as an important component of micellar solutions and microemulsions.

2.4.2.3. Film formation

The film formation occurs when a polymeric suspension gradually passes from a liquid stable dispersion to a continuous and dry film, via evaporation of water and other volatile paint components (such as coalescing agents). There are three different stages during the physical process of film formation: (1) evaporation of water and particle ordering; (2) particle deformation; and (3) inter-diffusion of polymers across particle-particle limits (see figure 2.5). Particle deformation occurs after water has been evaporated to form denser packing, in which the spherical particles assume a rhombic dodecahedral form. Afterwards, coalescence of the particles may take place, especially if there are no outer membranes in the polymer particles. The process of coalescence is here defined by an irreversible process of fusion of neighboring polymer particles by the inter diffusion of the core polymer, reflected by the breakage of the outer membranes. It is in this phase that surfactants tend to migrate from the core of the paint film.[20]

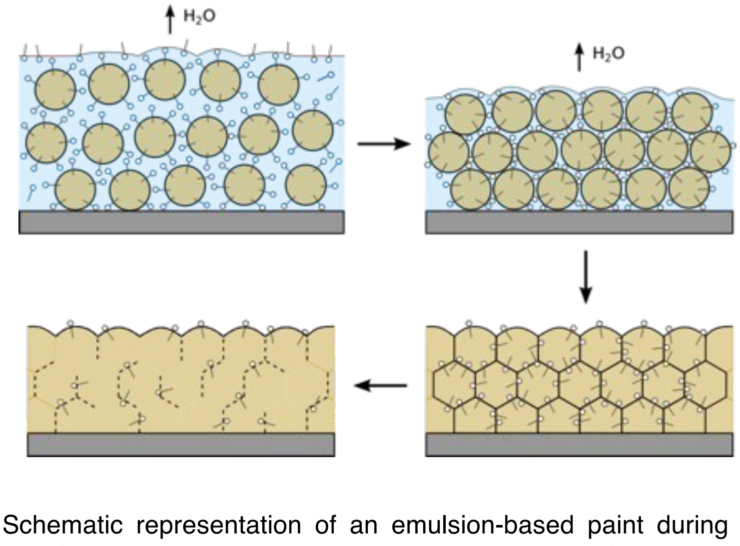

Figure 2.5. Schematic representation of an emulsion-based paint during film formation process. From left to right, according to arrows: early stage of applied emulsion paint; evaporation of water and particle organization; particle deformation occurring in the dried film; coalescence of polymer particles (adapted from[16]).

2.4.2.4. Additives

As stated before, the physical properties of the final paint can be adjusted just by copolymerization with a proper polymer or polymer blending. However, the polymer combination alone is not enough to give stability to the paint, mainly for what concerns protection from photo degradation, heat/cold, microorganisms attack, etc. In paint emulsions, mostly acrylic and vinyl base, additives are also important to consider since they improve specific properties and stabilize the forming emulsion paint. In particular, additives promote protection that may reflect in the maintenance of the optical and mechanical properties for a long time. Furthermore, almost all additives added remain in the dry paint film, so they may influence the paint behavior in the presence of cleaning systems.[1,21]

In general, paint emulsions can have a wide list of different additives, from the ones used specifically for the emulsion in the polymerization phase (e.g. pH buffers and protective colloids) to additives with the function of achieve certain paint features (e.g. coalescing agents, preservatives and thickeners). In fact, paint's characteristics can change significantly depending on which additives are present. Some of additives and their functions are schematized in table 2.2.

2.5. Effects of modern paints' ageing

According to literature[23–26], synthetic resins and, in particular, acrylic resins are considered to be resistant to ageing and to mechanical stresses if correct storage conditions are maintained. However, ageing processes and effects on the physico-chemical conditions of these materials are not yet well understood, mostly due to the variety and complexity of the paint systems.

Studies on the durability of synthetic resins in the field of conservation started in the mid-50s, when Feller presented data regarding the durability of acrylic polymers as potential materials for conservation varnishes. He observed cross-linking of methacrylates during an accelerated ageing experiment (ultraviolet radiation at 60ºC) that reflected in a decrease in polymer solubility.[27]

The two main causes of chemical degradation of polymers are hydrolysis and photo-oxidation. The photo-oxidation caused by the ultraviolet radiation may reflect in yellowing and loss in tensile strength, by the formation of reactive hydrogen peroxide that leads to chain scission and polymer oxidation. Acrylic polymers that have branched side chains with tertiary –CH groups, such as p*i*BMA, are expected to be more susceptible to photo-oxidation.[23,25]

Table 2.2. Common additives found in emulsion formulations.[1,22]

Additive type	Function	Examples
Antifoams	Reduce foam caused by surfactants, by lowering surface tension.	Dibutyl phosphate; Short chain alcohols; Mineral or silicon oils.
Coalescing agents	Reduce the minimum film-formation temperature to a temperature lower than the T_g.	Slow evaporation solvents: glycols; glycol ethers.
Dispersing agents	Aids the dispersion of pigments in the binder, by anchoring pigments surface to the solvent polarity.	Sodium and ammonium salts of poly(acrylic acid).
Freeze-thaw controllers	Lower the freezing point of water to avoid irreversible polymer coagulation.	Ethylene glycol; Propylene glycol.
pH buffers	Adjust the pH of the water system to alkaline.	Ammonia.
Preservatives	Prevent microbial growth.	Organo-mercurial and organo-tin biocides; Benzisothiazolinone derivatives.
Protective colloids	Enhance the emulsion stability during polymerization by avoiding agglomeration or flocculation	Cellulose derivatives; Poly(acrylic acid); Poly(vinyl alcohol)
Thickeners	Increase thickness of emulsion, by chain entanglement due to the formed hydrogen bonds.	Cellulose derivatives.

A relevant parameter to consider is the T_g of the paint. While in museum conditions this hardly effects on the physical integrity of paintings, in other conditions it may cause damage to the paint layers. In fact, if environment temperatures are high above paint's T_g, it becomes tacky and can easily capture air dust. On the other hand, at temperatures around and below 0ºC, the paint film may harden and become brittle or even crack.[25]

Since indoor (e.g. in museum conditions) and outdoor paintings (e.g. mural paintings) have different degradation processes, each one will be detailed separately.

2.5.1. Indoor paintings

Museum conditions are expected to be ideal for the long-term conservation of painted artifacts, since they limit daylight exposure and maintain constant temperature at around 24°C and relative humidity (RH) at ca. 50%. However, these conditions not always satisfy the demands of each single contemporary painting due to paint's different T_g's. One of the main concerns in conservation of this kind of paintings of indoor exposure is the dust pick-up. This may be induced by many factors, such as the static charge accumulation of resin paints that attract dust from the air; softening of the resin that entraps the air deposits and by the presence of migrated surfactants on the surface that, being hygroscopic, at certain RH can imbed soil particles and create a tacky grime layer.[26]

It is known that nonionic surfactants, in particular poly(ethylene oxide)-based surfactants (e.g. Triton X-100, an octyl phenol ethoxylate), may indeed migrate to the surface or to the paint layer/substrate interface.[16,26,28–30] This process is initiated shortly after film formation.[28] Surfactant migration has been observed also after only 1 year with p(*n*BA/MMA) Golden paint grade.[31] The main causes for surfactant migration have also been reported and may be surface tension of the substrate, water-flux during film formation, affinity between emulsion components and Tg.[32] The surfactant that is crystallized in the surface of a paint film is light sensitive, hygroscopic and soluble in water.

Studies have been carried out in order to study the influence that these water-miscible components have on the dried paint film. Hagan et.al.[31] have observed that surfactant washing-out cause a decrease in the elastic modulus in rubbery region.

2.5.2. Outdoor paintings

Many of the industrial synthetic resin paints (solvent-based and waterborne) were developed specifically for exterior use. The promise of paint durability and resistance to weathering had encouraged many artists to use these modern paints, which can be used for exterior sculptures and mural paintings. In particular, acrylic paints can form a semipermeable membrane that allow water vapor to pass through the wall or cealing.[24,33] Mural paintings are usually executed on cementitious materials. Acrylic-based paints have been applied on these cementitious surfaces because of their good adhesion to the alkaline substrates.[24]

The degradation of mural paintings is quite different of indoor paintings, since subject to severe atmospheric conditions (direct sunlight and rain). Evidences of painting degradation have been observed, such as cracks, chalking and discoloration of paint layers[34] (see for example the case of Keith Haring's mural painting in figure 2.6). Comparison of weathering resistance between vinyl, acrylic-styrene and acrylic paints have been carried out, which confirmed that vinyl paints are more susceptible to UV-induced degradation, mainly upon ester cleavage reactions and hydrolyzation, with formation of acetic acid.[35,36] Nonetheless, chain scission and photo oxidation of acrylic and acrylic-styrene paints have also been individuated.[34] Other major problem in mural paintings is associated with the acrylic paint permeability, since water-miscible pollutants can pass through and may remain trapped within the paint film.[24]

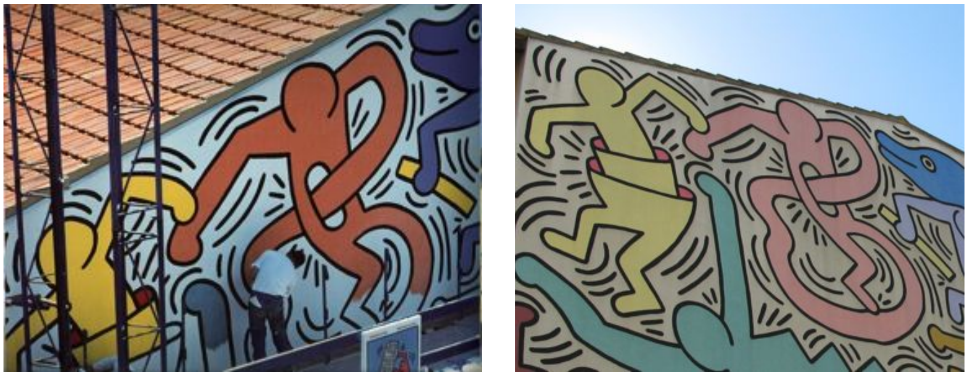

Figure 2.6. Keith Haring mural painting *Tuttomondo* in Pisa, Italy, during its making in 1989 (left) and 22 years later (right), where discoloration of paint is clearly visible.

2.6. Cleaning issues

Modern and contemporary paintings present indeed new concerns in cleaning interventions. Synthetic resin-based paints are, foremost, very sensitive to organic solvents since they may change surface texture, color or gloss by solubilization or swelling processes. A major concern is, likewise, related to the cleaning with water-based systems due to the possible interactions that water molecules have with polymeric materials, leading to swelling of dried paint films. Moreover, water and other solvent systems may lead to the extraction of paint components, so it is important to know whether the loss of these components contributes to any subsequent physical damage of the paint films.[37]

The need to evaluate changes in the physical properties of modern paints that may occur as a result of standard conservation cleanings, has recently been identified as a priority in cultural heritage conservation and preservation.[37] Several studies have been carried out concerning the study of the effects of wet cleaning, mainly in acrylic paints.[16,38–42] Recently research is being carried out in order to test effects and efficiency through the use of new cleaning systems based on commercial microemulsions.[43]

During a census[45] to determine the most commonly used methods and materials used by painting conservators in their treatment of acrylic paintings it was confirmed that there is not a deep knowledge on the materials to use and their interactions with surfaces of contemporary paintings. The major concerns that restorers had were the difficulty of grime removal, the sensitivity of the paint, leaching during aqueous cleaning, identifying the specific components of the media, the application and future removal of varnishes and the protection of unvarnished paintings from deterioration.[26]

Figure 2.7. Mural painting “Pulp Fiction Bananas” of Banksy at Old Street, London, in 2007 (above) and after a complete overpainting (below).

2.6.1. Removal of overpaintings

Overpaintings removal from contemporary paintings is up to now the most challenging problem in the conservation field. In fact, overpaintings are usually found to be of the same chemical nature of the underlying original paint layers. Finding overpaintings in contemporary art is surprisingly very common by several reasons, such as vandalism, ignorance of the artwork value, lack of knowledge on the materials and controversial ethical points of view (examples in figures 2.7-8).

Therefore, the major problem concerns the difficulty on the selective removal of the overpaints that are quite similar in composition to the original layers. The sensitivity of acrylic emulsion paint films to organic solvents clearly limits a conservator's choice of cleaning techniques.

Figure 2.8. Canvas painting "Black on Maroon" (1958) of Mark Rothko, vandalized with graffiti ink in October 2012. Restoration took place in 2014 using solvent blends.[44]

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CHAPTER 3

Nanostructured Fluids: Advanced Tools for Cleaning Cultural Heritage Artifacts

3.1. Introduction

Nanostructured fluids (shortly nanofluids) have a growing impact not only in the industry, but also in biotechnology and nanotechnology research. However, the detergency capacity is still, the most important feature of these systems. In fact, in the past decades, microemulsions and micellar solutions have been developed specially for the cleaning of Cultural Heritage artifacts, as much more viable tools with respect to the use of solvent technology by restorers. The combination of the advantages provided by nanofluids with the confining features of gels, gives rise to highly efficient cleaning tools. Nanofluids characteristics are briefly presented in this chapter, although it is not the main argument of this dissertation. In fact, nanofluids are relevant to introduce, due to their active cooperation with gels in the cleaning process of artifacts.

Surfactants, as active molecules in increasing the detergency capacity of liquids, are described, along with their classification and physico-chemical properties. Formation of micelles is an important factor for having a surface-active system, so subjects such as micellization process, micelle characterization and detergency are briefly described as well. A natural result of the dispersion of micelles in a fluid is the production of a nanostructured fluid with increased detergency properties. Relevant examples of these systems are microemulsions, which allow the isolation of an oil phase (e.g. organic solvent) from an aqueous phase and, therefore, allow the efficient cleaning of non-polar components using a solvent-confined system with reduced solvent amount. Examples of the use of these systems in the cleaning of Cultural Heritage artifacts are presented.

3.2. Solubilization process

First of all, to understand the thermodynamics involving a cleaning process, it is important to generally describe the solubilization process using pure and mixed liquids. It is natural to firstly make reference to the known phrase “like dissolves like”, as will be explained further. In general, a solubilization occurs when a liquid solvent dissolves a substance to form a homogeneous solution. In other words, when the attractive forces between liquid solvent and substance prevail over the cohesive intermolecular forces of the substance, then the solubilization process takes place. From the thermodynamic point of view, the solubilization by a solvent (S) of the substance (A) occurs spontaneously when the variation of the Gibbs free energy of the process (ΔG_{solub}) is negative:[1]

$$\Delta G_{solub} = G_{SA} - G_{SS} - G_{AA} < 0 \tag{3.1}$$

where G_{SA} is the Gibbs free energy of the solution, and G_{SS} and G_{AA} are the Gibbs free energies of the pure solvent and the pure solute, respectively.

There are three attractive forces influencing the solubilization process, according to the theory of intermolecular interactions: hydrogen bonds, dipolar interactions and dispersion forces.[2]

3.2.1. Polarity of solvents

According to the theory proposed by Hansen in 1966,[3] the interaction forces between A and S molecules are additive, that means that the cohesive energy density δ_t^2 for a solvent is given as a function of the three partial solubility parameters: δ_d, referred to dispersion forces, δ_p, referred to dipolar interactions and δ_h, referred to hydrogen bonds. The Hansen’s parameters can be represented in terms of fractional solubility parameters, as calculated elswhere,[1] f_d, f_p and f_h, respectively, where $f_d + f_p + f_h = 100$. The more similar are the singular fractional solubility parameters of two distinct substances (a solvent and a solute), the more mutually soluble they are.

3.2.2. Teas diagram

The fractional solubility parameters were introduced in order to provide the possibility of graphing Hansen parameters in a triangular diagram, named Teas diagram (see figure 3.1).[4]

This diagram is a very useful tool in restoration practice, since in most cases a selective removal is desirable. A selective removal, in this context, is intended as a choice of a solvent that has solubility parameters as similar to the substance to remove, while, at the same time, as different to the artifacts surface, in order to avoid solubilization processes of any kind with the materials to preserve. Solvents are situated in the Teas diagram according to their solubility parameters. Hydrocarbons, for example, are at the lower right corner, due to their non-polar feature, while ketones, being highly polar, are situated up along the left side of the diagram. A cleaning system composed by the mixture of solvents has a different position in the diagram with regard to the position of the singular solvents. It gives the possibility to choose of the optimal cleaning tool, in terms of both cleaning efficiency and toxicity of the solvents used.[1]

The Teas diagram solubility/swelling of various solid substances (e.g. polymers) is given In the literature.[5] It is possible to predict the solubility of a given substance using the Feller test, as described here:[1,6]

- Preparation of 13 mixtures composed of different amounts of cyclohexane toluene and acetone, which are thus characterized by different polarities;
- Application of the mixtures (by means of a cotton swab roll) onto 13 small areas of the painted surface, in a region representative of the surface conservation status;
- Identification of the mixture that provides the best performance by means of visual analysis;
- Choice of a solvent or solvent blend having a f_d value equal to the one of the best mixture. At this point, the main criteria that drive the choice of the solvent or blend are the low toxicity and the high volatility.

3.3. Nanostructured fluids

Nanostructured fluids (shortly nanofluids) are described in general as macroscopically homogeneous mixtures of oil, water and surfactant. They can be microemulsions or micellar solutions and present completely different features over emulsions, as they are thermodynamically stable systems based on surfactants self-assemblies. In the context of this thesis a difference between microemulsions and micellar solutions is made, that is, in the case of the firsts it is referred to a system where the oil is completely separated from the water by a monolayer of amphiphilic molecules, while micellar solutions are referred to systems where some part of the oil is water-soluble, and, consequently it is to some amount present in this phase.

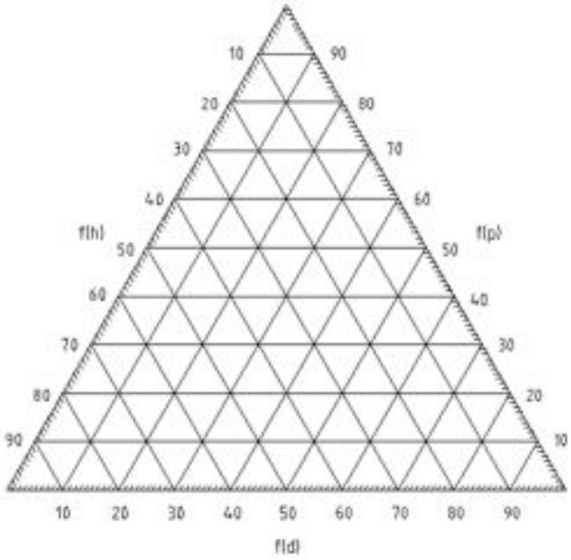

Figure 3.1. Teas diagram in function of the three fractional solubility parameters related to dispersion forces, f_d, dipolar interactions, f_p, and hydrogen bonds, f_h.

3.3.1. Surfactants

The term "surfactant" is a short word for the meaning "**surf**ace **act**ive **a**ge**nt**", which refers to a class of organic molecules that interact greatly at the interfaces, altering their physical-chemical properties. A common example regards the readily decrease of water surface tension when a surfactant is added. All surfactants are amphiphilic molecules, that is "oil and water-loving" molecules, because combine both polar and non-polar group into a single molecule, which makes them very versatile compounds with double affinity to different substances.[7] In the case of aqueous dispersions, these are commonly defined as hydrophilic and hydrophobic fractions, respectively.

3.3.1.1. Classification

Surfactants properties can vary widely, depending on the chemical composition. In fact, several different compounds exist by varying the combination of the two fractions of the surfactant: the “head” (polar group) and the “tail” (non-polar group). The head group can be charged or neutral, small and compact in size, or a polymeric chain. The tail group is usually a single or double, straight or branched hydrocarbon chain, although it may also be a more complex molecule, such as a fluorocarbon or a siloxane, or contain aromatic groups.[7] The simplest way to classify different surfactants is to distinguish the head group, thus, they are usually classified as anionic, cationic, zwitterionic and nonionic, as detailed below. Moreover, with the constant research on improving surfactant properties, new structures have recently been developed with remarkable aggregation properties. These novel molecules include catanionics, bolaforms, gemini surfactants and polymeric and polymerizable surfactants.[8,9]

Anionic. Anionic surfactants are compounds able to ionize in water solutions, originating negatively charged molecular species such as carboxylates ($-CO^{-2}$), sulfates ($-OSO^{-3}$) and sulfonates ($-SO^{-3}$) groups and positive counterions. This class of surfactants represents the first “soaps” of humankind, derived from fats and oils to obtain carboxylic acid that were neutralized with sodium or potassium salts, for example. The most common anionic surfactants are alkyl sulfates, carboxylates, sulfonates, and phosphates, which are moreover, the most used in detergents formulations for domestic use.[7,10]

Cationic. Contrariwise, cationic surfactants ionize in water solution, which produces positively charged molecules and a negative counterion. Simple amine salts, quaternary ammonium compounds, which one or more alkyl chains are attached to, and amine oxides usually constitute the polar head. Cationic surfactants started to gain some importance because of their antiseptic properties, which are used mainly in cosmetics, fabric softeners and hair conditioners.[10]

Zwitterionic. These surfactants (also named amphoteric) are compounds that contain two opposite charges on the same chemical structure. This class of surfactants has unique properties since they often show synergism when combined with other classes of surfactants. In addition, for uses that might involve the presence of charged polymeric species, the opposite charges of these compounds can reduce or eliminate the possibility of undesirable polymer-surfactant interactions. Phospholipids (lecithin) are one of most common examples. They are composed by a complex polar head, constituted by a glycerol group, which is composed by a phosphoric group (carrying a negative charge) and a choline (with a positive charge on the quaternary ammonium), and two alkyl chains. Zwitterionic surfactants are fundamental for biological membranes.[10]

Nonionic. Most of the nonionic surfactants belong to the poly(oxyethylene) family (POE) and are electrically neutral. Surfactants from this class exhibit an inverse temperature-solubility relationship, which means that if the solution temperature is increased, their solubility in water decreases. They can be classified as polyethoxylates fatty alcohols (e.g. Brij 35) and polyethoxylates alkyl phenols. Octyl phenol ethoxylate (commercially known as Triton X-100) is the most famous surfactant of the latter category. Nonionic surfactants are used for domestic purposes, as industrial detergents, and in textile industry.[10]

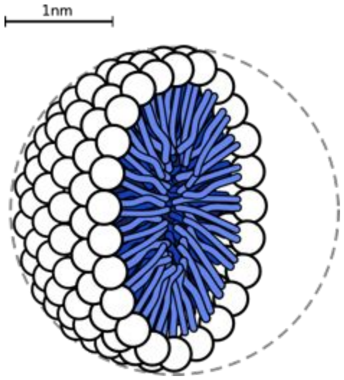

Figure 3.2. The structure of a direct micelle schematized.

3.3.1.2. Properties

The gradual addition of a hydrosoluble surfactant to water leads to the localized concentration of surfactant molecules at the liquid/gas and liquid/solid interfaces in order to minimize the contact between water and hydrophobic chains. At a certain surfactant concentration, a monolayer of oriented molecules is formed, reducing the liquid surface tension. The decrease of liquid surface tension leads to the decrease of penetrating power and capillary rise and to the increase of wetting power. This results from the hydrophobic effect,[11] that is, the expulsion of surfactant non-polar fraction from water, due to the fact that water-water intermolecular attraction is stronger than those between water and tails. Thermodynamics of surfactants adsorption and formation of molecular ordered monolayers at the interfaces has been widely studied.[7]

3.3.2. Micelles

One of the most interesting properties of surfactants is their capability of auto-associate to form supramolecular aggregates. In fact, since the interactions between tail chains and water have to be minimized, at a certain surfactant concentration, hydrocarbon tails of surfactant molecules confine themselves in globular aggregates, where they can only interact with affine groups. This feature is due to the formation of attractive interactions of the hydrophobic kind, such as Van der Waals forces.[7]

Surfactant molecules can form small oligomers or much more complex structures with up to 50-200 monomer units.[7] These aggregates are generally designated as “micelles”. In aqueous dispersions, micelles are termed “direct micelles”. In this case, the inner hydrophobic core is surrounded by a hydrophilic shell, which separates the alkyl chains from water molecules (see figure 3.2).

3.3.2.1. Critical micellar concentration

Micelles form when surfactant concentration in a liquid is above a critical value, called “critical micellar concentration” or *cmc*. If more surfactant is added to a solution at the *cmc*, the monomer concentration in solution remains almost constant, while the number of micelles increases, without appreciable changes in their size. The main factors that affect the *cmc* are related to the chemical structure of the surfactant, to solvent nature, to the addition of ions or other non-electrolytes substances, or to physical-chemical variables as temperature, pressure and pH. These are the main parameters that determine changes in the *cmc*:[12]

- *Hydrocarbon chain length.* The longer the aliphatic chain, the lower the *cmc*. In aqueous solutions *cmc* generally tends to decrease when a CH_2 group is added to the hydrophobic chain of a surfactant.
- *Ramifications and double bonds.* The presence of these groups on hydrocarbon chains leads to an increase in *cmc*.
- *Surfactant polar groups.* The more charges are present on the polar head, the higher is the *cmc*. In particular, ionic surfactants have a much higher *cmc* than nonionic ones.

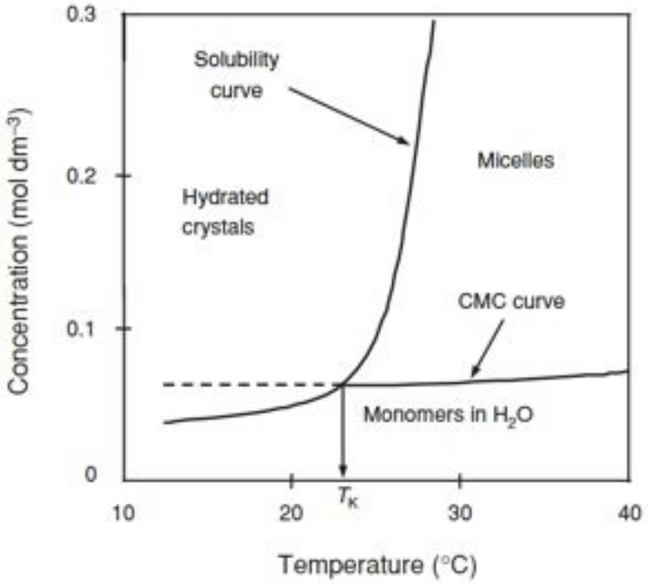

Figure 3.3. The Krafft temperature T_K is the point at which surfactant solubility equals the *cmc*. Above T_K, surfactant molecules form a dispersed phase by micelles formation, while below T_K, hydrated crystals are formed.[7]

- *Electrolytes.* The addition of these to the solution generally leads to a decrease in the *cmc*. Moreover, ionic surfactants are more sensitive to the presence of electrolytes than nonionic ones.
- *pH.* Surfactants with polar head charge may be influenced by the pH.
- *Temperature.* It may have some influence on the *cmc*, depending on the surfactant structure. In particular, in the 10-70°C range, with increasing temperature, the *cmc* tends to decrease to a minimum and, then, it increases again. Below a certain temperature value, called Krafft point (see below), micelles formation does not occur.

3.3.2.2. The Krafft temperature

As for most solutes in water, increasing temperature produces an increase in solubility. For ionic surfactants, which are initially insoluble, there is often a temperature at which the solubility suddenly increases in an exponential manner. This is known as the Krafft point or Krafft temperature, T_K, and is defined as the intersection of the solubility and the *cmc* curves, i.e. it is the temperature at which the solubility of the monomeric surfactant is equivalent to its *cmc* at the same temperature (see figure 3.3).[7]

Below T_K, surfactant monomers only exist in equilibrium with the hydrated crystalline phase, and above T_K, micelles are formed providing much greater surfactant solubility. The Krafft point of ionic surfactants is found to vary with concentration, alkyl chain length and chain structure. Knowledge of the Krafft temperature is crucial in many applications since below T_K the surfactant will not have the desired properties.[7]

3.3.2.3. The cloud point

A particular case concerns nonionic surfactants. Micellar solutions tend to become turbid at a well-defined temperature, the called cloud point, which indicates the temperature at which a phase separation occurs. Above the cloud point, the system consists of an almost micelle-free dilute solution at a concentration equal to its *cmc* at that temperature, and a surfactant-rich micellar phase. Since much larger particles are formed, the solution scatter light, giving rise to a turbid appearance. For nonionic surfactants from the polyoxyethylene (PEO) family the cloud point increases with increasing EO content for a given hydrophobic group.[7]

3.3.2.4. Micellization process

The thermodynamic principle that leads to micelles formation is the same that drives the migration of surfactant molecules to the liquid/solid and liquid/gas interfaces, that is, the interactions between tail chains and water have to be minimized.

Thermodynamics of micellization is a complex process and several models have been proposed.[7,13] However, the general equation related to micelles formation in thermodynamics is still based on Gibbs free energy equation:

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{3.2}$$

At room temperature, the process is characterized by a slight positive enthalpy and an highly positive entropy of micellization. The latter is considered as the main contribution to the negative free energy value. However, large values of ΔH_m would have been expected since hydrocarbon groups are poorly soluble in water.[7] One theory that may explain the controversial values for both entropy and enthalpy is related to the mechanism occurring when alkyl groups are surrounded by water, that is, water molecules may form clathrate cavities, increasing both strength and number of effective hydrogen bonds.[14] Therefore, the predominant effect of the hydrocarbon molecule is to increase the degree of structure in the immediately surrounding water. During the formation of micelles, the reverse process occurs: as hydrocarbon moieties aggregate, the highly structured water around each chain collapse back to ordinary bulk water. This accounts for the apparent large gain in entropy.[15–17]

3.3.2.5. Micelle structure

Several models describe the structure of surfactants supramolecular aggregates. In particular, the Tanford model is a practical tool to imagine the geometry of the surfactant aggregate structure. This model[18] is based on a parameter, named packing parameter (p), which is defined as:

$$p = \frac{v_i}{a_p l_i} \tag{3.3}$$

where v_i and l_i are respectively volume and length of the hydrophobic tail of a surfactant, while a_p is the area of the polar head. In this geometrical approximation, the surfactant is represented as a solid defined by the variables just described. Depending on the value of the packing parameter, and thus on this solid shape, different kinds of aggregates can be described (see figure 3.4):

- $p < 1/3$. Surfactants with one single hydrophobic chain and a big polar head. Resulting aggregates usually are spherical micelles.

- $1/3 < p < 1/2$. Surfactants with a single hydrocarbon chain and small polar head. Aggregates are rod-like micelles.

- $1/2 < p < 1$. Surfactants formed by a big polar head and two hydrophobic chains or one branched and voluminous chain. Aggregates are bilayer structures.

- $p > 1$. Surfactants with small polar head and voluminous double hydrophobic tail. Aggregates are inverse micelles.

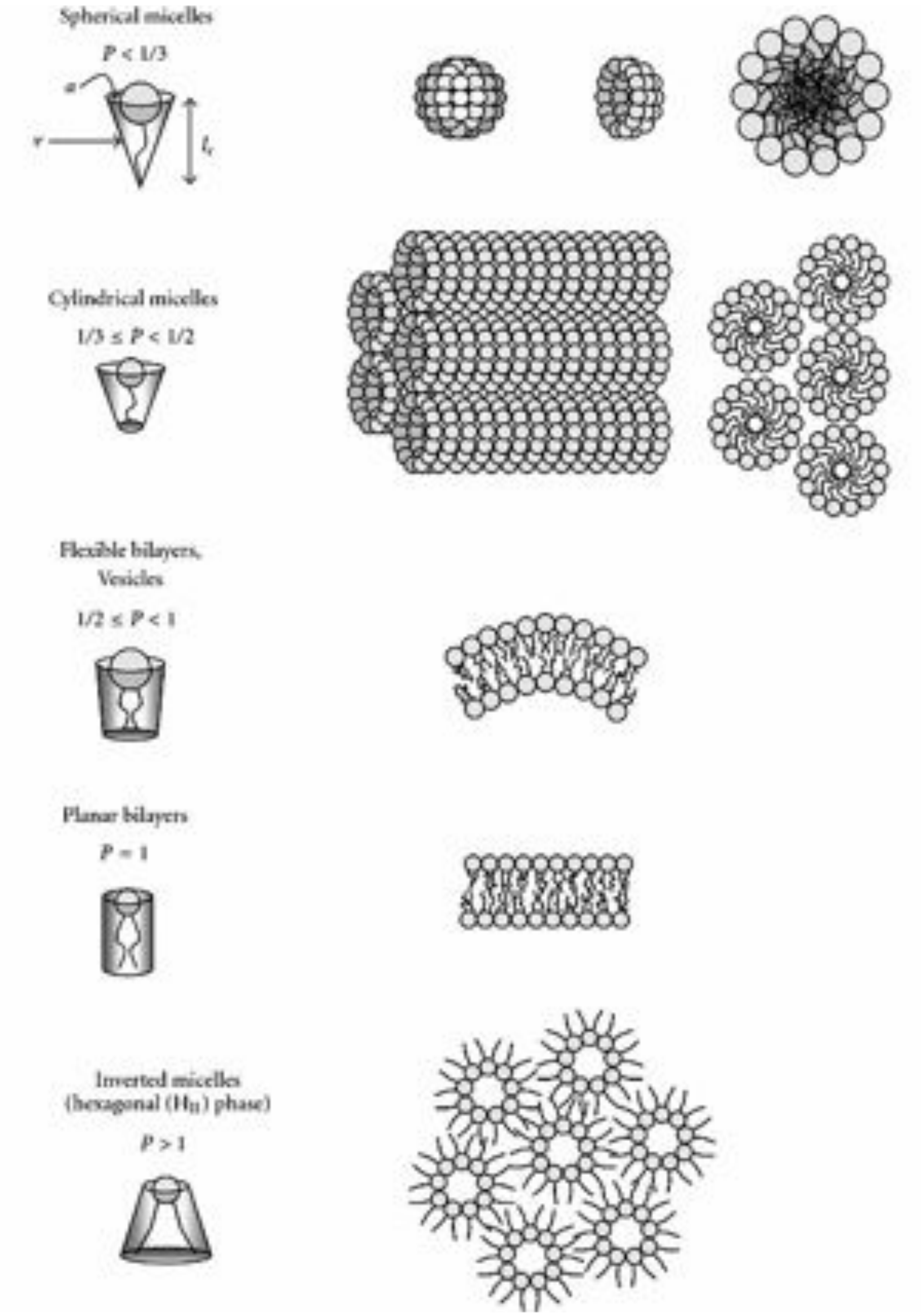

Figure 3.4. The various surfactants molecular structures and consequent shapes of the aggregates upon different values of the packing parameter *p*.[19]

3.3.3. Detergency

An aqueous micellar solution has a great detergent power towards grime and fatty materials. Direct micelles in water are able to capture in their hydrophobic core water-insoluble non-polar molecules, carrying them in the aqueous dispersion. In other words, surfactants can promote the solubilization of insoluble substances in water.

The three most important mechanisms for the removal of oily soil are described below and illustrated in figure 3.5.[20]

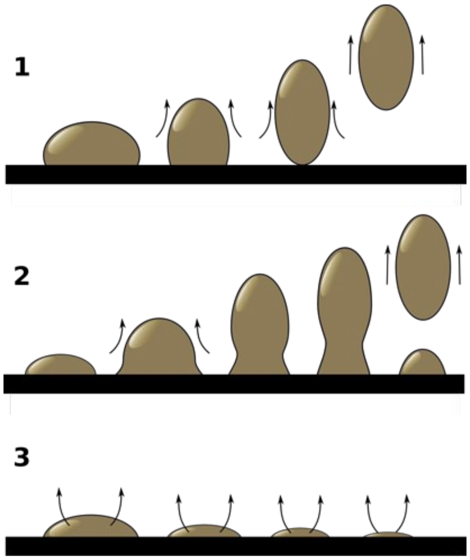

Figure 3.5. The three mechanisms for the removal of oily soils: 1) roll-up; 2) emulsification; 3) solubilization.[20]

- *Roll-up.* This mechanism is mainly related to fabric wetting. Good soil release is usually obtained when contact angle is larger than 90°. This is typically the case of non-polar oily soils on polar fibers, such as cotton.

- *Emulsification.* The mechanism involves surfactant oil interaction and is independent on the nature of the substrate. In this process, low interfacial tension is needed.

- *Solubilization.* The oily soil is solubilized into a microemulsion that is formed locally. This mechanism is independent from the nature of the surface from which soil has to be removed. In this process, a minor interfacial tension between oil and the surfactant solution is needed.

3.3.4. Microemulsions

Microemulsions are another important kind of amphiphiles-based colloidal systems.[21] The definition of microemulsion is not simple because of the complexity of its nature. Nowadays, discussions still arise about whether a system is a complex micellar solution or a true microemulsion. Some definitions have been tried, such as:

"*A microemulsion is defined as a system of water, oil and amphiphile, which is a single optically isotropic and thermodynamically stable liquid solution*".[22]

Microemulsions are, therefore, macroscopically homogeneous and optically transparent, though they are dispersed, discontinuous systems at the nanoscale. Furthermore, they are thermodynamic stable systems that are spontaneously formed.

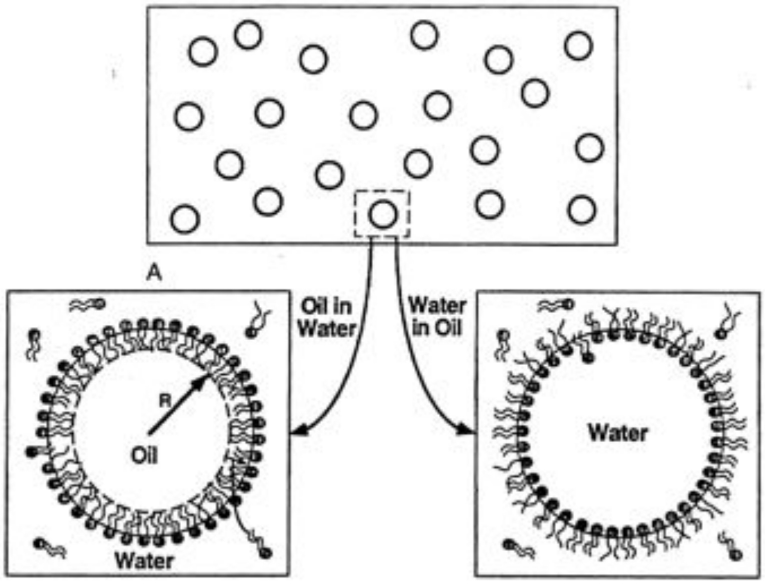

Figure 3.6. Aggregate structure of direct (o/w) and inverse (w/o) microemulsions.[13]

3.3.4.1. Properties

If the dispersed phase is an oil and the continuous phase is water, the resulting microemulsion is designated "oil-in-water" (o/w). Contrariwise, if the microemulsion is inversed, it is called "water-in-oil" (w/o) (see figure 3.6).

A microemulsion usually contains a surfactant and a co-surfactant, which is usually a long or medium-length chain alcohol that lowers the surface tension to extremely low values at the interface water/oil to allow spontaneous emulsification. Co-surfactants also contribute to the thermodynamic stability of the system. The main difference between microemulsions and emulsions is that the first undergo a spontaneous emulsification, while emulsions need a stirring action to emulsify. Other differences are that emulsions are inhomogeneous, form unstable systems and have droplets of higher size (200 nm up to some microns against microemulsion droplet diameter of 5-150 nm).[21] It is because of the nano-size micelles that microemulsions appear transparent.[23] Moreover, microemulsions have a high internal surface, due to the small size of micelles, which makes them extremely reactive.

3.3.4.2. Formation and stability

In a system constituted by two separated phases, oil and water, a surfactant and a co-surfactant, distributed in equilibrium between the two main components, dispersion of one phase to another may be observed. In fact, if this occurs in the form of droplets with same shape and size, the entropy of the system increases and a huge internal surface is formed. This increase in entropy leads to the adsorption of surfactant and co-surfactant at the newly formed interfacial area, which results in a lowering of surface tension at this interface. Assuming that volume variations are negligible and pressure is constant, the variation of total free energy of the system (per unit volume) associated to the dispersion of one phase into another is again given by the Gibbs equation:[21]

$$\Delta G_{form} = \Delta H_{surf} - T\Delta S_{conf} \tag{3.4}$$

or:[24]

$$\Delta G_{form} = \Delta A\gamma_{12} - \Delta TS_{conf} \tag{3.5}$$

where $\Delta A\gamma_{12}$ is the free energy for creating new surface, in which ΔA is the change in interfacial area and γ_{12} the interfacial tension between phase 1 and 2 (i.e. oil and water). ΔTS_{conf} is the configurational entropy change. If the energetic balance of these terms makes a negative ΔG_{form}, the microemulsion is spontaneously formed and the system is thermodynamically stable. This occurs when the variation of free energy (the negative term in equation 3.4) due to the configurational entropy is greater than the positive energy variation associated to the $\Delta A\gamma_{12}$ term, given by the increase in internal surface of the system. This condition is obtained if interfacial tension between oil and water is low enough.

In surfactant-free oil/water systems, γ_{ow} is of the order of 50 mN/m. Since during microemulsion formation the interfacial area highly increases (typically with factors of 10^4 - 10^5), interfacial tension should be very low (approximately 0.01 mN/m),[21] in order to obtain spontaneous formation of microemulsions. Some surfactants (ionic double chain[25,26] and some nonionic[27]) can produce particularly low interfacial tensions, such as 10^{-2} to 10^{-4} mN/m, although most of the available surfactants cannot reach values that low. An effective way to further decrease interfacial tension is to add a second compound (either another surfactant or a medium or long-chain alcohol), which acts as a co-surfactant that co-assists in lowering the interfacial tension to values that lead to the spontaneous microemulsion formation. Considering the free energy ΔG_{form} variation as a function of the dispersed droplets' radius, R, the optimal value of R can be calculated:[28]

$$\left[\frac{d(\Delta G_{form})}{dR}\right]_{R=R_0} = 0 \tag{3.6}$$

if the following condition is satisfied

$$\left[\frac{d^2(\Delta G_{form})}{dR^2}\right]_{R=R_0} > 0 \tag{3.7}$$

which individuates a minimum in the ΔG_{form} function. The formation process of the microemulsion is therefore spontaneous and the system is thermodynamically stable.

Internal contents of the microemulsion droplets are known to exchange, typically on the millisecond time scale.[29,30] They diffuse and undergo collision. If these are sufficiently strong, the surfactant film break and droplets exchange is thereby permitted. In other words, microemulsions are dynamic and kinetically unstable systems. Nonetheless, the shape and size of droplet in equilibrium are always maintained, which can be confirmed by several techniques.[21]

3.3.4.3. Winsor phases

Ternary mixtures formed by water, oil and a surfactant or quaternary systems, in which a co-surfactant is also present, can have different appearances and structures, depending on many conditions (e.g. concentration, temperature and pressure). Winsor described the possible types of microemulsive systems and catalogued them in a model called “Winsor phases”,[31] illustrated in figure 3.7 and described in the figure’s caption:

The simultaneous presence of two microemulsions phases, one in contact with water and other in contact with oil is also possible, and it has been considered as an extension of the Winsor’s classification to a fifth category.[32]

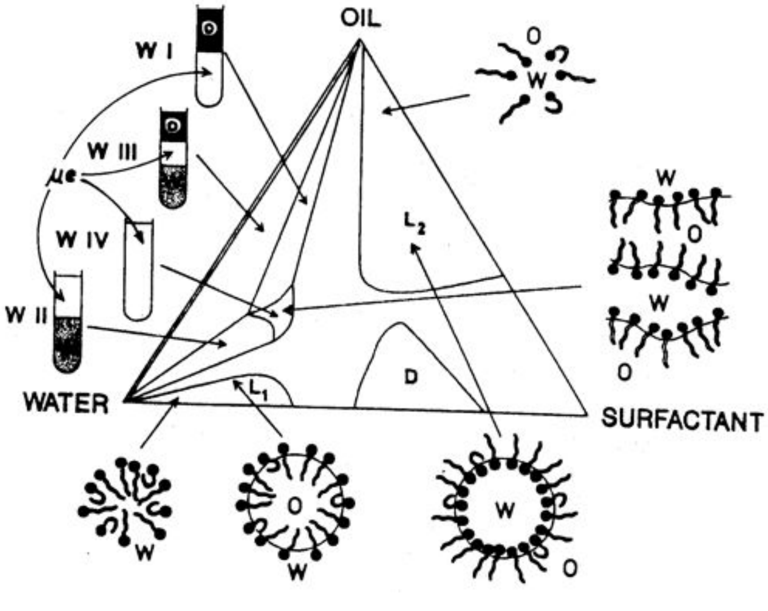

Figure 3.7. Schematic representation of the Winsor phases. **I -** The excess oil, less dense than water, is in equilibrium with an o/w microemulsion (*μ*e). **II -** the excess water is in equilibrium with a w/o microemulsion. **III -** The excess oil upper phase and the excess water lower phase are in equilibrium with a middle microemulsion phase with bicontinuous domains of o/w and w/o microemulsions. **IV -** Macroscopically, oil, water and surfactant are homogeneously mixed in a single phase.[32]

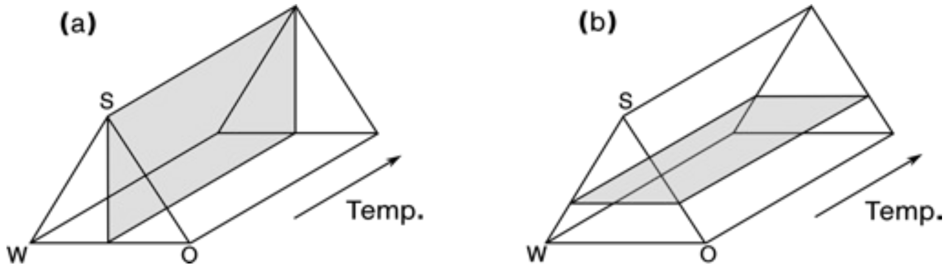

Figure 3.8. Phase prisms illustrating cuts at (a) a constant oil-to-water ratio, and (b) a constant surfactant concentration.[33]

Adjusting the different components proportions or varying the salinity (for ionic surfactants) or temperature (for non ionic surfactants) of a system it is possible to shift from a Winsor phase to another.[21]

3.3.4.4. Phase diagrams

Several types of phase diagrams can be identified depending on the number of variables involved. If the phase diagram is chosen properly, it is possible to describe the limits of existence of single and multi-phase regions and to characterize the equilibrium between different phases.[21]

At constant pressure the phase diagram can be represented as a prism, the so-called "phase prism" (see figure 3.8), which is the result of a triangular diagram translated along the temperature axis.[21]

For simple microemulsive systems, only composed by water, oil and a surfactant, the triangular diagram representation is the most convenient, in which every corner of the triangle corresponds to a single-component systems. At constant temperature and pressure the ternary phase diagram of a simple three-component system is divided into two or four regions, as shown in figure 3.9. In this kind of phase diagrams, every composition that is represented by a point placed above the demixing line is a microemulsion. Composition points below this line correspond to multi-phase regions, such as Winsor I, or II systems. If three phases coexist, the system is of Winsor III kind. If a system is made of more then three components, e.g. a second surfactant or a co-surfactant is present, a pseudo-ternary phase diagram can be used, in which one of the three corner is related to a constant ratio of two components, typically "surfactant + co-surfactant". Pseudo-ternary phase diagrams usually have more complex phase distributions then regular ternary phase diagrams. Several phase diagrams from different longitudinal sections in the phase prism are obtained, e.g. surfactant concentration vs. temperature, with constant oil/water ratio, or oil volume fraction vs. temperature with constant surfactant concentration (see figure 3.8).[21]

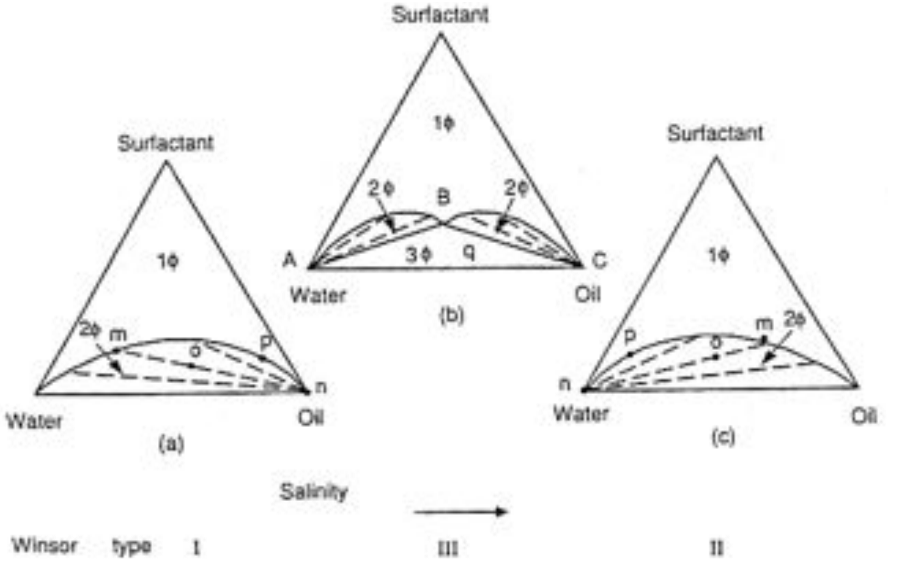

Figure 3.9. Ternary diagram representation of two and three-phase regions formed by simple water-oil-surfactant systems at constant temperature and pressure. (a) Winsor I type, (b) Winsor III type, (c) Winsor II type systems.[21]

3.3.4.5. Microemulsions' detergency

As already explained, a microemulsion may be formed during a cleaning operation with micellar solutions, if the grime is an oil that can be emulsified. Studies about detergency mechanisms seem to demonstrate that the best cleaning performances are obtained using surfactants-based aqueous solutions, which lead to the formation of microemulsions, after the interaction with the oily soil.[32,34–39] Nevertheless, microemulsions themselves also possess detergency properties and can be used for cleaning purposes. Less research has been carried out on microemulsions used as direct cleaning medium, but some examples exist in this subject (e.g. textile cleaning, hard surface cleaning, vehicle cleaning, dry cleaning).[40]

The detergency capacity of a generic o/w system is given by the combination of many factors, such as the detergency of micellar solutions, the solubilization power of organic solvents and the raised reactivity due to the high internal system's surface.

3.4. *Nanofluids for the removal of polymers from artifacts*

Micellar systems and microemulsions have shown to be highly performing aqueous systems for the cleaning of Cultural Heritage artifacts. Some examples are presented here to remark the importance of using these aqueous systems over pure or mixed solvents.

The first case reported of the use of nanofluids for the cleaning of unwanted materials from a painted surface is rather recent. Carretti et al.[41] proposed four different micellar systems and concluded that the microemulsion composed of water, sodium dodecyl sulfate (SDS), 1-pentanol, *p*-xylene and a mixture of hydrocarbons were able to remove an acrylic polymer coating, while a micellar solution containing water, SDS, 1-Pentanol and propylene carbonate was an efficient cleaning system for removing vinyl polymer coatings. The real case was a *fresco* by Pozzoserrato (16th century) from the Cathedral of Conegliano, Italy. Many other studies followed proposing new nanofluids formulations for the removal of polymers from wall paintings.[42–50]

A remark should be made to the efficient removal of Mowilith DM5 acrylic polymer covering the walls of an archaeological site of Mayapan in Mexico, by the use of the micellar solution composed by water, SDS, 1-Pentanol, propylene carbonate and ethyl acetate (named EAPC system).[44,45] The latter cleaning system has shown efficient removal of polymers in various other case studies since then, and it has been thoroughly studied. The advantages of using nanofluids over conventional methods are here detailed:[50]

- The continuous phase can be hydrophilic (o/w) or hydrophobic (w/o) allowing a control in the spreading of the continuous phase into the artifacts to be treated;
- The dispersed oil-in-water (o/w) or water-in-oil (w/o) nanodroplets provide an high surface area that increases the interactions with soiling materials, enhancing the solubilization or the swelling of the materials to be removed;
- The spreading of the solubilized material into the porous matrixes may be limited, because solubilization or swelling occurs into the core of nanodroplets and/or at the droplet interface. When dealing with hydrophilic substrates the aqueous continuous phase may act as a barrier, preventing the re-deposition of the hydrophobic coatings within the substrate porosity;
- Microemulsions are thermodynamically stable systems;
- The formulation of o/w microemulsions requires small amounts of solvents with a consistent reduction of the toxicity and environmental impact;

- The cleaning process allows a controlled action over the artifacts' surface.

The detergency process of nanofluids is described in figure 3.10 with the examples of microemulsion named XYL and the micellar solution named EAPC.

More recently, new complex fluids, containing biodegradable nonionic amphiphiles, to remove polymer coatings from porous substrates, such as wall paintings and stones, are being developed.[49]

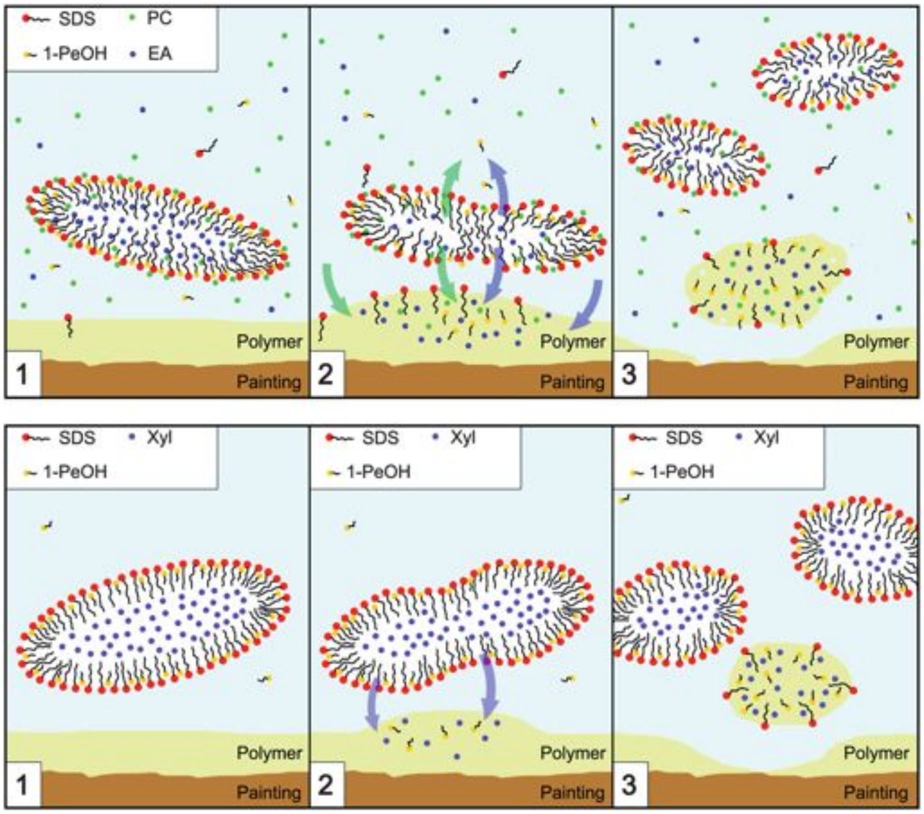

Figure 3.10. Schematic representation of the interaction mechanism between the nanostructured systems (top: EAPC; bottom: XYL) and the polymer coating.[46]

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CHAPTER 4
Gels:
Retentive Tools for Cleaning Cultural Heritage Artifacts

4.1. Introduction

In colloid science there is a class of materials termed lyophilic (liquid loving), characterized by the strong affinity that the solute macromolecular particles have with the surface molecules of the solvent phase. If the dispersed particles are cross-linked they form a network structure, in which all the dispersion phase is mechanically entrapped. Thus, they can be good carriers of fluids, having the mechanical features similar to those of a solid. Such colloids are known as gels.

There are a wide variety of gel types, which is mainly due to the ongoing research that is continuously developing new gel materials that cover a wide range of application fields. Gel materials are very complex systems, so their complete characterization is only possible through the use of multiple analyses able to characterize, among others, its polymeric structure, its liquid-polymer interactions, and its mechanical behavior. The in-deep knowledge of these features offers the possibility to tune gel properties through the addition of other components, such as fillers and plasticizers, or by varying the components ratios in gel's formulation, such as cross-linker, initiator, or liquid medium. Moreover, the gel preparation technique type has a major influence on the final gel characteristics.

The possibility of having versatile gels, with performing properties for application purposes, makes them potential materials for cleaning applications in the field of Cultural Heritage conservation.

4.2. Definition of gel

The simplest definition of a colloidal dispersion is that of a two-phase system, where molecules or polymolecular particles are dispersed in the continuous phase, i.e. the medium, and have at least in one direction a dimension usually in the range of 1 nm to 1µm, or that the discontinuities are found at distances of that order.[1] According to this definition, gels may be considered as colloidal systems due to the dimension of the interconnected long polymer chains, organic molecules or colloidal particles that entrap a fluid. The definition of colloidal systems covers a wide range of different materials though, so to define specifically the gel condition one must consider its structure, its phenomenology and its mechanical behavior.

According to IUPAC the general definition of gel is that of a "*non-fluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid*."[2] Curiously, there is a major description in the definition notes than in the definition itself, considering that, for example, this definition does not reflect its characteristic mechanical properties. In fact, the open debate on gel definition is mainly due to the fact that in some cases gels can resemble a viscous liquid, while others a soft solid. Moreover, the precise definition of the borderline system between these two conditions becomes somewhat ambiguous.

Lloyd in 1926 suggested that "*the colloidal condition, the 'gel', is one which is easier to recognize than to define*".[3] However, nowadays gels are not anymore that so easy to recognize, due to the variety of colloidal particles that are able to form gel networks and to the various kinds of polymer bonding interactions able of cross-linking, producing colloid systems that resemble to gels but with mechanical features typical of an highly viscous liquid, as is the example of the Highly Viscous Polymer Dispersions (HVPD), discussed further below. Many efforts to achieve an unique and covering definition of gel has been proposed since Lloyd, taking into account different points of view, such as the macroscopic behavior, the microscopic structure or rheological behavior, as summarized in table 4.1.

In order to give a clear understanding of what it is considered a "gel" further in this work, a mechanical point of view on the definition of the gel condition was adopted, according to Almdal et al.,[4] in which some measurable parameters are given for the classification of gels. In fact, he and his co-workers were the firsts to give a precise definition based on experimental data from rheological properties of gels. Their gel definition is based on the fact that the storage modulus, G', have a plateau and is always predominantly higher that the loss modulus, G'', over a wide range of frequencies. An example of such a system is presented in figure 4.1.

Table 4.1. Summary of the most cited proposed gel definitions.

Author/s	Year	Proposed gel definition
Lloyd, D.J[3]	1926	- Built up from two components: one is a liquid at the temperature under consideration, and the other is a solid; - Can maintain its form under the stress of its own weight, - Shows the phenomenon of strain, under any mechanical stress.
Bungenberg de Jong, H. G.[5]	1949	- Colloidal system of solid character; - The colloidal particles constitute a coherent structure, being interpenetrated usually by a liquid system consisting in kinetic units smaller than colloidal particles.
Hermans, P. H.[6]	1949	- Coherent colloid disperse systems of at least two components; - Exhibits mechanical properties characteristic of a solid; - Both the dispersed component and the dispersion medium extend themselves continuously throughout the whole system.
Flory, P. J.[7]	1974	- Solid-like behavior; - When deformed, its response is that of an elastic body; - The modulus of elasticity is low.
Ferry, J. D.[8]	1980	- A substantially diluted system, which exhibits no steady state flow.
Burchard, W. & Ross-Murphy, S. B.[9]	1990	- Possess a plateau in the real part of the complex modulus extending over an appreciable window of frequencies. - They are viscoelastic solids.
Almdal, K. et al[4]	1993	- Soft, solid or liquid-like material of two or more components, one of which is a liquid, present in substantial quantity; - Solid-like gels are characterized by the absence of an equilibrium modulus, by a storage modulus, $G'(\omega)$, which exhibits a pronounced plateau extending to times at least of the order of seconds, and by a loss modulus, $G''(\omega)$, which is considerably smaller than the storage modulus in the plateau region. - Materials with moduli of the order of 10^8 Pa are far too rigid to be called gel.
Nishinari, K.[10]	2009	- Intermediate state between a liquid-like rheological behavior and a solid-like rheological behavior; - Consists of a dispersed phase (polymers or colloids) and a dispersing medium (water or other solvents), and can be very close to a liquid or to a solid; - Liquid-like properties are due to the fact that the major constituent is water or other solvents; - Solid-like behavior is due to the network, which prevents the system from flowing, and characterized by a finite elastic modulus.

It was given a further recommendation about the borderline between solid-like gels and solids, that is, materials with moduli in the order of 10^8 Pa should not be considered gels, as they are too rigid. According to this definition, materials such as xerogels, aerogels and highly cross-linked polymers with low swollen degree must not be addressed as gels.

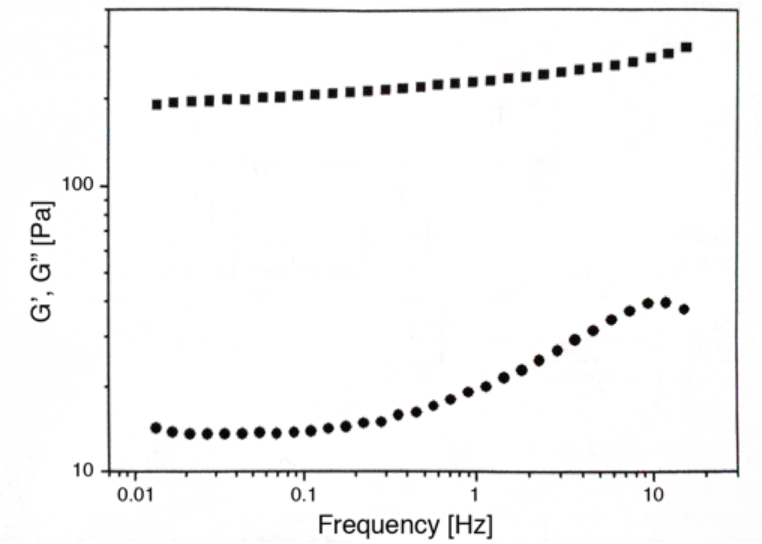

Figure 4.1. Frequency sweep of a gel composed by polyacrylic acid (1 w/w%), 1-propanol (20 w/w%) and water. Storage modulus *G'* (■) and loss modulus *G''* (●).[11]

4.3. *Classification of gels*

As well as for gel definition, also the classification of gels is not a well-defined subject, mainly due to the continuously new developed gel typologies, and to the different theoretical backgrounds of the professionals that study gels (such as chemists, physicists and engineers). Gels can be classified in various ways, depending if one is interested in the medium in which they were obtained; in the basis of the network' structure; in the thermal behavior; on the type of bonds in the three-dimensional network, among other possibilities for gel classification. Some examples of the above gel systems, along with a short description, are presented in table 4.2. The classification based on chemical gels and physical gels, is the most commonly used, which why is the one adopted here. However, it must be noticed that other terms may be used further in this thesis, depending on the addressed subject. Furthermore, in the context of this thesis' subject, importance will be addressed to hydrogels and Interpenetrating Polymer Networks (IPNs).

4.3.1. Crosslinking classification

Knowing the nature of the crosslinks in the polymer network is the most concrete way to distinguish gel materials. This is mainly due to the fact that the interaction type between the network primary units influence on the mechanical properties of the gel. In other words, the microscopic nature defines the macroscopic effect.

4.3.1.1. Physical gels

Physical gels are polymeric systems that are gelled by the presence of weak interactions between chains, such as hydrophobic, electrostatic, and Van del Waals kind, or the rather strong hydrogen bonds. Due to the weak nature of this kind of bonds, less energy is necessary to break them. On the other hand, physical bonds are easily reformed in certain conditions. Therefore, physical gels are also thermoreversible. Common examples of natural source physical gels are the ones based on polysaccharides and proteins. The usual procedure for the preparation of physical gels is to solubilize the macromolecules (i.e. the thickener) at an high temperature (60-70ºC), which causes the re-dispersion of the single molecules or aggregates in the solvent phase. During cooling, the molecular structures organize to form a 3D network. Moreover, physical gels can be molded and may grant a perfect adhesion to the surface, which are good characteristics for the cleaning of artifacts.[11]

4.3.1.2. Chemical gels

Chemical gels are composed of cross-linked polymer networks that are built by covalent bonds. In this case the polymer network forms a macromolecule with a very high molecular weight (M_w). The permanent nature of the covalent bonds connecting polymer chains is responsible for the thermoset nature of these materials: only over a critical temperature can the bond be break, yet the effect is irreversible. They behavior is similar to solids. In fact, chemical gels are able to load high amounts of liquid without undergoing polymer solubilization. Due to their cohesive force, chemical gels are easily removed from any surface, which is a very important characteristic for the cleaning of Cultural Heritage artifacts.[11]

Table 4.2. Classification of gels. Examples and description.[11,12]

Category	Sub-category	Description
Source	Natural	Found in nature. Can be formed simply by cooling of solutions of biological proteins (fish-glue) or polysaccharides (gelatin; pectin; agarose; carrageenan).
	Synthetic	Man-made to meet specific purposes (contact lenses; drug delivery systems; bone tissue; cosmetics; etc.).
	Hybrid	Mixture of natural and synthetic source polymers.
Medium	Hydro-	Three-dimensional networks constituted by hydrophilic polymers, generally covalently or ionically cross-linked, which interact with aqueous solutions.
	Organo-	Polymers made from an oil-medium, such as an organic solvent.
	Xero-	Born as liquid gels, xerogels are the result of a freeze-drying process that produce a porous solid with partially collapsed porosity. They must not be considered as gels, according to Almdal's definition.
	Aero-	Prepared as liquid gels which liquid phase has been replaced by a gas by means of the supercritical drying technique. They must not be considered as gels, according to Almdal's definition.
Thermal response	Thermoset	Gels with permanent cross-links. They do not melt when subject to high temperatures. These materials have improved mechanical properties, chemical resistance, heat resistance and structural integrity.
	Thermoplastic	Become more fluid when heat is applied. They are thermoreversible gels.
Crosslinking	Chemical	Polymer network constituted by permanent bonds, i.e. covalent bonds.
	Physical	Polymer network constituted by weak interactions that can be removed and reformed without any irreversible effects.

4.3.2. Multi-polymer combinations

The combination of two or more polymers can give rise to complex networks that can be classified in various ways, depending on how these polymers are interconnected in the polymer inner structure. These systems can be named multicomponent polymer materials, which comprise:[13] polymer blends (simple polymer mixing); graft copolymers (bonding between the end of one polymer with some portion of the backbone of an other polymer); block copolymers (chains bonded end to end); cross-linked copolymers (two polymers constitute the network); interpenetrating networks (IPNs), which are based on the synthesis of one or both polymers in juxtaposition, composing two or more networks from different polymers (IPN) or one network in the presence of other linear or graft polymer (semi-IPN), without any covalent bond between them (see figure 4.2).

4.3.2.1. Interpenetrating Polymer Networks (IPNs)

Since IPNs constitute the subject of this thesis they will be further described, for what concerns their classification. In fact, IPN can be produced in various ways, resulting in multicomponent polymer materials with different network structures:[13,14]

- *Sequential IPN.* First polymerization of polymer A is carried out using common methods. Then polymer B is polymerized in the presence of the previous formed network. Resulting network is schematized in figure 4.2(e).

- *Simultaneous interpenetrating network (SIN).* The monomers or pre-polymers, respective crosslinking agents and initiators are mixed together. The polymerization reactions are carried out simultaneously, with the condition that they to not interfere between them. The resulting network is the same as the previous.

- *Latex IPN (emulsion IPN).* The IPNs are made in the form of beads, usually with a core and shell structure, to form an emulsion film. An alternative is to mix two different beads and then form a film, which cross-links both polymers. This variant can be named as Interpenetrating Elastomer Network (IEN).

- *Gradient IPN.* The overall composition or cross-link density of the material varies from point to point on the macroscopic level.

- *Thermoplastic IPN.* They are hybrids between polymer blends and IPNs that contain physical rather than chemical crosslinks. They are temperature-responsive materials, since at a certain temperature they form crosslinks and behave like IPNs. Crosslinks types include block copolymer morphologies, ionic groups, and semicrystallinity.

- *Semi-IPN (SIPN).* 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.

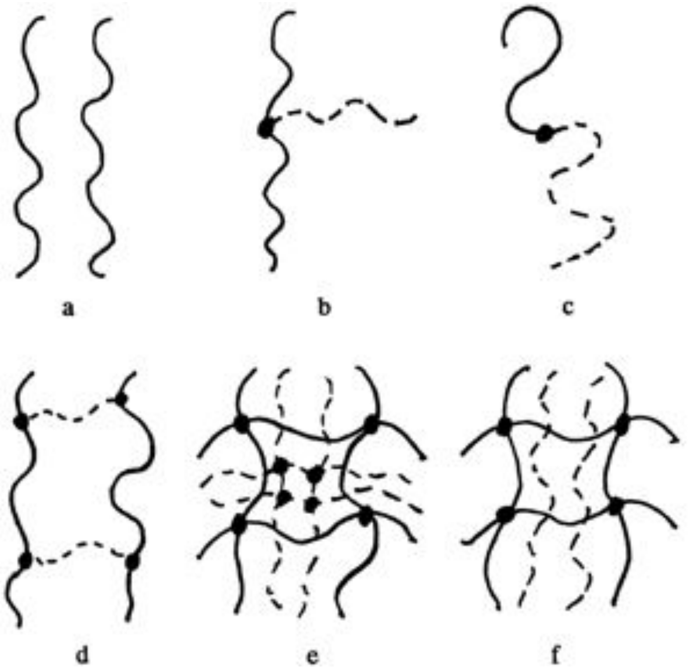

Figure 4.2. Possible structures resulting from the combination of two or more polymers: (a) polymer blend, no bonding between chains; (b) graft copolymer; (c) block copolymer; (d) AB-graft copolymer; (e) interpenetrating polymer network; (f) semi-interpenetrating polymer network. Structures from (a) to (c) are thermoplastic; structures from (d) to (f) are thermoset.[13]

4.4. Gelation process

The gelation process of a substance consists on the evolution of the polymer cluster growth until it reaches the gel point, which defines the moment of the sol-gel transition of the chemically crosslinking 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, it is called *gel* and it consists on an infinitely large macromolecule, which can only swell in a good solvent.[15]

Several theoretical approaches have been used for the prediction of the gel point and the modeling of the gel formation process. Two are relevant to consider: the classical theory based on branching models developed by Flory[16] and Stockmayer[17] and the percolation model introduced by de Gennes[18] and Stauffer et al.[19], as briefly discussed below (see also figure 4.3). Both gelation theories predict a critical point at which an infinite cluster forms, that is the sol-gel transition.

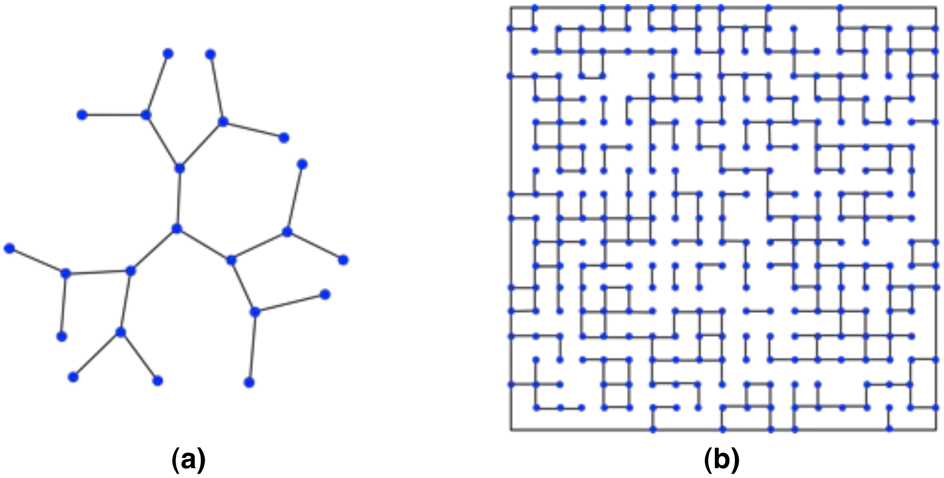

Figure 4.3. Comparison of a schematic structure of a Bethe lattice (a) with a $z = 3$ functionality and a two-dimensional square lattice (b). For the Bethe lattice, each possible bond is shown as a line connecting two monomers (blue dots). In the Flory-Stockmayer theory an actual bond of these possible bonds is formed with probability p. For the square lattice, each bond that has been formed is shown as a short line connecting two monomers (blue dots).[15]

4.4.1. Flory-Stockmayer theory

The mean-field branching theory established by Flory and Stockmayer is a classical statistical approach for the prediction of the gel point. It is based on the functionality of the system, z, i.e. the maximum number of z intermolecular interactions or bonds that a molecule can possess. Therefore, a z-functional molecule with $z > 2$, is a poly-functional molecule able to form 3D networks. The percolation is on a Bethe lattice or Caley tree, see figure 4.3(a).[11]

It is a simple statistical approach that assumes that all the functional groups of the forming chains have the same reactivity, that is, the reactivity is independent of the size or structure of the molecule or network. The second assumption is that intramolecular reactions do not take place, that is, reactions only between two separated molecules or networks are considered.[15,16]

The parameter, p, is related to the probability that a given functional group of a branched polymer has in being bonded with a chain of poly-functional units to form another branch in the polymer. It represents the ratio of the number of functional groups belonging to branch units to the total number of functional groups in the mixture, thus defining the overall extent of the reaction. There is, therefore, a critical extent of reaction, p_c, at which $M_w \rightarrow \infty$, that is, when the sol-gel transition occurs:[15,16]

$$p_c = \frac{1}{z-1} \qquad z > 2 \tag{4.1}$$

4.4.2. Percolation theory

Percolation statistical approach, on the other hand, describes the random growth of molecular clusters on a d-dimensional lattice, schematized in figure 4.3(b). The assumption for this theory is that there is no mobility of the clusters. A percolation defines the geometrical transition between disconnected and connected phases as the concentration of bonds in a network increases. The bond formation probability in random bond percolation, p, has as well a critical value, p_c, beyond which the probability of finding a cluster that spans all over the squared lattice is > 0, that is the percolation threshold, at which the formation of a infinite cluster occurs.[15]

4.4.3. Rheological behavior during gelation process

From a rheological point of view, it is possible to define the gelation process until a sol-gel transition is reached. Some of the rheological gel parameters here presented are described further on in this chapter (see under sub-chapter 4.6).

In the initial phase of a gelation process, as the crosslink sites increasingly develop, the viscosity starts to increase, and, at the same time, the polymer solution has an increasing ability to store energy, therefore increasing both loss (G'') and storage (G') moduli. Before reaching the sol-gel transition, the material presents more flow behavior than elastic behavior, so the loss modulus is higher than the storage modulus. The increasing rate of the storage modulus is higher than the loss modulus, thus at certain time during gelation, the viscosity tends to infinity and $G' \approx G''$, defining the *gel point* (see figure 4.4). Beyond the gel point, if the final compound is essentially an ideal solid, the connectivity of the polymeric network continues to increase, which means from a rheological point of view that the modulus will tend to infinity.[20]

Many studies have been elaborated in order to predict the gelation process using percolation theory on rheological behavior.[21,22] From figure 4.4, the complex shear modulus of gels, *G**, and the complex viscosity of the solution, η^*, are shown to follow a power law near the *sol-gel* transition point:[10]

$$G^* \sim \varepsilon^{t} \tag{4.2}$$

$$\eta^* \sim \varepsilon^{-k} \tag{4.3}$$

where $\varepsilon = |p - p_c|/p_c$ represents the relative distance of a percolation probability, p, from the gel point related probability, p_c. For this reason it is interesting to study the rheological behavior of gels in the vicinity of the *sol-gel* transition point.

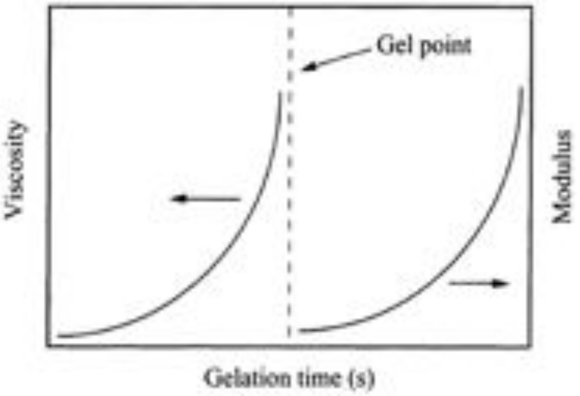

Figure 4.4. Schematic representation of the classical rheological definition at the gel point.[23]

4.5. Structural properties

Hydrogel's network structure is in direct relationship with the hydrophilicity of the system, that is, the ability of embedding and retaining considerably large amounts of water. So, in order to understand the application features of an hydrogel retaining a cleaning system, it is fundamental to understand the gel's network. According to Lowman and Peppas,[24] there are three main parameters to consider that define the structure and properties of swollen hydrogels:

- The polymer volume fraction in the swollen state ($v_{2,s}$);
- The molecular weight of the polymer chain between two neighboring crosslinking points (M_c) (see figure 4.5);
- The characteristic mesh size (ζ) (see figure 4.5).

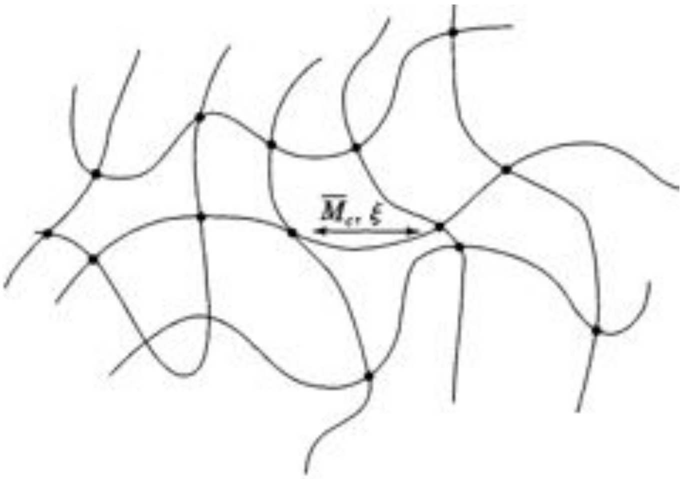

Figure 4.5. Schematic representation of the cross-linked structure of a hydrogel. M_c is the molecular weight of the polymer chains between cross-links (•) and ζ is the network mesh size.[24]

4.5.1. Polymer volume fraction

The polymer volume fraction in the swollen state refers to amount of the liquid fraction absorbed and retained by the gel. A direct way of measuring it is from the volume of the dry polymer, V_p, and the swollen gel volume, V_g as follows:[11]

$$v_{2,s} = \frac{V_p}{V_g} = \frac{1}{Q} \tag{4.4}$$

where Q is the volumetric swollen ratio. As higher is this value, the higher the polymer affinity to the solvent. Therefore, $v_{2,s}$ is strictly connected to the molecular affinity between a specific polymer and a specific solvent. Knowing the $v_{2,s}$ or the reciprocal Q, of the macromolecules, it is possible to tune the gel's affinity to a specific solvent by adding different monomers or different polymers to the gel's formulation. A parameter easily measured that is related to this property is the Equilibrium Solvent Content (*ESC*):[11]

$$ESC = \frac{W_w - W_d}{W_w} \times 100 \tag{4.5}$$

where W_w and W_d are the weights of swollen gel and dry gel, respectively. When the solvent is water, than it alters to Equilibrium Water Content (*EWC*). Furthermore, the *ESC* is proportional to the gel's porosity. In fact, gels having an increased porosity, i.e. the pore volume to polymer volume ratio is high, can load high amounts of solvent. For this reason, liquid medium is added during gel formation to create polymer voids, thus, for obtaining gels with high solvent affinity. The decrease of EWC over time or after dehydration/rehydration cycles, can be directly associated to some collapse of the gel's porosity.

4.5.1.1. Gel's porosity

The examination of the gel's porosity is an important analysis to consider, since it offers relevant information on the retention/release capacity of the gel system. Porosity ε is defined as the fraction of the apparent volume of the sample and is usually expressed in percentual:[25,26]

$$\varepsilon = \frac{U_P}{U} \tag{4.6}$$

where U is the bulk volume and U_P is the pore volume. If U_P refers to the absolute porosity, then also the non-interconnected pores are considered. However, for what matters the liquid flow through the porous medium, the effective porosity, and not the absolute porosity, is of interest. It is defined as the ratio of the interconnected pore volume $U_{P,e}$ to the total volume of the medium as in equation 4.6.[26] According to the IUPAC recommendations the pore size can be distinguished:[25]

- Micropores. Pore's dimensions smaller than 2nm;
- Mesopores. Pores with widths between 2 and 50nm;
- Macropores. Pore's dimensions greater than 50nm.

This classification accounts only for the porosity in the nanometer scale, considering that macropores cover all the greater sizes. There are several techniques for porosity quantification described in the literature.[25] The Scanning Electron Microscopy (SEM) is especially useful for the examination of the macroporosity.[24]

4.5.2. Molecular weight

Synthetic and natural polymers have a molecular weight distribution that differs depending on the method of synthesis and on the fractionation procedure. A method to obtain a measure of the polydispersity in molecular weight is to determine the average molecular weight between two consecutive cross-links, M_c. One approach is to calculate the number average molecular weight, M_n, as follows:[27]

$$M_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \tag{4.7}$$

where N_i is the number of molecules with mass M_i. M_n may be determined by freezing point depression, osmosis or chemical analysis of end groups.

An alternative molecular weight average is the weight average molecular weight, M_w, where w is the weighting factor for each molecular weight species, and is, thus, defined by:

$$M_w = \frac{\Sigma w_i M_i}{\Sigma w_i} = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} \tag{4.8}$$

M_w is sensitive to high molecular weight species and is always larger than M_n. For a monodisperse polymer $M_w \approx M_n$, so the ratio of the weight average to the number average molecular weights is a measure of the degree of polydispersity.[27]

M_c can define the degree of cross-linking of the polymer network, X, as follows:[11]

$$X = \frac{M_0}{2M_c} \tag{4.9}$$

where M_0 is the molecular weight of the repeating units in the polymer chains. As illustrated in figure 4.5, the M_c in chemical gels cannot vary with different swelling degrees as occurs for the mesh size value ξ, due to the chemical permanent topology.

4.5.3. Mesh size and inhomogeneities

The network mesh size ξ is defined by the distance between two consecutive cross-linking points, which depends on the swelling degree of the polymer network (see figure 4.5). Since there is a distribution of distances in a polymeric network, due to the random nature of the gelation process, the average mesh size values are average accounting for a 3D network system. Average mesh size is the same as the measure of the average porosity in the nanometer scale.[11]

Inhomogeneities in polymer gels are non-relaxing frozen polymer concentrations, which is dependent on the crosslinking density. The increase of inhomogeneities domains can lead to gel turbidity and can cause inhomogeneous responses in swelling and shrinking, as well as in rheological properties. According to Ikkai et al.[28] there are three types of inhomogeneities in polymer gels, as illustrated in figure 4.6.

The spatial inhomogeneities represent non-uniform spatial distributions of crosslinks. Topological inhomogeneities concern the defects on the topology of the polymer network (e.g. loops, trapped entanglements, dangling chains). The connectivity inhomogeneities are in relationship with the sizes and spatial distributions of clusters, which are predominant at the percolation threshold. Spatial inhomogeneities and mesh sizes can be examined through small-angle scattering techniques.

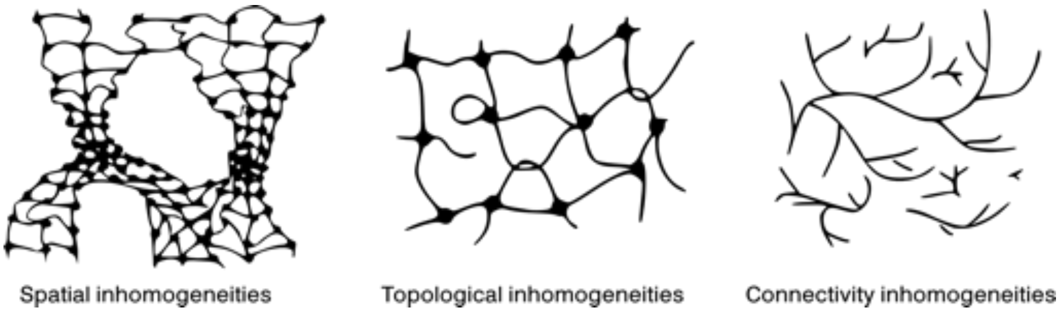

Figure 4.6. Types of inhomogeneities in gels.[28]

4.5.3.1. Scattering characterization techniques

Scattering technique is the simplest approach to study the structure of gels since it covers the entire size range of interest and is capable of measuring the structure dimensions, as well as to give detailed information on their interaction in a medium. The basics of a scattering experiment are evidenced in figure 4.7. In this experiment the intensity of the scattered radiation is measured as a function of the scattered angle, θ. The scattering vector intensity, q, is related to the scattered angle and wavelength:[29]

$$q = \frac{4\pi \sin\theta / 2}{\lambda} \tag{4.10}$$

The distances obtained from an experiment have a relation with the scattering vector intensity, that is distance ≈ $2\pi/q$. Therefore, larger structures are related to smaller q. In order to achieve small q, small scattering angle and large wavelengths are necessary (e.g. small angle X-ray and neutron scattering techniques). In Small-Angle Scattering (SAS), distances in the range 1nm-1μm can be measured. X-rays radiation induces scattering from the difference between electron densities, while neutron radiation is scattered by interaction with the nuclei, so they are independent of the atomic number.[29]

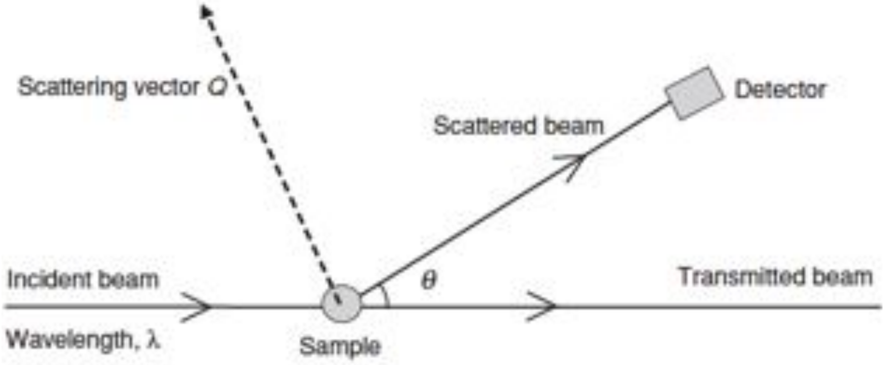

Figure 4.7. Schematic representation of a scattering experiment.[29]

Scattering techniques are non-destructive, since they do not need any sample preparation, such as out-gassing pre-treatment (needed in the case of Electron

Microscopy) that can irreversibly damage the internal structure of swollen gels. The average mesh and inhomogeneity sizes can be retrieved by using appropriate fitting models for scattering curves. In general, in a polymer network, the scattering intensity distribution, *I(q)*, can be defined as:[11]

$$I(q) = I_{Lorentz}(q) + I_{excess}(q) + bkg \tag{4.11}$$

The first contribution, $I_{Lorentz}(q)$, is a Lorentzian term, that is an Ornstein–Zernike function, accounting for the scattering associated of a tridimensional network where the correlation length ζ is the average distance between polymer chains. It can be expressed as follows:[30]

$$I_{Lorentz}(q) = \frac{I_{Lorentz}(0)}{1+q^2\zeta^2} \tag{4.12}$$

where $I_{Lorentz}(0)$ is the Lorentzian intensity at $q = 0$ and ζ is the average mesh dimension of the network. If the correlation length among the inhomogeneous regions is larger than the correlation length of the cross-links ($\Xi > \zeta$), an "excess" structure factor that takes into account of the scattering excess may be considered. This second contribution, $I_{excess}(q)$, is a Debye-Bueche function[31] that concerns the scattering at low q produced by inhomogeneities, as for example, solid-like polymer domains.

$$I_{excess}(q) = \frac{I_{excess}(0)}{(1+q^2\Xi^2)^2} \tag{4.13}$$

where $I_{excess}(0)$ is the excess intensity at $q = 0$ and Ξ is the average dimension of the inhomogeneity domains accessible by the SAS experiment.

4.6. Mechanical properties

Gels are viscoelastic materials from a mechanical point of view, which means that they possess contemporary mechanical behaviors typical of liquids and solids. As discussed before (see sub-chapter 4.2), the elastic fraction always prevails over the viscous behavior in gels. Therefore, there are two important parameters to consider, for studying the mechanical properties of gels: the elastic modulus and the viscosity. The elastic modulus, E, also known as Young's modulus, is defined as the fraction between the applied tensile stress, T, and the relative length of elongation, L_R:[11]

$$E = \frac{T}{L_R} = \frac{F/A}{\Delta L/L_0} \qquad (4.14)$$

where F is the applied force over an area A and L_0 is the initial length. The elastic modulus decreases with the increasing of mesh size, and, thus is dependent of the swelling degree, and with increasing in M_c, that is, with decreasing of crosslinking density.

The viscosity, η, is defined as the resistance of fluids to external mechanical stresses. When a perturbation is applied, the fluid starts to flow. This displacement is influenced by many factors, such as temperature, pH and the magnitude of the applied stress. However, the most important features that influence on gel's viscosity is the chemical nature of the fluid and the molecular interactions between the fluid's components. Therefore, gel's viscosity can be tailored as well.

4.6.1. Rheology of viscoelastic materials

Rheology is the science of material's flow behavior and deformation. It is directly in relation with the inner structure of the material. When a material is subject to outside forces (examples given in figure 4.8) it will yield a stress/strain response. In order to explain this phenomenon, the simple example of a shear stress on a cube is schematized in figure 4.9. The force is applied to the upper plane of the cube while the base is hold firmly. The resulting deformation shows a displacement with an angle α. The relation between the applied force and the deformation is due to the physical properties of the material. The deformation is called *shear strain*, γ, which is independent of the size of the material (dimensionless unit). The applied force is better explained by the *shear stress*, σ, which is the force divided by the upper area of the cube, expressed in Pa or $N \cdot m^{-2}$. The *shear modulus*, G, is now obtained:[32]

$$G = \frac{\sigma}{\gamma} \qquad (4.15)$$

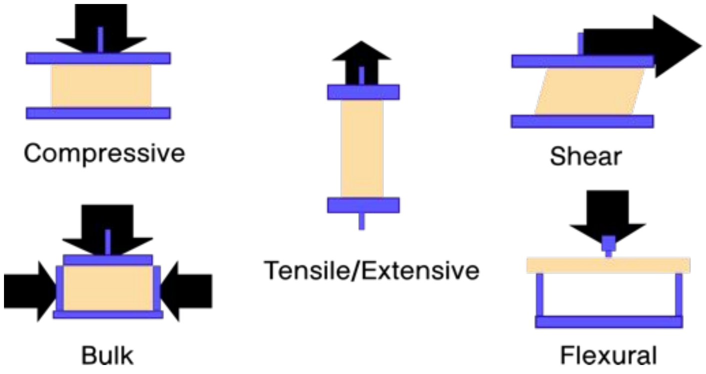

Figure 4.8. Examples of deformation modes. Geometric arrangements or methods of applying stress are shown.[33]

To distinguish between liquid-like and solid-like character of a gel, the viscoelasticity features of the system should be addressed. With imposing a constant strain, the size of the stress is determined by the shear modulus (see equation 4.15). Considering that the molecules that were forced to an higher energy state, rearrange in the material to return to the initial energy state, some of the stored energy is dissipated by viscous flow and some stress is reduced. The time for the relaxation is determined by the balance of elastic and viscous processes:[20,32]

$$\tau = \frac{\eta}{G} \tag{4.16}$$

where η is the viscosity of the material. The ratio of the relaxation time to the experimental observation time, t is defined by the Deborah number:

$$De = \frac{\tau}{t} \tag{4.17}$$

De reflects the tendency of the material to appear either more viscous or more elastic. Therefore, the classification of the gels' behavior can be:

$De >> 1$,	$De \sim 1$	and	$De << 1$
solid-like	viscoelastic		liquid-like

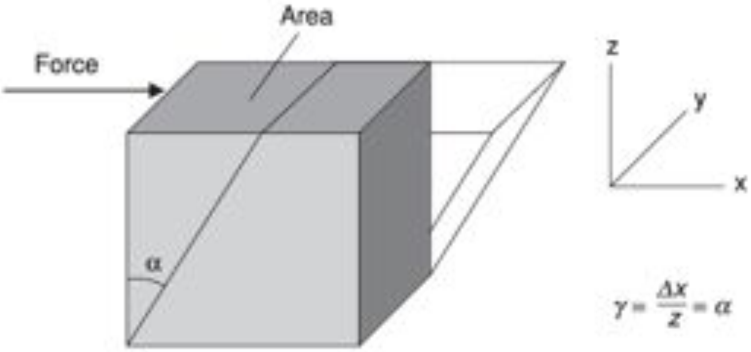

Figure 4.9. The shear stress and shear strain on a cube.[32]

Therefore, if observational times are rather small (in the order of seconds) and if t ≈ τ the material displays both elastic and viscous characteristic and is named viscoelastic.

4.6.1.1. Linear viscoelasticity

In the linear viscoelasticity region each applied stress yields a proportional strain, that is, a straight line is observed if the force applied is plotted in function of the deformation. Over a critical limit, the force applied causes irreversible modifications on the material and may eventually break with further increasing stress. The phenomenological rheological behavior of materials in the linear viscoelasticity region can be represented by combinations of Hookean springs and Newtonian dashpots. A Hookean spring obeys Hooke's law: the stress is linearly related to the displacement. An ideal Hookean solid has therefore an infinite elasticity, which is represented by *G*, accounting for the spring response (see equation 4.15). The dashpot is represented by a filled cup of Newtonian fluid with η viscosity, and a piston over the fluid. Therefore, the constant of proportionality is the shear viscosity:[20]

$$\sigma = \eta\dot{\gamma} \tag{4.18}$$

Viscoelastic materials are represented by the combination of these two models and they can be visualized in series or in parallel. In the Maxwell model, the spring and the dashpot are placed in series, while when in parallel they are represented by the Kelvin-Voigt model (see figure 4.10).

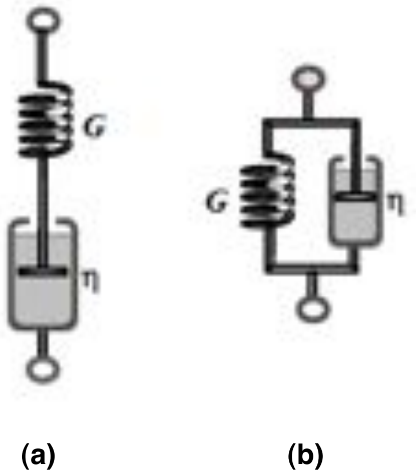

Figure 4.10. The Maxwell (a),and Kelvin-Voigt (b) models. The spring is related to materials' elasticity, while the dashpot represents the ability of the material to flow.

4.6.2. Dynamic mechanical analysis (DMA)

The deformation of a sample when subject to a dynamic force is related to both polymer elastic (spring-like) and viscous (dashpot-like) behaviors. Dynamic mechanical analysis (DMA) is based on the application of an oscillating force to a sample and the observation of the material's response to that force. When a material is loaded with a constant force and a sinusoidal oscillating stress or strain is applied, it will deform sinusoidally, which offers detailed information on material's characteristics, if this test is carried out within its linear viscoelastic region. The sinusoidally oscillating strain can be expressed by:[33,34]

$$\gamma(t) = \gamma_0 \sin\omega t \tag{4.19}$$

where γ is the strain at time t, γ_0 is the strain amplitude and ω is the oscillation or angular frequency. The strain rate, $\dot{\gamma}(t)$, becomes:

$$d\gamma/dt = \dot{\gamma}(t) = \omega\gamma_0 \cos\omega t \tag{4.20}$$

The applied strain generates two stress moduli represented by an elastic component, also named in-phase stress (strain in line with stress) and by a viscous component, also called out-of-phase stress (δ = π/2) (see figure 4.11), which sum express the generated total stress (σ_0):

$$\sigma_0 = G'\gamma_0 \sin(\omega t) + G''\gamma_0 \cos(\omega t) \tag{4.21}$$

In a viscoelastic material, the generated stress shows a difference between the applied strain, showed by a phase lag of δ radians. Therefore, the viscoelastic stress response, $\sigma(t)$, of the materials to the applied strain over time in the linear viscoelastic region is as follows:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \tag{4.22}$$

By combining the previous equations it is possible to obtain:

$$G' = \left[\frac{\sigma_0}{\gamma_0}\right]\cos\delta \tag{4.23}$$

$$G'' = \left[\frac{\sigma_0}{\gamma_0}\right]\sin\delta \tag{4.24}$$

where G'(Pa) is the storage modulus associated with the elastic response of the material, and G''(Pa) is the loss modulus, associated to the energy loss in internal motion. Therefore, for an ideal elastic solid, G'' is zero, while for an ideal liquid, there is not any elastic component, so G' is zero. The vector sum of these two moduli provides with the complex shear modulus:[33]

$$G^* = G' + iG'' = \sqrt{G'^2 + G''^2} \tag{4.25}$$

If $G' >> G''$ the material behaves more like a solid, i.e. the deformations are essentially elastic or recoverable. If $G'' >> G'$ then the energy used to deform the material is dissipated by the viscosity of the system, so the material behaves more like a liquid. The viscoelastic moduli determined over a range of frequencies can indicate transition zones (e.g. sol-gel transition), which correspond to relaxation processes dependent on the material's structure.[33]

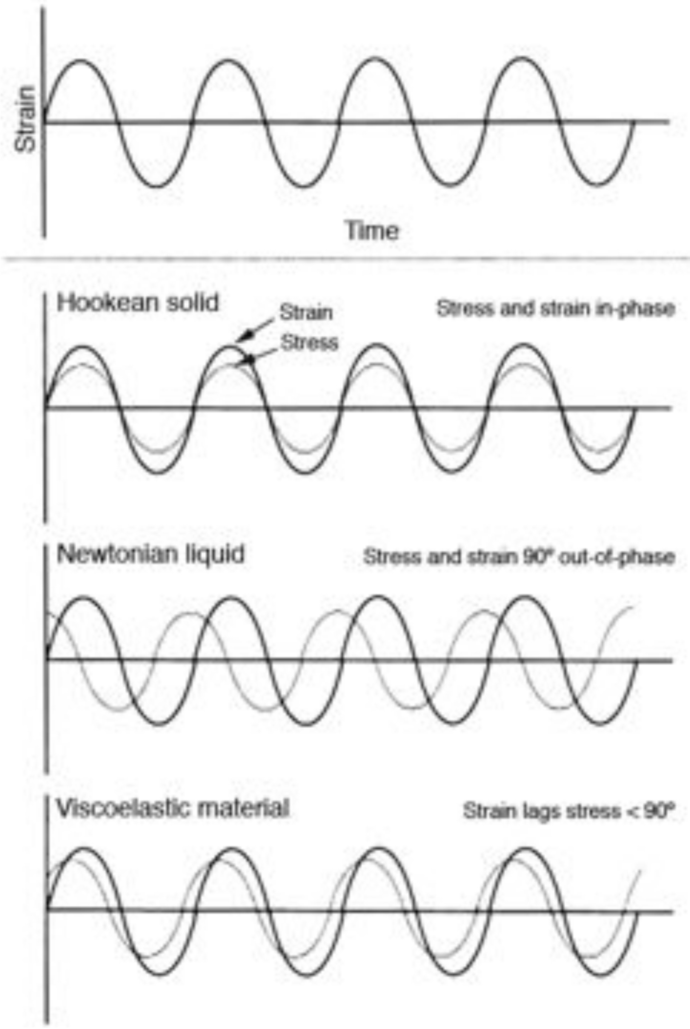

Figure 4.11. Stress and strain responses of an ideal solid, an ideal liquid and a viscoelastic material.[34]

The tangent of the phase angle (δ), also called damping factor, can define how efficiently the material loses energy to molecular rearrangements and internal friction. In other words, it is the ratio of the energy dissipated to that stored per cycle of deformation, therefore:[34]

$$\tan \delta = G''/G' \tag{4.26}$$

In addition, the complex viscosity, η^*, can be calculated:[23]

$$\eta^* = \frac{\sqrt{G'(\omega)^2 + G''(\omega)^2}}{\omega} \tag{4.27}$$

Since there is an extensive literature among numerous scientific and technologic areas on this subject, the viscoelastic parameters are usually expressed in various ways. The parameters used in this thesis are the ones related to the shear deformation, and are summarized in table 4.3.

Table 4.3. Summary of the viscoelastic parameters from shear deformation.[34]

Parameter	Shear deformation
Oscillating strain	$\gamma(t)$
Stress-relaxation modulus	$G(t)$
Creep-compliance	$J(t)$
Storage modulus	G'
Loss modulus	G''
Complex modulus	G^*
Dynamic viscosity	η'
Complex viscosity	η^*

4.6.2.1. Classification according to rheological behavior

Polymer solutions can be classified according to their rheological behavior in oscillatory measurements, i.e. according to the frequency dependence of storage and loss shear moduli:[10]

- *Strong gels*. G' is far larger than G'' and both moduli are independent of frequency (e.g. agar gels);
- *Structured liquids*. Also called weak gels (even if they fail to fulfill the definition of a gel). G' is slightly larger than G'' and both moduli are slightly dependent on frequency (e.g. xanthan gels);
- *Entangled polymer solutions*. G' is smaller than G'' at lower frequencies but both moduli increase with increasing frequency and show a crossover. After the crossover G' is higher than G'';
- *Non-entangled polymer solutions*. G' is far smaller than G'' at all the frequencies and both moduli are strongly dependent on the frequency.

It is important to remark that only the first case fulfills the requirements of a true gel. However, other types of polymer solutions have been used to retain liquid for cleaning procedures in Cultural Heritage artifacts, so they will also be addressed here.

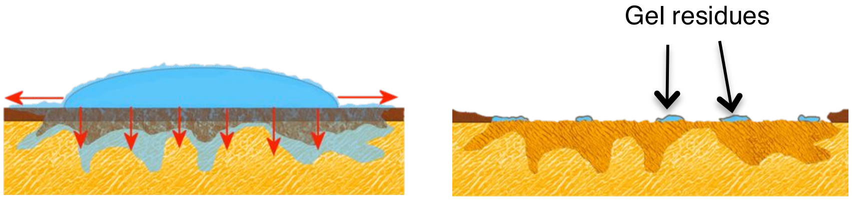

Figure 4.12. Schematic representation of the drawbacks of using conventional cleaning methods.

4.7. Gels for the cleaning of Cultural Heritage artifacts

In the conservation of Cultural Heritage artifacts, gels have the essential role of carrying a cleaning agent and containing its penetration into the artifacts surface, thus, controlling the cleaning action. Convectional methods in cleaning artifacts are the use of cotton-swabs and poultices of cellulose. However, with respect to gels, they are more aggressive (higher friction) and less retentive. In the past decades conservators devised several methods for the confinement of solvents, with the aim of increasing the control over the cleaning process. Penetration of the solvent via capillary action may be decreased using thickeners like cellulose ethers (e.g. Klucel, which is a hydroxypropyl cellulose; ethyl cellulose) and polyacrylic acids (e.g., Carbopol). Unfortunately, the retention features of those systems are as well unsatisfactory, and high evaporation rates of the solvents themselves can lead to formation of dry films of solid material on the treated surface.[35] Solvent gels (solvents in their thickened state) introduced by R. Wolbers,[36] are one of the most used retentive cleaning tools. The capillary penetration of the solvent into the artifact is reduced through immobilization of the solvent within the polymer network forming the solvent gel, characterized by weak intermolecular bonds that are responsible for the viscosity of the dispersion. The most important drawback concerning the use of solvent gels is related to the residues that might remain on the works of art after the cleaning (see figure 4.12). Following the treatment with a solvent gel system, it is always necessary to perform an appropriate cleaning procedure, which is usually carried out through organic solvent blends.[35] Furthermore, after mechanical removal and solubilization of the solvent gel system, residues of surfactant may remain on artifacts surface.[37]

A solution to the gel residue has been pursued by formulating completely innovative gel systems. Hence, some new confining systems such as Highly Viscous Polymer Dispersions (HVPD) and physical gels (e.g., rheoreversible polyallylamine based organogels,[38] viscoelastic polyvinyl alcohol-borate based gels[39–41]) and chemical gels (e.g., polyacrylamide networks, which can be functionalized with magnetic nanoparticles) have been recently developed in the CSGI research group.[42–44] In the latter class of gelled systems (chemical gels), the polymeric network is characterized by the presence of covalent bonds. With respect to physical gels, chemical gels exhibit improved mechanical properties; they can be shaped in a well-defined form and can swell in a liquid medium without gel solubilization.

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PART II

Experimental

CHAPTER 5

Synthesis of Innovative Hydrogels for the Cleaning of Water-Sensitive Artifacts

5.1. Introduction

Taking into account the recent doctoral research[1] in this field, the state-of-the-art of gel development and research for applications in the cleaning of Cultural Heritage field is the following:

- Chemical gels, due to their permanent structure, are potential materials for application in the cleaning of artifacts, since no residues of gel are left after cleaning procedures.

- It Is important that chemical gels have an high Equilibrium Water Content (EWC), that is, high enough to release sufficient liquid on the surface, so that a detergency process can take place.

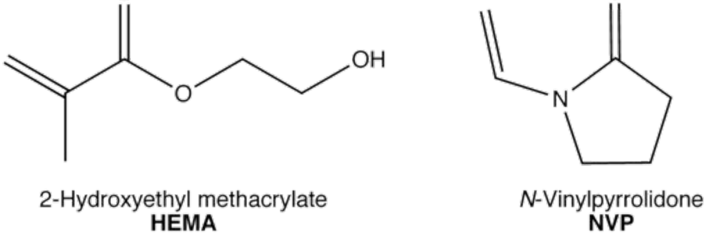


Figure 5.1. Chemical structures of the monomers HEMA and NVP.

- Acrylamide-based chemical gels have already been applied for the cleaning of Cultural Heritage artifacts, since they provide good mechanical features and have an high EWC (~90% w/w).[2,3] However, acrylamide monomer is a very toxic compound (oral LD_{50} (rat): 124 mg/kg and dermal LD50 (rat): 400 mg/kg).[4]

- 2-Hydroxyethyl methacrylate (HEMA) based gels are potential substitutes for polyacrylamide gels due to their low toxicity (oral LD_{50} (rat): 5050 mg/kg).[5] PHEMA gels are extensively studied and have a wide range of applications in medical and pharmaceutical areas.[6,7] PHEMA hydrogels exhibit a high degree of chemical stability and mechanical integrity.[8] In fact, it was the first synthetic hydrogel intended for producing biomaterials, such as contact lenses, described and synthetized by Lim and Wichterle in 1960.[9] A description of the synthesis and properties of pHEMA hydrogels has been given by Refojo and Yasuda.[10] Nonetheless, hydrogels made only of HEMA are rather poor hydrophilic: water content is thermodynamically limited to barely 40% w/w.[11]

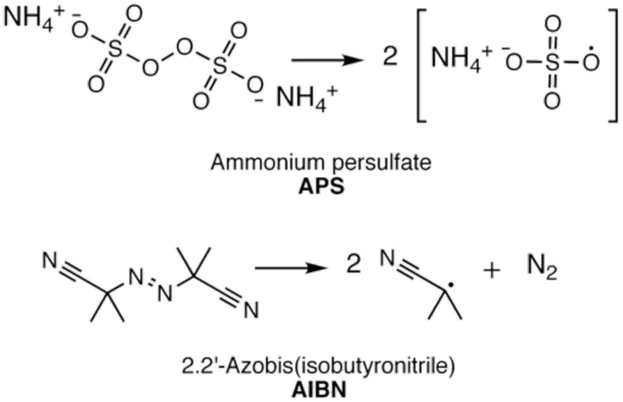
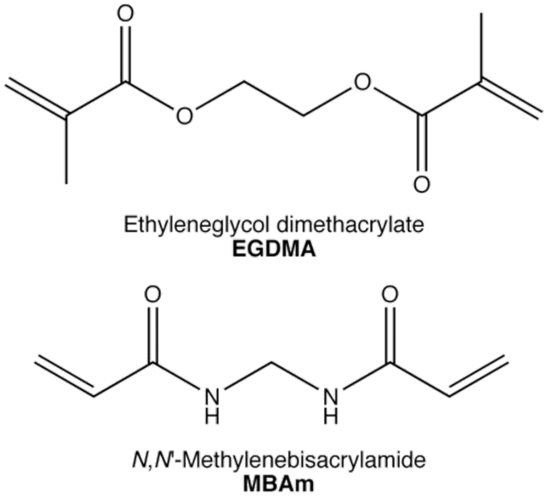


Figure 5.2. Chemical structures and decomposition reactions of initiators APS and AIBN.

- Copolymerization of HEMA with a less toxic hydrophilic monomer was carried out using *N*-vinylpyrrolidone (NVP) (oral LD_{50} (rat): 830 mg/kg and dermal LD_{50} (rat): 1040 mg/kg).[12] As pHEMA, it is a biocompatible polymer and it is widely used in the pharmaceutical, cosmetics and food industries.[13] Chemical hydrogels obtained from the copolymerization of NVP and HEMA, whose chemical structures are presented in figure 5.1, have been reported to have scarce mechanical features.[14] Moreover, the reactivity ratios of each monomer for the copolymerization of HEMA and NVP are considerably different: considering HEMA as monomer-1 and NVP as monomer-2, r_1 and r_2 are 3.12 and 0.05, respectively.[15] This may reflect in a low reaction yield and in high inhomogeneities in the polymer network.

- The free-radical polymerization is the easiest method to obtain hydrogels. There are many types of initiators that undergo homolysis reaction to form radicals. Ammonium persulfate (APS) has been noted to be common for the reaction polymerization of HEMA.[16] APS has a low decomposition rate, so usually is generally in association with the catalyst *N*,*N*,*N*',*N*'-tetramethyl ethylenediamine (TEMED) that initiates the APS chemical homolysis even at room temperature. Another extensively used initiator is 2,2'-azobis(isobutyronitrile) (AIBN),[17] which has an higher decomposition rate, and activates at lower temperature with respect to APS.[18,19] The use of AIBN to activate HEMA's monomer has been already reported.[17,20] Chemical structures of APS and AIBN, along with their homolysis reaction are described in figure 5.2. Polymerization reaction may take place under thermal conditions or by radiation induction.



Ethyleneglycol dimethacrylate
EGDMA

N,*N*'-Methylenebisacrylamide
MBAm

Figure 5.3. Chemical structures of crosslinking agents EGDMA and MBAm.

- Crosslinking of HEMA in a polymerization reaction is done in the presence of a crosslinking agent. The most commonly used is ethyleneglycol dimethacrylate (EGDMA), and the crosslinking with HEMA has been reported for a long time.[11,21] The amount and cross-link type have been reported to influence the swelling ratio and the polymer-water interaction parameter.[22] Another important crosslinking agent is *N*,*N*'-methylenebisacrylamide (MBAm) (see figure 5.3), which is specially used with acrylamide gels, yet its combination with HEMA has also been proposed for creating highly absorbent gels.[16]

The previous doctoral research[1] on chemical gels based on HEMA and VP gave interesting results, so the focus of this thesis lied on these materials, with the aim of developing a new synthesis method that could improve hydrogel's characteristics, and, in particular, to produce suitable retentive gel systems for the removal of unwanted layers from water-sensitive artifacts.

5.2. Design of highly-retentive hydrogels for the cleaning of water-sensitive artifacts

The synthesis design of a new class of hydrogels for the cleaning of water-sensitive artifacts began having as starting point two selected gel formulations of HEMA-NVP copolymers from the previous PhD thesis[1], which formulations are presented in table 5.1. Both gels have shown interesting results during the application on canvas for the removal of aged polymers. In particular, they are both transparent, which is a required characteristic for controlled cleaning interventions.

Table 5.1. Composition (wt%) of the two selected hydrogels from previous research work.

Gel	NVP (wt%)	HEMA (wt%)	H_2O (wt%)	MBA (wt%)	APS* (wt%)
B1	13.96	5.99	79.80	0.20	0.05
C2 NaCl	26.82	2.98	69.53	0.60	0.07

* The *N*,*N*,*N*',*N*'-tetramethyl ethylenediamine (TEMED) catalyst of the homolysis reaction of ammonium persulfate (APS), is added with a fixed volume of 50μL in both formulations.

The most evident disadvantage about these hydrogels is their friable nature under some manipulation. Contrariwise, studies have reported the successful application of copolymers of HEMA-NVP as biomaterials, but with gel formulations having an EWC from 40 to 60% (w/w).[14] The increase of water content beyond this limit may be responsible for the gel friability, since the polymer chains that are organized by the copolymers with rather distinct chemical structures, may not be elastic enough for high grades of water swelling. For this reason an alternative method for obtaining hydrogels with high EWC based on pHEMA and pVP was pursued.

Another important aspect to the restoration field is the retention capability of the liquid containing system. In drug delivery field, the control of the liquid diffusion in hydrogels is important as well.[23] Several approaches have been tried to change the microstructure of the hydrogel in order to have hydrogels able to diffuse liquid in a controlled way. The immediate method is to increase the crosslinking agent, which produce highly cross-linked gels that may, however, exhibit undesirable mechanical properties. A more sophisticated method is the production of interpenetrating polymer networks (IPNs). IPNs can be formed by the crosslinking reaction of an hydrogel in the presence of a pre-polymerized polymer network (IPN), or, by the entrapment of linear or branched polymers within the forming polymer network (semi-IPN, or SIPN),[24] as illustrated in figure 5.4. Linear polymers incorporated into a cross-linked network can act as dangling chains, producing softer gel systems.[25]

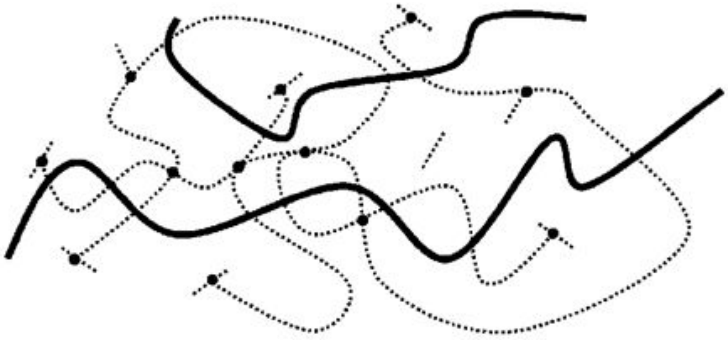


Figure 5.4. Schematic representation of a SIPN network. Solid lines are the embedded linear polymer, dashed lines are the polymer cross-linked network and filled dots are the cross-links.[26]

Among the various advantages of IPNs with respect to conventional cross-linked gels, there are the efficiency in loading different systems and the possibility to tune pore sizes and surface chemistry, which are in relationship with liquid release features and gel mechanical properties.[27] The IPNs versatility is also based on the hydrophilicity of the interpenetrating phases that can be tuned in order to meet different swelling responses of hydrogels and, thus, specific liquid release kinetics.

These characteristics are highly compatible with restoration and conservation demands. So, to benefit from the characteristic mechanical strength of HEMA and the hydrophilicity of VP the polymerization reactions have been carried out in order to obtain SIPN hydrogels, where linear polymer PVP with high molecular weight ($M_w \approx 1.3 \times 10^6$ Da) are interpenetrated during the polymerization of HEMA's monomer. The combination of HEMA and PVP with different molecular weights to form SIPN hydrogels has also been presented here.[28,29] Several considerations were made during synthesis trials and SIPN hydrogel formulation boundaries were evaluated qualitatively. A summary of such synthesis design is presented here.

5.2.1. Radical initiator

In order to choose which initiator was the most suitable, considering that decomposition rates affect the final morphology of hydrogels, APS/TEMED and AIBN were used in a 0.18wt% amount in relation to HEMA monomer weight. The chosen gel formulation for this trial was a SIPN gel with 38wt% of water, a HEMA/PVP weight ratio of 9:1, and 1wt% of MBA (crosslinking agent) with respect to HEMA weight. A remark should be make to AIBN, which is almost insoluble in water, but this seems not to compromise the formation of radicals and the initiation phase of the polymerization reaction. This may be due to the presence of the polymer phase (PVP), which could offer extra solubility for AIBN.

Both initiators originated transparent hydrogels. However, even if the prepared reaction mixture was homogeneous, the APS cured hydrogels showed a white deposit in the bulk of the system, most probably due to a phase separation of PVP. For this reason the use of AIBN was preferred. Going further with synthesis trials, low values of gel content were noticed, mainly with increasing PVP weight percentage (see sub-chapter below). For this reason AIBN amount was increased to have the right amount of radicals during the initiation phase of polymerization reaction, in order to contribute to a complete polymerization of the activated monomers. Lower initiator concentrations also mean slower polymerization rates. If polymerization rate is slow, oxygen may inhibit polymerization of monomers, resulting in gels that are mechanically weak. Too much initiator, on the other hand, could give rise to shorter average polymer chains and oligomers, which may produce turbid gels with low elasticity, or in limit cases, gel solutions that does not seem to have been polymerized. Considering the obtained results, HEMA/AIBN molar ratio of 1:0.01 was considered to be suitable.

5.2.2. Interpenetrating polymer PVP

Considerations on the PVP quantity and molecular weight were made alongside. In the literature[28,29] semi-IPNs made of HEMA, as the network, and PVP, as the linear polymer, are already reported, even if only rather small amounts of PVP are considered. It has been reported that in a PVP water solution (60wt%) with a molecular weight of $1x10^6$–$1.5x10^6$ Da all water is bounded, while in other grades of PVP with lower molecular weights, some of the water in solution acts as free water. Considering these results, and in order to restrain the variables, an higher molecular weight PVP (≈$1.3x10^6$ Da) was used in these trials and further in this work for mainly two reasons related to its hydrophilicity: it can potentially produce hydrogels with high water content and it can retain water-based systems in order to avoid excessive spreading during the cleaning of water-sensitive surfaces.

Table 5.2. Compositions (wt%) of SIPN gel formulations for the two PVP series (XPVP38 and XPVP60, "X" refers to the weight percentage of PVP with respect of HEMA). Weight ratios of HEMA and PVP and of H_2O and PVP are presented.

Gel	PVP (wt%)	HEMA (wt%)	H_2O (wt%)	MBAm (wt%)	AIBN (wt%)	HEMA/PVP ratio	H_2O/PVP ratio
0PVP38	0	61.55	37.72	0.62	0.11	-	-
10PVP38	5.60	55.99	37.75	0.56	0.10	1:0.1	1:0.15
20PVP38	10.27	51.36	37.77	0.51	0.09	1:0.2	1:0.27
30PVP38	14.23	47.42	37.79	0.47	0.09	1:0.3	1:0.38
40PVP38	17.62	44.06	37.80	0.44	0.08	1:0.4	1:0.47
50PVP38	20.57	41.13	37.82	0.41	0.07	1:0.5	1:0.54
0PVP60	0	39.81	59.72	0.40	0.07	-	-
10PVP60	3.62	36.21	59.74	0.36	0.07	1:0.1	1:0.06
20PVP60	6.64	33.20	59.76	0.33	0.06	1:0.2	1:0.11
30PVP60	9.20	30.66	59.78	0.31	0.05	1:0.3	1:0.15
40PVP60	11.39	28.48	59.80	0.28	0.05	1:0.4	1:0.19
50PVP60	13.29	26.58	59.81	0.27	0.05	1:0.5	1:0.22

Two hydrogels series were considered to evaluate the effects that PVP has on the hydrophilicity of the produced gels. On both series the cross-linker content was maintained constant with respect of HEMA quantity (1wt%), while the weight percentage of PVP with respect to HEMA's monomer weight increased from 0 to 50%. One series was made with 38wt% of water, in order to compare them with a conventional HEMA homopolymer (formulation 0PVP28). The second series was made with 60wt% of water, which is much over than a HEMA homopolymer can support without going into phase separation during synthesis,[1] to evaluate how PVP influence the equilibrium water content. The compositions of these two series are presented in table 5.2.

Table 5.3. General observations of the obtained SIPN hydrogels from XPVP38 and XPVP60 series, after EWC is reached. The water release from gels is expressed.

Gel	Appearance after reaching EWC	Water release (mg/cm^2)
0PVP38	Transparent.	7
10PVP38	Transparent.	8
20PVP38	Transparent/opalescent.	8
30PVP38	Opalescent, slightly slippery.	8
40PVP38	Opalescent, slippery	8
50PVP38	Opalescent, slippery	7
0PVP60	White, opaque.	8
10PVP60	White, opaque, slightly slippery.	7
20PVP60	White, opaque, except for a thin lower transparent layer, slippery.	8
30PVP60	Phase separation: white, opaque upper phase; transparent lower phase, slippery.	8
40PVP60	Phase separation: white, opaque upper phase; transparent lower phase, slippery.	9
50PVP60	More transparent than opaque. The transparent phase swells more.	10

The most relevant observations on the first series (XPVP28) is that the increasing of PVP increases the water content of gels, as highlighted by the enhanced swelling of hydrogels with higher PVP amount (see figure 5.5.). On the other hand it seems not to influence on the release capacity of hydrogels, since the water release trials, as reported in table 5.3, did not show considerable changes between the hydrogels of this series, proving the retention capability associated with the PVP quantity, and therefore, to a certain H_2O/PVP ratio.

The hydrogel series of XPVP60 have highlighted the fact that PVP can increase the water content of hydrogels over the limit of ~40wt% of HEMA. The 0PVP60 hydrogel, which is a pHEMA homopolymer, is totally opaque, because the excess of water goes in phase separation during synthesis, leading to the formation of macro-pores. This polymer's macro discontinuity leads to the scattering/refraction of light due to the different refractive indexes of pHEMA and water. The increase of PVP amount in the hydrogel formulations, in fact, decreases the opacity caused by the water-phase separation. Furthermore, with hydrogels having 60wt% of water, the water release begins to be influenced by the increasing of PVP, mainly after a PVP 10wt% content (see table 5.3).

Figure 5.5. SIPN hydrogels after reaching EWC with two different water ratios in gel formulation: 38 wt% (first row) and 60 wt% (second row), with increasing PVP weight percentage in the HEMA/PVP mixture (from 0 to 50 wt%). Full gel compositions in table 5.2.

In order to obtain fully transparent and homogeneous hydrogels, PVP was increased and water content was decreased to 50wt%, The PVP content with respect to HEMA was therefore increased (table 5.4). In this new series the AIBN initiator content was added in a 1:0.01 HEMA/AIBN molar ratio, because in the previous hydrogel's series a low reaction yield had been observed. The cross-linker was maintained with 1wt% with respect to HEMA amount.

The main reason for this hydrogel series was to evaluate qualitatively how much PVP could be embedded in the HEMA's network. From the observation summarized in table 5.5 is clear that the available area of the HEMA network, which interacts with PVP chains, at a specific HEMA/PVP ratio is not enough to contain further PVP. This happens mainly after a 1:2.3 HEMA/PVP ratio (w/w), so this ratio was considered the borderline. The hydrogel 100PVP50* has good mechanical properties and potential application features.

The water release test showed that from 233PVP50* gel formulation there is a sudden increase of water diffused from the gel to the filter paper. This may be due to the excessive PVP quantity in the formulation that during synthesis prevent the polymer network to form in an homogeneous manner, losing in structure character.

Table 5.4. Compositions (wt%) of SIPN gel formulations for the PVP series XPVP50*, "X" refers to the weight percentage of PVP with respect of HEMA. Weight ratios of HEMA and PVP and of H_2O and PVP are presented.

Gel	PVP (wt%)	HEMA (wt%)	H_2O (wt%)	MBAm (wt%)	AIBN (wt%)	HEMA/PVP ratio	H_2O/PVP ratio
100PVP50*	24.86	24.86	49.72	0.25	0.31	1:1	1:0.5
150PVP50*	29.86	19.91	49.78	0.20	0.25	1:1.5	1:0.6
233PVP50*	34.88	14.95	49.83	0.15	0.19	1:2.3	1:0.7
400PVP50*	39.91	9.98	49,89	0.10	0.12	1:4	1:0.8

* AIBN is added in a 1:0.01 HEMA/AIBN molar ratio.

Table 5.5. General observations of the obtained SIPN hydrogels from XPVP50* series, after EWC is reached. The water release from gels is expressed.

Gel	Appearance after reaching EWC	Water release (mg/cm^2)
100PVP50*	Transparent, homogeneous, slippery.	8
150PVP50*	Transparent, homogeneous, very slippery, soft. A small part of PVP is not embedded.	9
233PVP50*	Opalescent, translucid, homogeneous, very slippery, soft. Some PVP is not embedded	28
400PVP50*	Opalescent, translucid, inhomogeneous, very slippery, very soft, friable. High amount of PVP is not embedded.	20

5.2.3. Water content

The water amount in the composition has been noticed to influence on the final hydrophilicity and retention/release capacity of the gels. Since water is the only non-solid component of the reaction mixture, and furthermore, does not participate in the polymerization reaction, it is the major contributor to final hydrogel porosity. The formed voids in the polymer are liquid containers able to diffuse liquid when in contact with a surface, as it will be addressed further on.

In order to study the maximum water amount possible in the reaction mixture, able to produce stable and homogeneous gels a hydrogel series was made by varying water content (wt%) in hydrogels with 1:1 HEMA/PVP ratio and 1wt% cross-linker content with respect to HEMA amount (see full composition in table 5.6).

Table 5.6. Compositions (wt%) of SIPN gel formulations for the PVP series 100PVPY*, “Y” refers to the weight percentage of water in the composition. Weight ratios of H_2O and PVP are presented.

Gel	PVP (wt%)	HEMA (wt%)	H_2O (wt%)	MBAm (wt%)	AIBN (wt%)	H_2O/PVP ratio
100PVP55*	22.39	22.39	54.72	0.22	0.28	1:0.41
100PVP60*	19.91	19.91	59.73	0.20	0.25	1:0.33
100PVP65*	17.43	17.43	64.75	0.17	0.22	1:0.27
100PVP70*	14.95	14.95	69.76	0.15	0.19	1:0.21

* AIBN is added in a 1:0.01 HEMA/AIBN molar ratio.

Table 5.7. General observations of the obtained SIPN hydrogels from 100PVPY* series, after EWC is reached. The water release from gels is expressed.

Gel	Appearance after reaching EWC	Water release (mg/cm^2)
100PVP55*	Transparent, homogeneous, slippery.	9
100PVP60*	Opalescent, translucid, slightly inhomogeneous, slippery, soft.	10
100PVP65*	Opalescent, less translucid, inhomogeneous, very slippery, very soft.	12
100PVP70*	Opaque, water phase separation.	10

According to this series there is a limit of PVP amount in the H_2O/PVP ratio, under which the water in the gel formulation goes into phase separation (see table 5.7). To simplify, gel formulations having PVP content under 27wt% with respect to water quantity were not considered further on.