

Polymeric Coatings for Protection of Historic Monuments: Opportunities and Challenges

Mehdi Sadat-Shojai,¹ Amir Ershad-Langroudi²

¹Department of Polymer Science, Iran Polymer and Petrochemical Institute, 14965/115 Tehran, Iran

²Department of Colour, Resin and Surface Coating (CRSC), Iran Polymer and Petrochemical Institute, 14965/115 Tehran, Iran

Received 8 June 2008; accepted 16 November 2008

DOI 10.1002/app.29801

Published online 18 February 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The conservation and protection of historic monuments or culturally significant structures have recently attracted much attention from material scientists. This review is given of the various aspects of the monuments protection such as the main reasons of damaging and spoiling of the historical monuments, the factor of contact angle as one of the essential parameters in the selection of polymeric coatings, and some of usual types of polymeric materials used for monument protection. There has been growing interest in developing novel materials for using in protective fields. Nowadays, the polymeric coatings, especially those with high hydrophobicity, are widely used to decrease or even stop further deteriora-

tion of historical monument. This review presents some of the most well-known polymers used as protective materials such as acrylics, alkoxy-silanes, fluorinated polymers, and hybrid organic-inorganic coatings. Furthermore, hybrid organic-inorganic coatings as a new class of materials are increasingly interesting materials because of their extraordinary properties deriving from the combination of the different building blocks and it is attempted to focus on this materials. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2535–2551, 2009

Key words: transparency; coatings; nanocomposites; polysiloxanes; fluoropolymers; monument protection

INTRODUCTION

The protection of historical monuments is the multidisciplinary approach and is a collision of two incompatible worlds that is the old and new world.¹

Historical monuments are mostly made from one of the following building materials^{2,3}:

- Stone such as marble
- Mud and mud brick
- Sandstone
- Masonry
- Ceramic and glass.

The protection of historic or culturally significant stones has recently attracted much attention from material scientists.⁴ In the past, the consolidation of monuments by using unsuitable means, such as iron dowels, staples, lime mortar, cement, plaster, and unsuitable resins, often caused negative effects on appearance of monument and further damage.

In recent years, various synthetic polymers have been widely used in the treatment of construction

materials of historical monuments for consolidation and conservation of such structures.⁵ However, protection of monument by using polymeric coatings has created serious challenges for the surface science and technology. Some of the challenges are as follows^{1,4–9}:

1. Because of the role of water in damaging and spoiling of monuments, polymeric coatings must be capable to stop the liquid water entry and let it escape as vapor;
2. A synthetic polymer must be soluble in convenient solvents during the synthesis and coating steps. Water-based coatings with neutral pH are usually preferred. Moreover, the temperature of polymerization and crosslinking reactions on the surface of the monument is preferred to be close to the ambient temperature, and the final coating must be removable (e.g., via a suitable solvent) whenever problems had arisen or when a new and better product is available. It is very important that the removing of coating will be not damaged the original monument;
3. The protective material should be performed at the optimal thickness. Thickness of polymeric coating must be as high as possible to increase the hydrophobic properties and the durability. However, transparency of coating has a

Correspondence to: A. Ershad-Langroudi (a.ershada@ippi.ac.ir).

tendency to decrease with increasing of its thickness. Thus, precise control of the thickness is required to satisfy hydrophobicity, transparency, and durability;

4. Polymeric coatings must be stable to the alterations of climatic conditions and to the negative effects of the ultraviolet radiation from sunlight;
5. Coating film must be compatible with the surface of monuments; for this reason, the evaluation of interaction between the new and historical materials is very important.
6. Protective materials must have a whole set of simultaneous properties such as physical and mechanical properties, service life, and aging history; unfortunately, some of these properties are competitive with each other;
7. A key function of protective coatings on surface of monument maybe blocking the liquid water entry. This property predominantly is affected by hydrophobicity of coating film. The hydrophobicity of solid surfaces with liquids is governed by the chemical composition and the geometric microstructures of the surface. It is well known that the water-repellent property is enhanced by the surface roughness. Unfortunately, hydrophobicity is competitive with transparency because it is the source of light scattering. When the surface roughness increases, hydrophobicity increases and transparency decreases. Moreover, the increase of roughness of the films may lead to a lower durability of the coating film and poorer mechanical properties than flat surfaces against scratching and abrasion. Thus, the polymeric coatings must be applied with an optimal thickness to satisfy hydrophobicity, transparency, and durability.

Surfaces with a water contact angle higher than 150° , which in literatures is known as superhydrophobic surface, have attracted much attention because of their potential practical applications, such as self-cleaning property.^{4,6}

It is necessary to mention that before the performing of polymeric coating, the surface of monument must be cleaned by a suitable method. In fact, cleaning is often one of the first steps of historical monument protection. In the past, the cleaning procedure is performed by acidic solutions followed by neutralization, which resulted in the generation of salts that increased the deterioration. The unsuitability of many of these methods caused to develop new methods for the surface cleaning of historical monuments. Nowadays, the most important methods for cleaning of monument involved the lasers, biological cleaning, and targeting the dirt.¹⁰

In this review, we consider the present state of historical monument protection. This review is not a detailed and intended to give a general overview about the monument protection. However, it focuses on various polymeric coatings used in protective applications. It presents first the various factors causing to deteriorate stones. Then, because of the importance of contact angle factor in monument protection, it is preferred to explain this aspect of the subject. We would like and persist to introduce some historic monuments of Asian countries, especially those in Iran, that their protection by suitable coating material is very important. Finally, in another important section, the different types of polymeric materials used for monument protection is presented. In this section, in addition to introducing polymeric coatings, it is tried to recommend areas of strength and weakness in different polymeric coatings.

SPOILING OF THE HISTORICAL MONUMENTS

Before we present any procedure for protection of historical monuments, it is necessary to introduce spoiling factors causing the deterioration of historical structures. Moreover, it must be emphasized that protective materials can only slow down but not stopped the deterioration of building materials of historical monuments. Parallel to researches in other countries, Iranian researchers also survey on the pathology of Persian monuments such as deterioration causes and environmental impact assessment; For instance, Zabihi¹¹ studied the pathology of decorative bricks of Chahar Bagh school of Isfahan.

There is a very wide range of factors which cause the spoiling of monuments. The four broad categories of deterioration in historical structures are as follows^{2,3,9-25}:

1. Natural factors namely climatic factors, earthquake, fire, and corrosion. The most important climatic factors include flood, wind, rain, frost, and temperature fluctuations. The water freeze/thaw cycles, which maybe from the rain water, are a very important factor to result in material decay. Natural phenomena such as earthquakes and temperature variations cause the displacement of foundation and change the geometry of monument. Small changes in geometry can seriously alter the equilibrium of a monument and may cause it to collapse.
2. Human factors such as road traffics (for bridges), vandalism, terrorism, neglect, and tourism;
3. Biological factors such as various types of bacteria and fungi. The biodeterioration of building materials of monuments through the action of

biological organisms has been recognized over a long period. The biodeterioration is determined by two main factors, which are the bioreceptivity of building materials and their microbial contamination. The bioreceptivity of the building materials is described by its structure and also its chemical composition, whereas the microbial contamination is determined by the climatic factors. Biological organisms produce the colloidal biofilms on surface of the monuments. Shrinking and swelling of these biofilms can cause mechanical stress and finally weakening of the mineral lattice. Moreover, acidolytic and oxidoreductive biocorrosion processes also cause biodeterioration of building materials and may be very harmful, especially to limestone.

4. Air pollution and salt growth: It is believed that the atmospheric pollution is the main agent responsible for stone decay, and in industrial countries attention to the field of protective materials should also be increased parallel to increasing pollution. The danger of the air pollution is more serious in humid regions because moisture can collect environmental pollutants on the surface of the monuments. The most corrosive materials in the highly polluted urban or industrial areas are dusts suspensions and gaseous products such as SO₂, NO, and CO₂. Gaseous products are capable of dissolving in water to produce an acidic solution such as sulfuric acid and nitric acid and then react with calcareous building materials. Moreover, carbonate-based stones such as marble suffer from the attack of sulfur dioxide in polluted environments because of the transformation of CaCO₃ into gypsum as final product. For example, most Greek cultural heritage objects in Acropolis of Athens and also Taj Mahal in India have been constructed with marble. At the present time, Taj Mahal is suffering from yellowing of marble and dissolution because of acid rain. Experts of the archaeological survey of India have named it "marble cancer." Since January 2002, the suspended particulate matter level in the area has doubled, drastically increasing erosion of the white marble surface of Taj Mahal. Moreover, every year during the months of May and June, winds blowing at speeds ranging from 40 to 70 km per hour and carrying sand particles damage the marble.

Kapalos et al.²³ evaluated the ability of an acrylic copolymer, Paraloid B-72, and a small siloxane molecule to protect cultural heritage monuments against corrosion caused by the SO₂ dry deposition.

However, the effects of air pollutants on stone decay are very complex. If a monument is washed by rain, the corrosion products are washed and the surface of the stone is cleaned. On the other hand, the water source from rain causes some freeze/thaw cycles of water, and so it does the further damage. Moreover, in the highly polluted urban areas, the rain maybe acidic and it causes further deterioration.

In fact, air pollutants increase the salt content in building materials, and it is believed that the deterioration of many of the world's famous monuments is due to the crystallization processes of salts. The growth of salt crystals in the porous building materials can generate microcracks because of significant changes of salt volume and finally destroy the monument. It must be emphasized that there are many sources of salts generation such as air pollution, soil, wind; unsuitable cleaning materials and incompatible building materials.

Van Hees and Brocken¹⁵ evaluated the salt growth in brick masonry specimens, coated with a water repellent, during a salt crystallization test. They demonstrated that the behavior of different salts on development of salt damages is completely different.

However, it is demonstrated that the adsorption of dusts suspensions and water-soluble air pollutants decreases with increasing hydrophobicity of the surface of building materials. For this reason, superhydrophobic coatings have become a focus of interest in the field of protective coatings.

THE FACTOR OF CONTACT ANGLE

Surface wettability is opposite of hydrophobicity of the surface and can be described by the contact angle.^{9,17} The hydrophobicity of surfaces is essentially dependent on the surface tension or surface free energy of polymeric coating.²⁶⁻²⁸ Because of the different interfacial forces between solid and liquid for various solid films, the shape of the water drop is varied in different cases. When a drop of water settles on a surface with low hydrophobicity or high wettability immediately spreads and wets the surface. But in the case of hydrophobic surface, the drop contracts and makes an angle with the surface ($\theta > 90^\circ$).^{2,26,29} The equilibrium angle between drop and surface is controlled by a balance between the interfacial forces for the solid-liquid, liquid-vapor, and solid-vapor interfaces. This equilibrium angle is reached to minimize the surface free energy.²⁹

The hydrophobicity of surface can be evaluated by the measurement of static and dynamic contact angles against water.^{9,28} However, the measurement of contact angle by static method for determining of hydrophobicity is only applied for the materials whose surface roughness is previously reduced or standardized and later coated with the protective

materials.⁹ In fact, the reduction of the surface roughness by means of an abrasive is not identical for various building materials, so the specific protective material will give different contact angles on different building materials. Brugnara et al.⁹ demonstrated that, in some cases, the measurement of the advancing angles can only indicate the presence of the protective, not its effective protecting ability.

There are two basic methods to alter the contact angle. The usual method to change the contact angle is to decrease surface energy by changing its surface chemistry. A typical example of such approach is to use fluorinated groups in protective coatings.^{17,27} The small atomic radius and the high electronegativity of fluorine lead to the formation of a strong covalent bond between the fluorine and carbon and consequently a surface with low energy.¹⁷

The other approach to change the contact angle is to change the morphology or the geometry of the surface.^{2,17,30} However, surface morphology is frequently explained by surface roughness.^{2,29,30} It is demonstrated that the effective surface area and consequently nominal surface energy increase with increasing the surface roughness.¹⁷ The alterations of surface morphology cause to alter the relative contribution of the solid–liquid interface to the surface free energy.²⁹

There are various approaches to reach surface roughness such as sol–gel process,³¹ plasma etching and polymerization,²⁷ chemical vapor deposition,²⁷ incorporation of the particles,^{2,27,28,30} reaction in hot water,²⁷ layer-by-layer (LBL) process,³¹ and phase separation.^{6,27,29,31}

In fact, the high hydrophobicity of composite films is due to the specific pattern of its surface.^{2,28} For example, the roughness of these hydrophobic surfaces is induced by incorporation of silica particles in surface coating.^{28,30} Moreover, the degree of surface roughness is controlled by size, degree of aggregation, and concentration of particles.^{28,30} Pilotek and Schmidt²⁸ investigated the hydrophobicity of hydrophobic surfaces in terms of surface morphology by using different kinds and concentrations of silica nanoparticles.

It must be emphasized that in superhydrophobic protective coatings, both changes in surface chemistry and surface roughness must be optimized.^{17,27,30}

THE FUTURE AND PAST OF THE HISTORICAL MONUMENTS AND THE IMPORTANCE OF CONSERVATION

The conservation of the cultural heritage is of high value for the future of all countries. We are delighted to state that the ancient Asian made great contributions to the development of world civilization. The civilizations of the Asian countries are one of the oldest civilizations in the World; for example,



Figure 1 The image of Persepolis, the most important Persian monument, which is located in Shiraz. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

8000 years ago, there was a civilization which lived in today's Khoozestan (Iran) and was called "Shoosh Civilization" or in English "Susa Civilization." In fact, there are several precious monuments in Asian countries such as Taj Mahal, Great Wall of China, Arg-e-Bam, and Persepolis (Fig. 1). The list of the historical monuments of the Asian countries is endless; these monuments define a great history of the Asian countries in which they are situated.

The historical Citadel of Bam (Arg-e-Bam) covers ~ 200,000 m² and has had around 20 centuries of habitation, making it one of the most ancient earthen structures. It was made from mud brick containing a very resistant type of clay. An earthquake measuring 6.3 on the Richter scale occurred on December 26, 2003 led to the destruction of Citadel of Bam and loss of many human lives.³² It must be emphasized that Persian monuments in Iran such as Choghazanbil temple in Shoosh, Persepolis, Pasargad and Naghshe Rostam in Shiraz, Alighapou, Sepah Salar Mosque, Siosepol (bridge) in Isfahan, and Yazd's grand mosque are required to be conserved immediately by protective materials. So far, several studies have done on the Persian monuments of Iran; these studies have frequently focused on the building materials of old structures, the pathology of monuments (deterioration causes, environmental impact assessment, etc), and conservation and restoration techniques (planning intervention techniques, selecting materials strategy, earthquake protection, etc.).^{11,18–22} Figure 2 shows the effect of a protective coating based on modified oligomer of alkylalkoxysiloxanes on the diminishing of the depth of diffusion of rain water on the surface of the Choghazanbil temple in Shoosh.

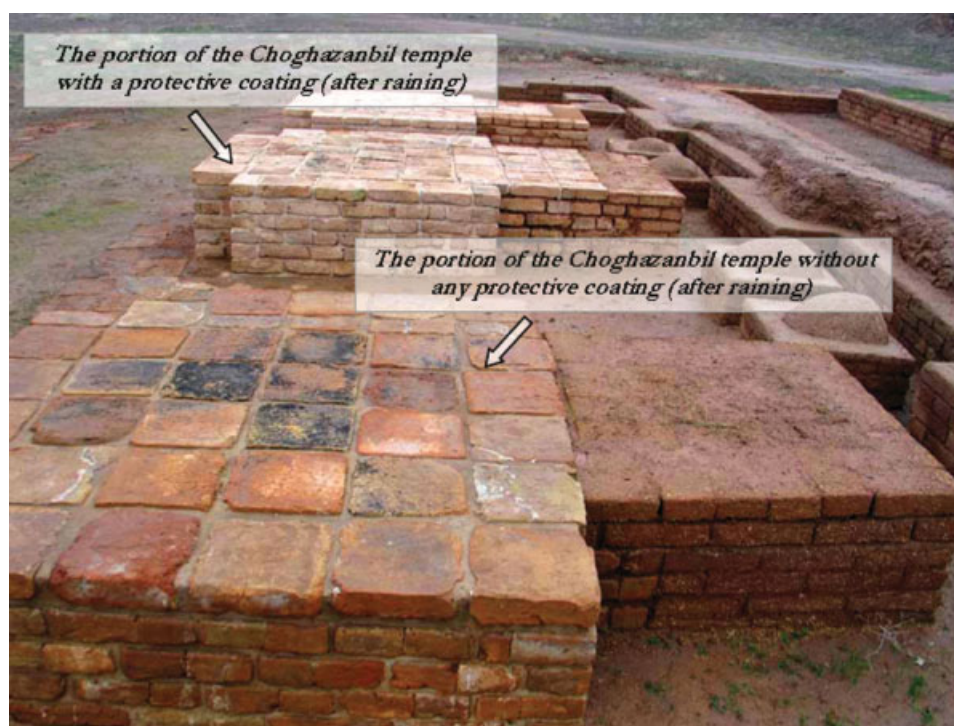


Figure 2 The image of the effect of a protective coating based on modified oligomer of alkylalkoxysiloxanes on the diminishing of the depth of diffusion of rain water on the surface of the Choghazanbil temple in Shoosh (Iran). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

DIFFERENT KINDS OF POLYMERS FOR MONUMENT PROTECTION

Nowadays, the polymeric coatings, especially those with high hydrophobicity, are widely used to decrease (or stop) further deterioration of historical monuments.¹³ In fact, most modern materials, which have been applied as stone treatments in the recent years, have been mainly developed for other purposes, mostly industrial applications, and their application to monument protection has been secondary.^{1,5}

All polymers which are used as protective materials in conservation fields such as monument protection have the performance parameters of the coating material such as transparency, absence of color, good chemical stability, good penetration, solidification strength, and antiflaking properties. These polymers frequently consist of synthetic organic polymers such as acrylic and silicon-based products and hybrid organic-inorganic materials. Moreover, some inorganic materials such as silicates of sodium, potassium, and lithium and also various compound materials have successfully been applied in protection fields.^{1,5,7,13,33-36}

Sodium, potassium, or lithium silicates are the generic names for a series of compounds derived

from soluble silicate glasses. They are water solutions of metal oxide (Na_2O , K_2O , or Li_2O) and silicon dioxide (SiO_2) combined in various ratios. By varying the proportions of SiO_2 to metal oxide and the solids content of solutions, products of definite but widely different properties are produced, and it is important to specify the silicate ratio and concentration when discussing an application.³⁷⁻³⁹

The solution of silicates has physical and chemical properties that are useful in coating applications. When the solution of silicates applied as a thin layer on surfaces of other materials, the silicate solution dries to form a tightly adhering inorganic film; in fact, silicates are converted to solid films by two methods: (1) evaporation of water (dehydration) or (2) chemical setting mechanism. These can be used separately or in combination. Chemical setting is often used to improve film moisture resistance, to reduce setting time, and to increase ultimate bond strength as needed. When the alkalinity is decreased or removed by neutralization, the siliceous species will polymerize at a rate dependent on the silica concentration and pH value. Once the film is formed, the protection is maintained as long as silicate treatment is continued; if stopped, the protection is gradually lost; if damaged, the film is self-healing, as long as the silicate feed is continued.³⁷ These films are

nonflammable, resistant to high temperatures, bondable to metals, particles, glass, and ceramics, odorless and nontoxic, stable to UV light exposure, and strong and rigid. Because silicate coatings are inorganic aqueous polymers, they perform most effectively on hydrophilic, nonoily surfaces, where they achieve proper wetting and, hence, maximum adhesion.³⁶⁻⁴³

Although potassium or lithium silicates have properties and uses similar to sodium silicate, but certain differences offer advantages in many uses, forming a basis for selecting potassium or lithium silicate in place of sodium silicate. For example, potassium silicate is more soluble than sodium silicate of equal levels of alkalinity, making blends with potassium silicate more life-cycle stable, more washable, and offers the potential for higher concentration formulations. Moreover, potassium silicate solutions are not as sticky or tacky as sodium silicate solutions and are therefore easier to handle and use.³⁹⁻⁴²

Most important commercial acrylic polymers used as water repellent include Paraloid B72 and Paraloid B67. However, it is necessary to evaluate the suitability of the new materials to be used in the monument protection, and it must be performed by standard methods which provide comparative results.^{1,5} Favaro et al.⁵ evaluated the performances of Paraloid B72 and Paraloid B67 and a silicon-based product for monument protection. They demonstrated that the structural changes are related with the color changes of the weathered specimens and with the loss of consolidation efficiency of the polymeric coatings. Amin-Shirazi Nejad¹⁸ investigated the performance of some paraloids as a consolidant material at climatic conditions of Iran. In the sequel of the review, we will focus on the synthetic organic polymers.

Acrylics

Polymers based on various acrylics, which are known as Paraloids, are widely used in the conservation of monuments. Polyacrylics are synthesized by the addition polymerization of the corresponding monomers.⁴⁴

Acrylic-based protective materials have the moderate hydrophobicity and well adhering property. They are polymerized usually *in situ* to form the optically clear films.^{10,44} However, most of the pure acrylic polymers have high rigidity and T_g , making them unsuitable in conservation applications.¹⁰ These applications require durability and resistant to spoiling factors such as temperature fluctuations, sunlight, moisture, and air pollution agents for long periods of times⁴⁴; for these reasons, acrylic polymers are usually blended or copolymerized to

improve the protective and physical properties. The molecular structure of some acrylic copolymers used in conservation fields is shown in Table I.

Chemical decays of acrylic-based polymers such as photooxidative reactions lead to the formation of oxidized species such as γ -lactones, which finally cause to yellowing appearance of the polymeric coating on the stone surfaces.^{5,45}

The photooxidative stability of a series of commercial acrylic polymers such as B66 and B67 has been investigated by Chiantore and Lazzari.⁴⁵ They concluded that the stability of the acrylic polymers is strongly influenced by the alkyl side groups. In fact, oxidation usually occurs in hydrogen atoms on the two methylenes of the *n*-butyl groups in B66, or on the one methylene of the tertiary carbon of the isobutyl groups in B67 (Table I), and the photooxidative stability of Paraloids is dependent on the reactivity of such hydrogens.⁴⁵

As stated earlier, two procedures used to improve the properties of acrylic resins include copolymerization and blending. The comonomers used in copolymerization are frequently fluorinated monomers. Yoshida et al.⁴⁷ prepared a series of methacrylate random copolymers that contained of fluorinated group to attain a high hydrophobicity, trialkoxysilane groups as an anchor to the surface, and epoxy groups as the crosslinking agent (Table I). They reported that these random copolymers have high hydrophobicity and mechanical durability. The procedure of copolymerization with fluorinated comonomers will be explained in detailed in section of "fluorinated polymers as protective coatings."

The other procedure is the blending of acrylic resin with some other resins. For example, dissolving of B72 in an alkoxy silane such as MTMOS leads to high adhesive properties because of the existence of acrylic component and deep consolidation and alkoxy silane component.¹⁰

Alkoxysilanes

The alkoxy silanes (or silanes) such as methyltrimethoxysilane (MTMOS) and tetraethoxysilane (TEOS) have widely been used as protective materials in the last 20 years.¹⁰

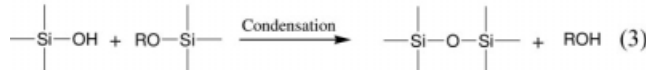
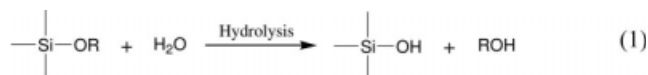
The reactions of alkoxy silanes that lead to the formation of network on the surface of the monuments have been recognized. After the application of the protective coating on the stone surface, the alkoxy silanes are hydrolyzed by water to produce alkoxy silanols [eq. (1)]. Then, alkoxy silanols condense to form a polysiloxane (or silicone) polymer with the elimination of water or alcohol [eqs. (2) and

TABLE I
Chemical Formula of Some Important Acrylic Resins

Commercial name	Formula	Reference
B66	$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_3 \end{array} \right)_x \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOC}_4\text{H}_9 \end{array} \right)_y$	45
B67	$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_2\text{CH}(\text{CH}_3)_2 \end{array} \right)_x$	45
B72	$\left(\begin{array}{c} \text{H} \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_3 \end{array} \right)_x \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOC}_2\text{H}_5 \end{array} \right)_y \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOC}_4\text{H}_9 \end{array} \right)_z \quad \{z \lll m, n\}$	45
B82	$\left(\begin{array}{c} \text{H} \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOC}_2\text{H}_5 \end{array} \right)_x \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_3 \end{array} \right)_y \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOC}_4\text{H}_9 \end{array} \right)_z \quad \{z \lll m, n\}$	45
—	$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_3 \end{array} \right)_x \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOC}_4\text{H}_9 \end{array} \right)_y \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COO}(\text{CH}_2)_2\text{OCOCF}_2\text{CF}_2\text{H} \end{array} \right)_z$	26
—	$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_3 \end{array} \right)_x \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOC}_4\text{H}_9 \end{array} \right)_y \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COO}(\text{CH}_2)_2\text{OCOCH}_2\text{CH}_3 \end{array} \right)_z$	26
—	$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_3 \end{array} \right)_x \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOC}_4\text{H}_9 \end{array} \right)_y \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COO}(\text{CH}_2)_2\text{OH} \end{array} \right)_z$	26
—	$\left(\begin{array}{c} \text{F} \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_3 \end{array} \right)_x \left(\begin{array}{c} \text{H} \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_3 \end{array} \right)_y$	44
—	$\left(\begin{array}{c} \text{F} \\ \\ \text{C} \\ \\ \text{F} \end{array} \right)_x \left(\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C} - \text{C} \\ \\ \text{OCOCH}_3 \end{array} \right)_y \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C} - \text{C} \\ \\ \text{OCO}(\text{CH}_2)_3\text{Si} \begin{array}{l} \\ \text{CH}_3 \\ \\ \text{CH}_3 \end{array} \end{array} \right)_z \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{O} - \text{Si} \\ \\ \text{CH}_3 \end{array} \right)_n \text{C}_4\text{H}_9$	46
—	$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_3 \end{array} \right)_x \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_2\text{-Rf} \end{array} \right)_y$	47 ^a
—	$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_3 \end{array} \right)_x \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_2\text{-Rf} \end{array} \right)_y \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \end{array} \right)_z$	47 ^a
—	$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_3 \end{array} \right)_x \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH}_2\text{-Rf} \end{array} \right)_y \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3 \end{array} \right)_z \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C} - \text{H}_2\text{C} \\ \\ \text{COOCH} - \text{O} \\ \\ \text{C} \\ \\ \text{H}_2 \end{array} \right)_y$ <p style="text-align: center;">Hydrolysable portion Hydrolysable portion Crosslinkable portion</p>	47 ^a

^a Rf ≡ CH₂(CF₂)₆CF(CF₃)₂, CH₂(CF₂)₂CF₃, CH₂(CF₂)₅CF₃, CH₂(CF₂)₃CF₃, and CH₂CF₃.

(3)].^{10,34,48} However, the alkyl-modified alkoxy-silanes-based coatings are mostly known as organic-inorganic hybrids systems because of their alkyl groups as organic component and silicon backbone as inorganic one. Figure 3 shows the structure of these polymers as protective coating on the surface of monument.



The procedure which is used to form silicon network is usually *in situ* sol-gel process. Some of the parameters such as temperature, pH, and reactant concentrations must be controlled to obtain a best silicon network.⁴⁸ For example, the hydrolysis rate is directly affected by pH.⁴⁸ However, the hydrolysis step is catalyzed with either acids or bases. It is possible to evaluate the effect of pH on the rate of network formation by means of the gel time.⁴⁸

Ni et al.⁴⁸ synthesized the organic-inorganic hybrid coating system based on the isocyanurate as organic component and prepolymerized oligomers of TEOS as inorganic component. They demonstrated that the *para*-toluene sulfonic acid catalyzes the formation of the hybrid coating system and leads to enhancement of the adhesive properties of the hybrid coatings. In fact, the crosslinking density increases and the crystallinity of the organic phase decreases by the addition of acid catalyst.⁴⁸

Distinctions should be made between the ordinary alkoxy-silanes ($\text{Si}(\text{OR})_4$) and alkyl-modified alkoxy-

lanes ($\text{R}_x\text{Si}(\text{OR}')_y$).^{20,25,30,31} Xu et al.⁴⁹ investigated the hydrophobic films synthesized by the polymer of methyltriethoxysilane (MTES), the polymer of dimethyldiethoxysiloxane, and hexamethyldisilazane (HMDS) as mono-, di-, and trimethyl modifiers, respectively. They concluded that the contact angles of hydrophobic films synthesized by mono- or dimethyl-modified silica sol are less than 120° . But it reaches 165° when using trimethyl-modified silica sol.

Wu et al.³⁰ modified a silica-based sol-gel coating. They attempted to modify the hydrophobicity of coating by incorporation of a long side-chain alkyl-trialkoxysilane such as octyltriethoxysilane into the coating solution (chemical modification) and also by the addition of silica filler into coating (morphology modification). They demonstrated that the contact angle is affected by chemical properties and surface morphology, and the addition of silica filler leads to increase in contact angle.³⁰

Shirtcliffe et al.²⁹ prepared the superhydrophobic foams with contact angles greater than 150° from MTES by using a sol-gel phase-separation method. The phase-separation process leads to the formation of a porous and rough surfaces and finally production of superhydrophobic films.

Mahltig and Bottcher⁵⁰ prepared the hydrophobic textiles by coating with different modified silica sols. First, they prepared sol using TEOS and 3-glycidylpropyltriethoxysilane and then incorporated the hydrophobic additives into the liquid sol. They used alkyltrialkoxysilanes, polysiloxane derivatives, and a fluorine-containing silane as hydrophobic additives.⁵⁰

Han et al.³¹ described three approaches for producing superhydrophobic surfaces: micellization of a specific block copolymer, nanoparticle-assisted micelle stabilization, and simple hydrophobization. They synthesized poly(*tert*-butyl acrylate)-*block*-poly(dimethylsiloxane)-*block*-poly(*tert*-butyl acrylate) (PtBA-*b*-PDMS-*b*-PtBA) triblock copolymer as polymeric

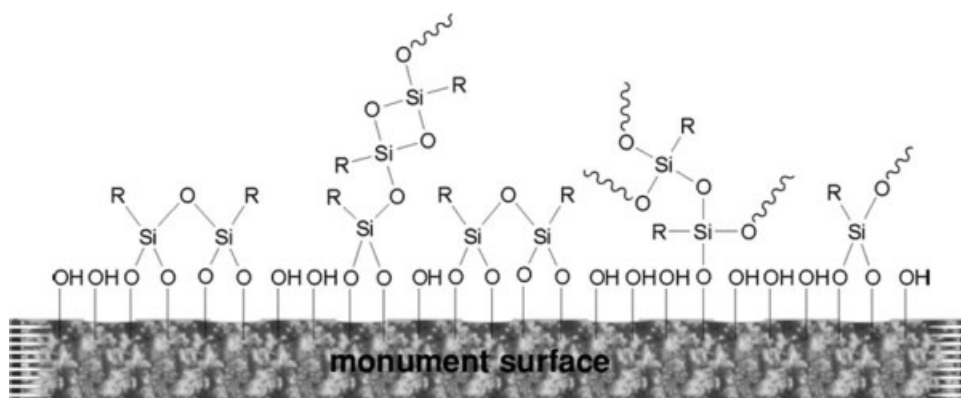
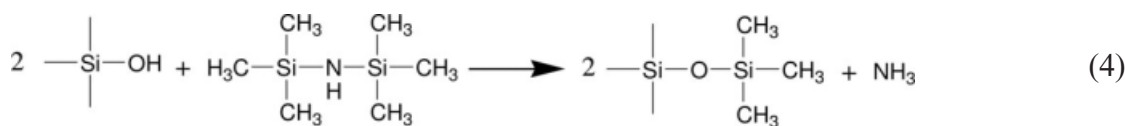


Figure 3 Schematic representation of the silicon polymer as protective coating on surface of monument.

surfactant by atom transfer radical polymerization. They dissolved this triblock copolymer in a solvent above the critical micelle concentration to form micelles and then controlled the surface roughness via changing the solvent power and nanosilica-mediated stabilization of the triblock copolymer micelle structure during film formation. They also attempted to stabilize PtBA-*b*-PDMS-*b*-PtBA micelle solution by hydrophilic silica nanoparticles and by hydrophobization of the surface.³¹

Huang et al.⁵¹ prepared the mesoporous silica films by sol-gel coating process through nonionic surfactant and triblock copolymer templating synthesis. They used TEOS as silica source to produce the hydrophilic mesoporous films and then modified these hydrophilic films to achieve the hydrophobicity through *in situ* trimethylchlorosilane silylation during the preparation of precursor sols and post-treatment with HMDS vapor, according to the following reaction:



As stated earlier, one approach to raise the contact angle is the surface roughness increasing. Nakajima et al.⁶ prepared the crater-like structure on surface of films by utilizing phase separation in the sol-gel process. They reported that hard and superhydrophobic films could be prepared by using combined phase separation of TEOS induced by the addition of an acrylic polymer and subsequent fluoroalkylsilane coating.⁶

Fluorinated polymers as protective coatings

One of the ways to increase surface hydrophobicity is to change the surface chemistry by lowering the surface energy.^{17,26} However, some of chemical alterations in surface chemistry such as introduction of polar groups like hydroxyl and ester into polymeric coating leads to hydrogen bonding with moisture and consequently diminishing contact angle.²⁶ Among various polymers that are known as protective materials with critical surface tension less than water, fluoropolymers are well known because of their unique properties such as photostability, oil and water repellency, antifouling property, and minimized critical surface tension.²⁶ In fact, introduction of fluorinated groups into polymer backbone leads to decrease in surface free energy and consequently critical surface tension because of stability of covalent bond between the carbon and fluorine, resulting in small bond polarization.^{17,26} Moreover, higher stability of the C—F bonds compared with C—H bonds leads to resistance toward photo-degradation.^{26,44}

Silicon-based and acrylic-based coatings are bonded on the monument surface via covalent bond and dipole bond, respectively. However, fluorine-based coating has lower adhesion to the surface,

because such coatings are bonded on the surface via very weak van-der-Waals forces.^{17,26} For this reason, it is attempted to produce the copolymers or blends of fluoropolymers with acrylic or silicon polymers. The blending involves introduction of fluorinated component into the mix and then migration of fluorinated component to the surface, and finally cross-linking of hydrophobic agent. The usual example for blending involves the preparation of a series of blends based on polyvinylidene fluoride (PVDF) and acrylic polymers. In the protecting applications, where long-term exposure to the exterior environment is inevitable, it is common to apply a PVDF coating to the surface of building. It was found that this polymer can easily be dissolved in acetone or ester solvents. Moreover, PVDF is removable using the polar solvent, such as acetone. Unfortunately, this material affords very poor adhesion to the substrate, a common problem with fluoropolymer coatings. To increase adhesion of the PVDF, it must be blended with an acrylic polymer. The PVDF/acrylic blend increases adhesion to an average range.^{52–57}

However, a more usual approach is the introduction of fluorine into the backbone or side chain of silicon-based or acrylic-based polymers to prepare a polymer with properties of both fluoropolymers and silicon or acrylic polymers.^{7,26,44,46,47} Brugnara et al.⁹ reported that fluorinated polymers show hydrophobicity significantly higher than the usual acrylic polymers. From a chemical point of view, fluorine groups in the main chain and in the side chain can be distinguished by chemical properties. For example, the acrylic polymers that are fluorinated at the main chain are more photostable than fluorinated polyacrylates at the ester side groups.⁴⁴

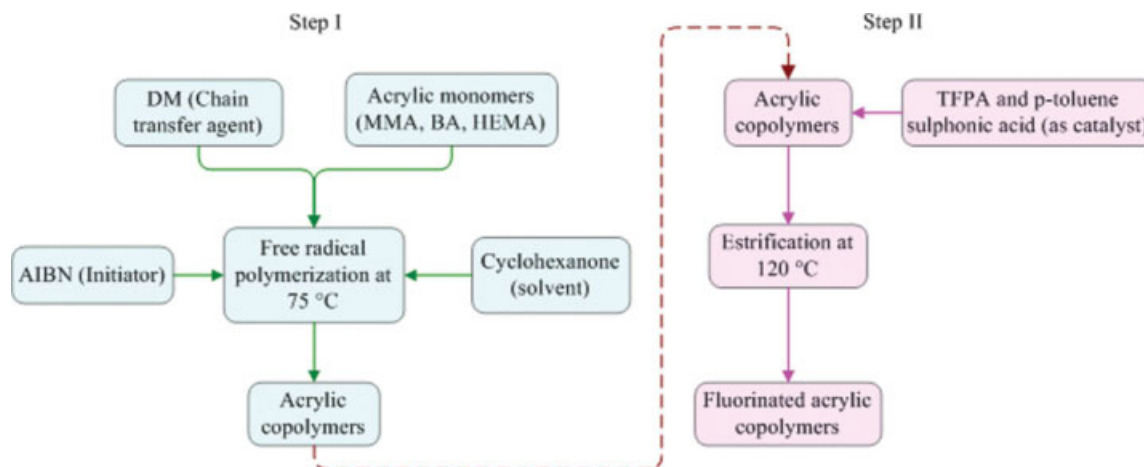


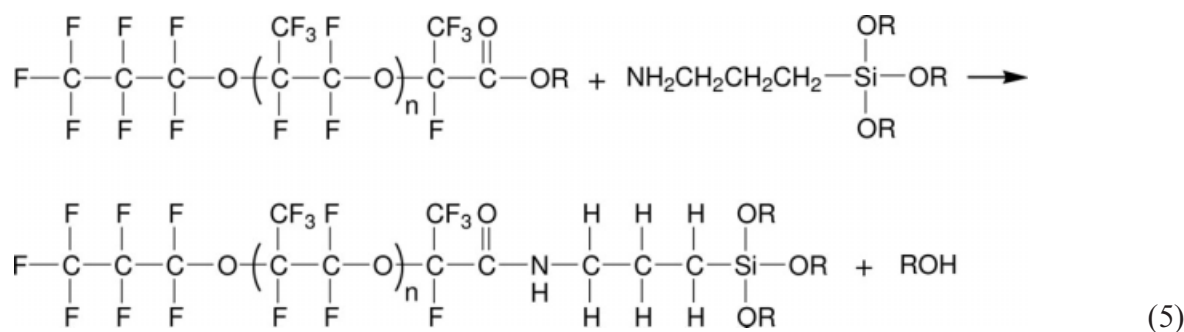
Figure 4 Synthesis of fluorinated acrylic copolymers²⁶ (Reproduction based on Malshe and Sangaj, *Prog Org Coat*, 2005, 53, 207). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Like the silicon-based polymer, the usual method for polymerization of fluorocopolymers such as fluoroalkyltrialkoxysilane is a sol-gel process.⁷

Polytetrafluoroethylene (PTFE) has widely been used in coating fields because of its small surface energy. However, because of the rheological behavior of the melt state of PTFE such as high viscosity and insolubility in usual solvents, it is attempted to synthesize the other perfluoropolymers with similar properties but a suitable rheological behavior. These polymers usually are acrylic-based and silicon-based polymers with

long fluoro groups in the backbone or side chain of the polymers.^{44,47,58}

Krukovsky et al.⁵⁹ developed methods for the synthesis of oligomer perfluorocarbonic acid amides as protective materials. These oligomers had fluorine groups that were directly bonded to the backbone of the molecule. These compounds were soluble in organic and fluorinated solvents. The contact angle for treated limestone by using one of these fluorinated siloxanes ($n = 1$, $R = -C_2H_5$) was 138° for both water and decalin. In this procedure, the reactive trialkoxysilyl groups were used according to the following equation:



Malshe and Sangaj²⁶ prepared the fluorinated acrylic copolymers through esterification of functional monomer. They synthesized acrylic copolymers based on methyl methacrylate (MMA), butyl acrylate, and functional monomer, 2-hydroxy ethyl methacrylate (HEMA). Then, the pendant OH was partially esterified with tetrafluoro propanoic acid to produce the fluorinated acrylic copolymers (Table I and Fig. 4).

Mazzola et al.⁴⁴ synthesized polyacrylic esters containing different amounts of fluorine in the α -position of the backbone of the acrylate polymers (Table I). These products were obtained through the copolymerization of ammonium 2-fluoroacrylate and acrylic acid. The relevant procedure is shown in Figure 5.

Gu et al.⁶⁰ prepared the organic-inorganic hybrid composite based on polymethacrylate (PMMA)/SiO₂ hybrids. They reported that *in situ* derivatization of the precursor solution by perfluoroalkylsulfonyl

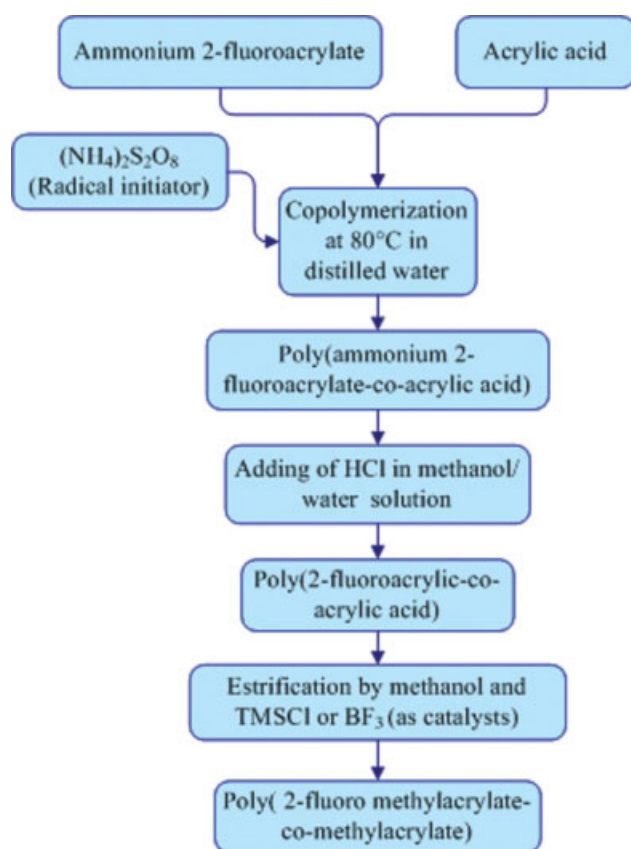


Figure 5 Synthesis of fluorinated acrylic copolymers⁴⁴ (Reproduction based on Mazzola et al., *Eur Polym J*, 2003, 39, 1995). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

alkyl trialkoxy silane $C_8F_{17}SO_2NHC_3H_6Si(OCH_3)_3$ leads to increases in contact angle to values beyond 100° .

Recently, novel hydrophobic fluoro-terpolymers were developed by Baradie and Shoichet.⁴⁶ They synthesized a series of thermally stable and hydrophobic fluoro-terpolymers of tetrafluoroethylene (TFE), vinyl acetate (VAc), and poly(dimethylsiloxane) methyl acrylate-terminated (PDMSMA), P(TFE-ter-VAc-ter-PDMSMA), in supercritical carbon dioxide (Table I).

Shang et al.¹⁷ prepared the superhydrophobic silica-based coatings by using the sol-gel method and self-assembly. In fact, they used both approaches to make superhydrophobic films that were chemical method and geometrical one. They prepared a series of films using materials such as TEOS, methacryloxypropyltrimethoxysilane, and MTES. The surfaces of these films were rough resulting in packing of monosized spherical silica and stacking of nanoclusters. Superhydrophobic silica-based film was produced by modifying the surface chemistry using chlorotrimethylsilane and tridecafluoro-1,1,2,2-tetrahydrooctyldimethylchlorosilane.¹⁷

Hybrid organic-inorganic based coatings

As mentioned in the previous section, so far many studies have been focused on the fluorine-based coatings because of their properties such as high hydrophobicity and photostability. However, fluorinated compounds are expensive materials and maybe dangerous to human health and environment.⁶¹ Moreover, the perfluoropolymers usually display unsuitable rheological behavior such as high viscosity and high temperature process. As a result, although the study on the fluoropolymers has not yet come to a definite point, there has been an attempt to produce new nonfluorinated hydrophobic surfaces at low temperatures.⁶¹ Hybrid organic-inorganic materials (known as ceramers) as a new class of materials have increasingly attracted much attentions because of their extraordinary properties deriving from the combination of the different building blocks.^{33,35,62,63} In such systems, polymer blocks lead to good adhesion, toughness, flexibility, and ease of processing and inorganic blocks improve the mechanical properties such as abrasion resistance, optical properties, and heat resistance.⁶²⁻⁶⁴ Meanwhile the presence of Si-OH groups in inorganic blocks leads to the durable adhesion.⁶⁴ Zielecka and Bujnowska² prepared silicone-containing polymer matrices as coating materials. They used the fluoropolymers, polyolefins, and acrylic resins as organic components of the hybrid system and demonstrated that such coatings have higher protective properties than those prepared by pure silicone.

Recently, Daoud et al.⁶¹ reported the synthesis of a nonfluorinated silica nanocomposite as environmental friendly superhydrophobic coatings and investigated the formation, morphology, chemical structure, and physicothermal properties of these nanocomposites.

So far, several applications have been developed for these hybrid systems in the field of protective coatings.^{33,34,62,65-68} However, organic-inorganic hybrids, because of their unusual mechanical, optical, electrical, and magnetic properties, offer a wide range of interesting applications for the future generation of materials.^{33-35,65,67-69}

Unfortunately, the final properties of the hybrid systems are not only determined by the volume fractions of organic and inorganic components,⁶³ but also affected by several parameters such as size, morphology and size distribution of inorganic particles, homogeneity of dispersion of organic and inorganic phases, amount of phase separation, morphology of hybrid system, molecular weight of organic polymer and its solubility in the sol-gel solution, and the number of reactive groups and coupling agents.^{33,34,63,65}

Alkyl-modified alkoxy silanes ($R_x\text{Si}(\text{OR}')_y$) have been widely used to construct a structural silica particles in hybrid systems during the last years.⁶¹ However, the optical transparency of the hybrid systems in coating applications such as conservation of historical monument is a very critical property,^{63,66} and to approach this goal, it is attempted to produce a series of hybrid coatings with nanoscale inorganic clusters or particles.^{33,63,66}

From the structural point of view, several ways to obtain the organic–inorganic hybrid materials have been developed. The relatively simple approach to construct these materials is incorporation of inorganic particles (mostly in nanometric scale) into the organic phase and then *in situ* formation of an organic network.^{33–35,65} This approach leads to the production of nanoparticle-reinforced polymers (also called nanomers).⁶⁵ The interfacial interaction between the dispersed and continuous phases is a critical point.⁷⁰ For this reason, so far various coupling agents such as organofunctional silanes have been developed to improve the interface of inorganic moiety with organic polymer and also to increase adhesive bonding of dissimilar surfaces.^{35,65,70,71} In fact, without any coupling agent, the interactions between organic and inorganic moieties are weak (van-der-Waals or dipole interactions) and using of coupling agents leads to the formation of strong covalent bond.^{33,35,70}

The other approach to obtain the hybrid systems is fabrication of hybrids from organically modified silicates (also called ormosils).^{33,35,61,65} These hybrids may include interpenetrating organic polymers.^{33,65} The usual example for ormosils maybe hybrids fabricated from TEOS and alkyl-modified alkoxy silanes.^{63,65} In this case, the dimension of the produced inorganic particles is usually in nanometer size, and therefore, these hybrid systems maybe called nanocomposites or molecular composites.^{34,63,66,69,70}

We synthesized organic–inorganic hybrid nanocomposite coatings from 3-glycidoxypropyl-trimethoxysilane (GPTMS), crosslinking agent and bisphenol A (BPA) in previous studies.⁶³ The characterization of this nanocomposite showed that these hybrid systems had a network structure and inorganic phases had a size of less than 100 nm.

From the structural point of view, the mixing of inorganic and organic phases in the molecular scale is very important to attain the desired properties.⁶⁹ The most commonly employed technique for preparation of organic–inorganic hybrid materials is the sol–gel process which leads to the formation of the separation organic and inorganic phases on nanometer scale.^{33,35,63,66,70,72} However, these hybrids systems are macroscopically single-phase.^{33,67,70}

The sol–gel procedure involves the production of a colloidal suspension named “sol” from liquid precursors such as TEOS and organic oligomers and then conversion of this sol phase to a gel phase to form an inorganic network.^{33,63,70} The most important advantage of the sol–gel process is that the reaction proceeds at temperatures below 150°C.^{34,70,72–74} The other advantages of sol–gel process include excellent control of stoichiometry of precursor solutions, the possibility of reaction performance at atmospheric pressure, ease of chemical modifications by incorporating of various functionalized precursors, ease of structural modifications by controlling of reaction conditions, the possibility of coating on large-area substrates such as historical monuments, and simple and inexpensive equipment.^{70,72,75}

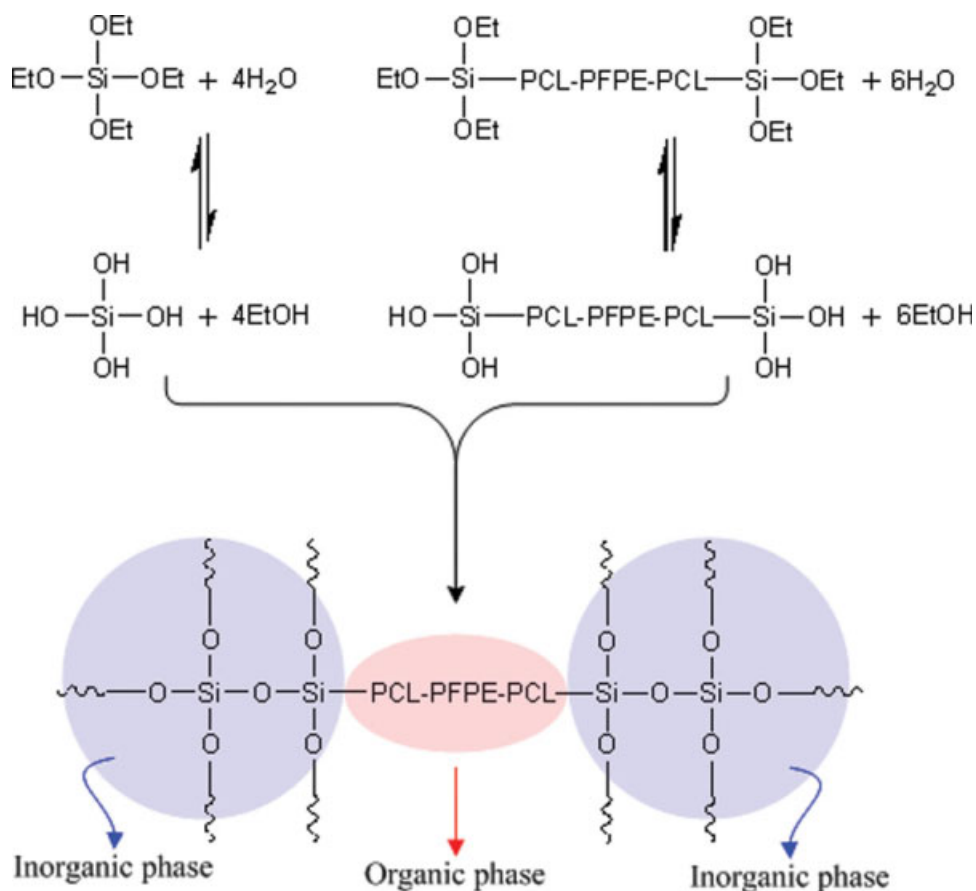
Because of high reactivity of organofunctional alkoxy silanes such as GPTMS to the water, they are widely employed in hybrid systems as precursors for synthesizing the sols.^{33,63,70,73,74,76} The sol–gel process involves two separate reactions: Hydrolysis of organofunctional silanes to form organofunctional silanols and then condensation of these silanols to form a hybrid material.⁶³ The hydrolysis and condensation reactions are very similar to those mentioned in alkoxy silanes section [eqs. (1)–(3)].

The structure and morphology of inorganic phase obtained by the sol–gel process are strongly controlled by pH of solution.⁶³ For example, the acid-catalyzed reaction leads to extend the chain, whereas the base-catalyzed reaction leads to agglomerate the chain to form particles. In fact, in the acid-catalyzed reaction, the hydrolysis step is faster than the condensation step, whereas in the base-catalyzed one, condensation is faster than hydrolysis.⁶³

The other parameters in sol–gel process affecting the hybrid properties involve the type and amount of solvent, the ratio of water to inorganic component, the ratio of organic to inorganic component, aging, concentration of crosslinking agent, and drying methods.^{63,69,70}

However, it is possible to synthesize hybrid materials from various polymers such as fluoropolymers or acrylics. Fabbri et al.³³ made the hybrid coating by using α,ω -triethoxysilane-terminated poly(caprolactone-*b*-perfluoropolyether-*b*-caprolactone) block copolymer as organic component with structure of $(\text{EtO})_3\text{Si-PCL-PFPE-PCL-Si}(\text{OEt})_3$, where PCL represents the poly(caprolactone) and PFPE represents the perfluoropolyether and TEOS as inorganic component. They prepared organic–inorganic hybrids by the sol–gel technique. The relevant reactions are shown in Scheme 1.

We synthesized the hybrid systems based on 3-trimethoxysilyl propyl methacrylate, tetramethylorthosilicate, and MMA for moisture protection of glass objects. Meanwhile for achieving superhydrophobic



Scheme 1 Synthesis schema developed for the preparation of the organic-inorganic hybrid system based on $(\text{EtO})_3\text{Si-PCL-PFPE-PCL-Si}(\text{OEt})_3$ and TEOS. [Color scheme can be viewed in the online issue, which is available at www.interscience.wiley.com.]

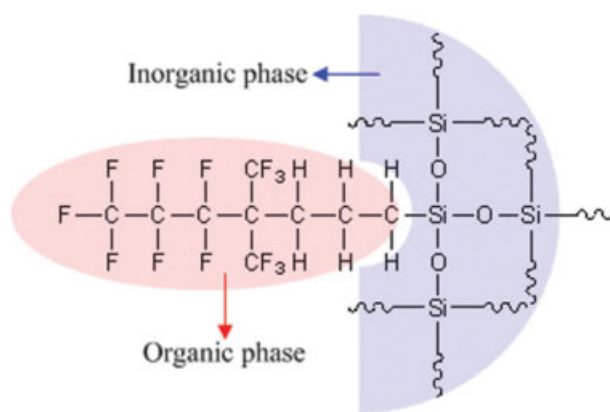
properties, the fluorinated precursors can be introduced in the hybrid system; such coatings have good optical transparency, resistance to cracking, and excellent adhesion.⁶²

Monde et al.⁵⁸ synthesized polyfluoroalkylsilane-modified SiO_2 films from branched chain polyfluoroalkylsilane and TEOS by the sol-gel process. These films had thermal stability and surface energy as low as PTFE to 400°C . The structure of hybrid system is shown in Scheme 2.

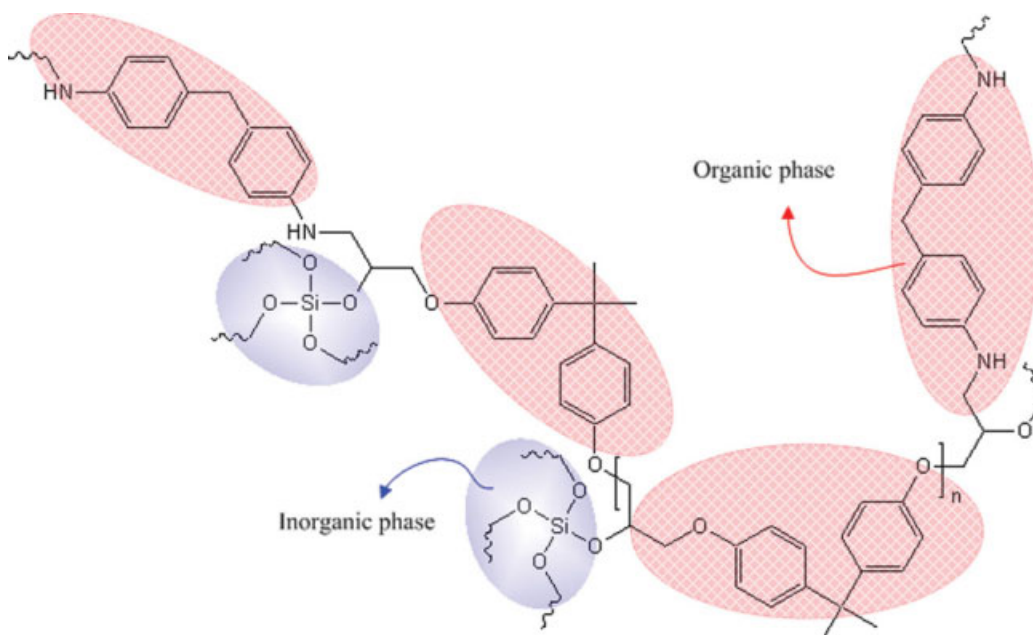
Satoh and Nakazuni⁷ reported the synthesis of superwater-repellent fluorinated organic-inorganic coating films from poly(methyl methacrylate) (PMMA), TEOS, and perfluorooctylethyltriethoxysilane by the sol-gel method.

Recently, Han et al.⁴ synthesized a superhydrophobic organic-inorganic nanocomposite through LBL deposition of poly(allylamine hydrochloride) (PAH) and ZrO_2 nanoparticles coated with poly(acrylic acid) (PAA), allowing facile control of surface roughness and hydrophobicity. Superhydrophobic behavior was developed by deposition of silica nanoparticles and fluorination of the surface. In this method, the superhydrophobic surface can be devel-

oped by a simple procedure of about 10 deposition cycles of PAH- and PAA-coated ZrO_2 nanoparticles and deposition of 1.5 bilayers of PAH and silica nanoparticles, followed by a simple fluorination.



Scheme 2 The structure of organic-inorganic hybrid system based on polyfluoroalkylsilane and TEOS. [Color scheme can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 3 The structure of an interpenetrating network of the organic-inorganic hybrid system based on diglycidyl ether of bisphenol A and an aromatic amine as organic components and TEOS as inorganic component. [Color scheme can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Shen et al.⁷⁷ prepared organic-inorganic hybrid coatings with high hydrophobic properties from nano-TiO₂ and fluoroalkylsilane. The thickness of such coatings was on nanometer size.

Recently, protective coatings with repellency to both water and oil have attracted much attention. Hikita et al.²⁷ developed the film that its surface exhibits repellency to both water and oil. They prepared sol-gel films containing optimized fractional amounts of colloidal silica nanoparticles to increase surface roughness and fluoroalkylsilane coupling agent to decrease surface energy.

In addition, the organic-inorganic hybrid systems based on the plant oils were also investigated. The hybrid films exhibited the higher modulus, but the films were formed using high temperature cure.⁷³ The UV-curable organic-inorganic hybrid films based on epoxynorbornene linseed oils and TEOS were studied by Zong et al.⁷³ They also demonstrated that the hybrid film properties were affected by the level of TEOS oligomers and the hybrid structures.

We prepared an interpenetrating network of the organic-inorganic hybrid system composed of diglycidyl ether of bisphenol A and an aromatic amine as organic components and TEOS as inorganic component by a sol-gel process.⁷⁰ The structure of the hybrid system is shown in Scheme 3. We demonstrated that this hybrid network has excellent optical transparency. Moreover, crosslinking between epoxy resin and silica increases the thermal stability of the sample.⁷⁰

Although the hydrophobicity is the most important properties of protective materials, it is not their only significant property. In this respect, an efficient protective material for monument protection must have a whole set of simultaneous properties such as aging history, good long-term adhesion, high compatibility with the surface of monuments, excellent scratch and abrasion resistant, ability to be removed from the surface monument (e.g., via a suitable solvent), stability against weathering, and resistance toward corrosive delamination as well as high hydrophobicity.^{4-9,76} As stated earlier, unfortunately some of these properties are competitive with each other.

In previous sections, we reviewed the key properties of various polymeric coatings. However, it may be questioned that finally which of these polymeric materials are more suitable for historical monument protection. In general, all protective materials must have good optical transparency and hydrophobicity although the degree of hydrophobicity is different for various polymeric coatings. In this respect, fluorinated polymers are more suitable.

In the section of acrylics, we alluded to the polymers based on various acrylics used in the protection of monuments. However, these materials are nowadays used less than before because of its fast degradation due to chemical decays of acrylic backbone such as photooxidative reactions leading to the formation of oxidized species, and finally yellowing appearance of the coating film on the monument surface.^{5,9,45} For this reason, scientists attempted to

design materials with no sensitivity to environmental factors such as sunlight. Among the wide ranges of new materials that may be considered as candidates for protective applications, the most useful materials are hybrid systems and alkoxy-silanes.

If the primary concern is the hydrophobic properties, the introduction of fluorine atoms in lateral chains of polyacrylates strongly increases the hydrophobicity⁹; however, other properties such as photo-oxidative stability are not significantly affected, and similarly these acrylic coatings are not efficiently perfect for monument protection. Only hybrid systems and alkoxy-silanes however show similar or better hydrophobic properties.⁹

In the last few years, dilute solution of Wacker BS 290, which is based on silane/siloxane, has widely been used in protection fields especially for highly alkaline substrates. Brugnara et al.⁹ investigated the efficiency of various acrylic- and silicon-based coatings. They also studied the effect of fluorinated groups and various surfactants on final properties of coating films. They demonstrated that after a prolonged UV-aging, surface of all kinds of polymeric films (acrylic, fluorinated-acrylic, and silicons) strongly changes in time, which is revealed by diminishing contact angles.⁹ They showed that stability of contact angles is higher for Paraloid B72 than for BS290. In fact, Wacker BS290 showed a rapid decrease in contact angle values. Moreover, the copolymers of fluorinated acrylics also showed strong reductions in contact angle after a prolonged UV-aging. These phenomena occurred during aging process, because of increase in surface temperature of the samples. For Paraloid B72, the final temperature is near T_g . In general, the chain mobility increases as a function of increasing temperature as the molecules can move to modify the distribution at the surface and the bulk. However, BS290 is a high crosslinked polymer and is locked in its position. Such high crosslinked polymers suffer crack formation or material degradation because of temperature-induced dilations and contractions during the aging test.⁹

Although the cationic surfactants show significant hydrophobic characteristics, Brugnara et al.⁹, however, demonstrated that these materials cannot be considered as protective agents, because of their high water solubility.

It has been well documented that adding an inorganic material to a polymer enhances the mechanical properties of the system, and so the hybrid organic-inorganic systems were produced. As stated earlier, one of the most important properties of polymer for application in monument protection is adhesion properties. To this point, hybrid systems and alkoxy-silanes are unique. The good adhesion of such coating films to the surface of monument is due to the

formation of Si—O—Si chemical bonds between Si—OH groups from polymeric coating and the Si—OH of the monument surface. It is important to note that unfortunately the adhesion property and ability to remove the films from the surface of the monuments are inversely related. However, the hybrid organic-inorganic systems are preferred in most of the protective applications. The main preferred aspects of the hybrid systems, in comparison with the alkoxy-silanes, include higher plasticity because of the presence of organic chains, more compatibility with the nature of the monuments, prevention of the crack formation during the drying step because of the presence of organic phase, and increasing the mechanical properties of monuments by filling the surface flaws and blunting the crack tips.^{62,76} As mentioned earlier, the hybrid organic-inorganic polymers are compatible with historical monuments because hydroxyl and alkoxy groups of the coating material can react with the Si—OH groups of the surface monuments to produce bonds between the hybrid layer and monument surface.⁷⁶ Kron et al.⁷⁶ demonstrated that the hybrid systems are stable in weathering tests and have good long-term adhesion, excellent scratch and abrasion resistance, stability against weathering, and resistance toward corrosive delamination. The hybrid organic-inorganic coatings have optical transparency, an indication that no macrophase separation may occur.⁶²

Moreover, fluorinated chains can be introduced in the hybrid system to produce superhydrophobic films without much significant changes in adhesion property.^{9,62}

The unsuitability of many of organic solvents used in various coatings has encouraged research efforts to develop water-based coatings. In recent years, water-based coatings have become increasingly important because of very low volatility of the organic compounds and virtually of no hazardous air pollutants.⁷⁴ Moreover, by applying water-based coatings, the equipment can be cleaned easily by only water flow.⁷⁴

Recently, Mosher et al.⁷⁴ presented a new water-based coating of GPTMS-based. They synthesized organic-inorganic water-based nanocomposite coatings, which were relatively hard and abrasion resistant with very good adhesion. The as-produced coatings are useful for protecting UV-sensitive materials such as historical monument surfaces from harmful UV irradiation. They also demonstrated that incorporation of nanoparticle colloids into the coating formulation leads to minimal catalyst use because of the function of particles as nucleation sites for precipitation of silicate polymers, and so provide easy and environmentally friendly synthesis of coating sols.

At the end of this article, we introduce an interesting example of monument protection to emphasize

the importance of hybrid systems as protective coatings. "Last Judgment Mosaic" in Prague has made from 1 million glass tiles, or tesserae, embedded in mortar.⁷⁸ These glass tiles are exposed to corroding factors such as air pollution, temperature fluctuations, and rain. All previous protection attempts using various organic polymers could not stop deterioration of this valuable historical monument. In fact, these organic coatings all have poor durability, low adhesion property, and low blocking properties of water and air pollutants. After reviewing various protective materials, the selected coating for treatment of the monument is a multilayer system composed of a hybrid organic-inorganic functional layer made from organofunctional alkoxysilanes and oxide nanoparticles, placed between the glass substrate and a fluoropolymer coating. This hybrid nanocomposite is much more effective than all tested organic polymers.⁷⁸

CONCLUSIONS

It can be concluded that the protection of historical monuments is the multidisciplinary approach, and also the search for new optimal protective materials has not yet come to an end. Furthermore, the new fluorinated and hybrid polymers are certainly among the most promising challenges in protective fields in the near future, and consequently, the research effort put in their development continue to increase.

The authors are grateful to Ms. H. Mivehchi at Iran Polymer and Petrochemical Institute as well as Mr. A. Vatandoust, Mr. H. Fadaii, and Mr. R. Vahidzadeh at Research Center of Tehran for Conservation of Cultural Relics, Cultural Heritage, Handicraft and Tourism Organization.

References

1. Michoinová, D. New Materials for the Protection of Cultural Heritage. Available at: http://www.arcchip.cz/w10/w10_michoinova.pdf.
2. Zielecka, M.; Bujnowska, E. *Prog Org Coat* 2006, 55, 160.
3. De Lorenzis, L.; Nanni, A. International Workshop on Preservation of Historical Structures with FRP Composites, National Science Foundation Arlington, VA 22230. Available at: <http://www.iifchq.org/publications/REPORT%20LECCE%20WORKSHOP.pdf>.
4. Han, J. T.; Zheng, Y.; Cho, J. H.; Xu, X.; Cho, K. *J Phys Chem B* 2005, 109, 20773.
5. Favaro, M.; Mendichi, R.; Ossola, F.; Russo, U.; Simon, S.; Tomasin, P.; Vigato, P. A. *Polym Degrad Stab* 2006, 91, 3083.
6. Nakajima, A.; Abe, K.; Hashimoto, K.; Watanabe, T. *Thin Solid Films* 2000, 376, 140.
7. Satoh, K.; Nakazumi, H. *J Sol-Gel Sci Technol* 2003, 27, 327.
8. Krage, L. Research and Investigation of Historic Materials in Latvia. Available at: http://www.arcchip.cz/w09/w09_krage.pdf.
9. Brugnara, M.; Degasperi, E.; Della Volpe, C.; Maniglio, D.; Penati, A.; Siboni, S.; Toniolo, L.; Poli, T.; Invernizzi, S.; Castelvetro, V. *Colloids Surf A* 2004, 241, 299.
10. Price, C. A. Stone Conservation: An Overview on Current Research, Dinah Berland, USA, 1996. Available at: http://www.getty.edu/conservation/publications/pdf_publications/stoneconservation.pdf.
11. Zabihi, Sh. Pathology of Brick-Made Decoration of Chahar Bagh School of Isfahan; Art University of Isfahan: Isfahan, 1997.
12. Ghedini, N.; Sabbioni, C.; Pantani, M. *Thermochim Acta* 2003, 406, 105.
13. Le Metayer-Lévrel, G.; Castanier, S.; Oriol, G.; Loubiere, J.-F.; Perthuisot, J.-P. *Sediment Geol* 1999, 126, 25.
14. Warscheid, Th.; Braams, J. *Int Biodeter Biodegr* 2000, 46, 343.
15. Van Hees, R. P. J.; Brocken, H. J. P. *Constr Build Mater* 2004, 18, 331.
16. Bortolotti, V.; Camaiti, M.; Casieri, C.; De Luca, F.; Fantazzini, P.; Terenzi, C. *J Magn Reson* 2006, 181, 287.
17. Shang, H. M.; Wang, Y.; Limmer, S. J.; Chou, T. P.; Takahashi, K.; Cao, G. Z. *Thin Solid Films* 2005, 472, 37.
18. Amin-Shirazi Nejad, Sh. Investigation of Paraloid as Adhesive and Consolidant Material at Climatic Conditions of Iran; Art University of Isfahan: Isfahan, 1998.
19. Khakban, M. The Examination of Renovation Materials for Application in Historic Work Conservation in Guilan Region; Art University of Isfahan: Isfahan, 1997.
20. Bater, M.; Abed Esfahani, A.; Paidar, H. *Iran J Cryst Miner* 2005, 13, 155.
21. Vahidzadeh, R. The Examination of Glaze Decorative Production Process Related to Architectural Middle Elam and Analysis of its Damages; Art University of Isfahan: Isfahan, 2005.
22. Khakban, M. The Examination of Picture Walls of Shrines at Lahijan Region. Available at: <http://dbase.irandoc.ac.ir/00188/00188516.htm>.
23. Kapalos, J.; Bakaoukas, N.; Koliadima, A.; Karaiskakis, G. *Prog Org Coat* 2007, 59, 152.
24. Pouli, P.; Fotakis, C.; Hermosin, B.; Saiz-Jimenez, C.; Domingo, C.; Oujja, M.; Castillejo, M. *Spectrochim Acta A* 2008, 71, 932.
25. Rastogi, V. K. Taj Mahal has "Marble Cancer." Available at: <http://sify.com/news/fullstory.php?id=13196248>.
26. Malshe, V. C.; Sangaj, N. S. *Prog Org Coat* 2005, 53, 207.
27. Hikita, M.; Tanaka, K.; Nakamura, T.; Kajiyama, T.; Takahara, A. *Langmuir* 2005, 21, 7299.
28. Pilotek, S.; Schmidt, H. K. *J Sol-Gel Sci Technol* 2003, 26, 789.
29. Shirtcliffe, N. J.; McHale, G.; Newton, M. I.; Perry, C. C. *Langmuir* 2003, 19, 5626.
30. Wu, L. Y. L.; Soutar, A. M.; Zeng, X. T. *Surf Coat Technol* 2005, 198, 420.
31. Han, J. T.; Xu, X.; Cho, K. *Langmuir* 2005, 21, 6662.
32. Ono, K.; Andaroodi, E.; Einifar, A.; Abe, N.; Matini, M. R.; Bouet, O.; Chopin, F.; Kawai, T.; Kitamoto, A.; Ito, A.; Mokhtari, E.; Einifar, S.; Beheshti, S. M.; Adle, C. *Prog Inform* 2008, 5, 99.
33. Fabbri, P.; Messori, M.; Montecchi, M.; Nannarone, S.; Pasquali, L.; Pilati, F.; Tonelli, C.; Toselli, M. *Polymer* 2006, 47, 1055.
34. Haas, K.-H.; Amberg-Schwab, S.; Rose, K.; Schottner, G. *Surf Coat Technol* 1999, 111, 72.
35. Kickelbick, G. *Prog Polym Sci* 2003, 28, 83.
36. Conservation of Ancient Sites on the Silk Road. Available at: http://www.getty.edu/conservation/publications/pdf_publications/silkroad1.pdf.
37. Asrar, N.; Malik, A. U.; Ahmed, S. Corrosion Prevention with Sodium Silicate. Available at: <http://www.swcc.gov.sa/files%5Cassets%5CResearch%5CTechnical%20Papers%5CCorrosion%5CCORROSION%20PREVENTION%20%20WITH%20%20SODIUM%20SILICATE...8.pdf>.
38. The OxyChem Sodium Silicates Handbook. Available at: http://www.oxy.com/Our_Businesses/chemicals/Documents/silicates/silicate.pdf.

39. Potassium Silicate vs. Sodium Silicate. Available at: <http://www.buzzle.com/articles/potassium-silicate-vs-sodium-silicate.html>.
40. Satoh, Y. U.S. Pat. 6,464,774 (2002).
41. Maschhoff, B. L.; Armstrong, N. R. *Surf Interface Anal* 2004, 14, 76.
42. Johnson, S. M.; Lamoreau, R. H.; Loehman, R. E. *J Am Ceram Soc* 2005, 78, 1115.
43. Šefčík, J.; McCormick, A. V. *AIChE J* 2004, 43, 2773.
44. Mazzola, M.; Frediani, P.; Bracci, S.; Salvini, A. *Eur Polym J* 2003, 39, 1995.
45. Chiantore, O.; Lazzari, M. *Polymer* 2001, 42, 17.
46. Baradie, B.; Shoichet, M. S. *Macromolecules* 2005, 38, 5560.
47. Yoshida, N.; Abe, Y.; Shigeta, H.; Takami, K.; Osaki, H.; Watanabe, T.; Hashimoto, K. *J Sol-Gel Sci Technol* 2004, 31, 195.
48. Ni, H.; Skaja, A. D.; Soucek, M. D. *Prog Org Coat* 2000, 40, 175.
49. Xu, Y.; Wu, D.; Sun, Y. H.; Li, Z. H.; Dong, B. Z.; Wu, Z. H. *J Non-Cryst Solids* 2005, 351, 258.
50. Mahltig, B.; Bottcher, H. *J Sol-Gel Sci Technol* 2003, 27, 43.
51. Huang, K.-Y.; He, Z.-P.; Chao, K.-J. *Thin Solid Films* 2006, 495, 197.
52. Shedlosky, T. J.; Stanek, K. M.; Bierwagen, G. On-Line Survey Results of Techniques Used for Outdoor Bronze Conservation. Available at: <http://www.ncptt.nps.gov/pdf/2002-18.pdf>.
53. Bierwagen, G.; Shedlosky, T. J.; Stanek, K. Developing and Testing a New Generation of Protective Coatings for Outdoor Bronze Sculpture. Available at: <http://www.ncptt.nps.gov/pdf/2002-18.pdf>.
54. Greigger, P. P.; Wilson, P. High Performance Fluoropolymer Coatings. Available at: <http://corporateportal.ppg.com/NR/rdonlyres/B52891CF-321B-421C-8602-8C415D7C253C/0/AAMA.pdf>.
55. Fluoropolymer Finishes: Kynar® 500-Hylar® 5000. Available at: http://www.wph.com/pdf/White_Papers/Fluoropolymer-Finishes-White-Paper.pdf.
56. Wood, K. A.; Gaboury, S. R. *Surf Coat Int B* 2006, 89, 231.
57. Wood, K. A. *Eur Coat J* 2005, 9, 48.
58. Monde, T.; Fukube, H.; Nemoto, F.; Yoko, T.; Konakahara, T. *J Non-Cryst Solids* 1999, 246, 54.
59. Krukovsky, S. P.; Yarosh, A. A.; Glazkov, A. A.; Batizat, D. V.; Redina, T. N. *J Fluorine Chem* 1999, 96, 31.
60. Gu, G.; Zhang, Z.; Dang, H. *Mater Res Bull* 2004, 39, 1037.
61. Daoud, W. A.; Xin, J. H.; Tao, X. *Appl Surf Sci* 2006, 252, 5368.
62. Ershad-Langroudi, A.; Mai, C.; Vigier, G.; Vassoille, R. *J Appl Polym Sci* 1997, 65, 2387.
63. Zandi-Zand, R.; Ershad-Langroudi, A.; Rahimi, A. *Iran Polym J* 2005, 14, 371.
64. Kron, J.; Schottner, G.; Deichmann, K.-J. *Thin Solid Films* 2001, 392, 236.
65. Schmidt, H. *Macromol Symp* 2000, 159, 43.
66. Haas, K.-H.; Amberg-Schwab, S.; Rose, K. *Thin Solid Films* 1999, 351, 198.
67. Schottner, G. *Chem Mater* 2001, 13, 3422.
68. Sanchez, C.; Julian, B.; Belleville, P.; Popall, M. *J Mater Chem* 2005, 15, 3559.
69. Sanchez, C.; Lebeau, B. *Pure Appl Opt* 1996, 5, 689.
70. Farhadyar, N.; Rahimi, A.; Ershad-Langroudi, A. *Iran Polym J* 2005, 14, 155.
71. Li, Y.-S.; Wright, P. B.; Puritt, R.; Tran, T. *Spectrochim Acta A* 2004, 60, 2759.
72. Huang, Y.; Zheng, H.; Forsyth, I. Application of Functional Ceramic and Hybrid Nanostructure Coating Fabricated Via Sol-Gel Processes. Available at: <http://www.chemat.com/solgelinfonewsitem2.tpl?cart=%5Bcart%5D>.
73. Zong, Z.; He, J.; Soucek, M. D. *Prog Org Coat* 2005, 53, 83.
74. Mosher, B. P.; Wu, C.; Sun, T.; Zeng, T. *J Non-Cryst Solids* 2006, 352, 3295.
75. Muromachi, T.; Tsujino, T.; Kamitani, K.; Maeda, K. *J Sol-Gel Sci Technol* 2006, 40, 267.
76. Kron, J.; Amberg-Schwab, S.; Schottner, G. *J Sol-Gel Sci Technol* 1994, 2, 189.
77. Shen, G. X.; Chen, Y. C.; Lin, L.; Lin, C. J.; Scantlebury, D. *Electrochim Acta* 2005, 50, 5083.
78. Bescher, E.; Pique, F.; Stulik, D.; Mackenzie, J. D. *J Sol-Gel Sci Technol* 2000, 19, 215.