

CoPVDF membranes for protection of cultural heritages

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Abstract

The study focuses on the possibility of using polymeric membranes to protect cultural heritages from biological degradation and from corrosive action exhibited by atmospheric agents. These membrane systems may be utilized as intelligent coatings on the porous lithoid material surfaces, which constitute a great part of the heritage and in recent years have suffered from an increase in attack phenomena. In particular vinylidene fluoride copolymer has been used in this study. The hydrophobic character of CoPVDF membranes has been used to avoid direct liquid water contact with *Serena* stone surfaces. The *Pietra Serena* is a porous sandstone which has been frequently used to construct balconies, stairs and decorations of Italian monuments.

The possibility of modifying the gas and liquid permeability by introducing a mixture of liquid crystals in the CoPVDF polymeric matrix has been also analyzed. In particular, a mixture of liquid crystals has been introduced in the nematic phase in a polymeric matrix. Because of their fluidity and nematic intrinsic anisotropy, those materials are applicable in the electro-optical field, but their gas transport behaviour is also interesting. They can control and facilitate the gas passage through a polymeric film. We have characterized the selectivity of modified CoPVDF membranes for several gases (O_2 , N_2 , CO_2).

Keywords: PDLC; Gas permeation; Vapor permeation; Selectivity

1. Introduction

The preservation of cultural heritages is receiving growing attention and also attracting also new technical knowledge (for example chemistry, chemical engineering, process control, system analysis, etc. ...). Among the main factors that cause deterioration are the action of H_2O and corrosive gases attack as well as that of some micro-organisms, such as bacteria, fungi, lichens, etc. ..., which during their metabolic process can be very significant. For example the formation of oxalates of organic acids and chelating agents, included in this last phenomenon, can solubilize and wear away stone matrix and contribute to dissolution of the objects. The conservation approach as the treatment of

stone monuments affected by deterioration have been various. New materials and methods are still under investigation to improve their quality and performance with time. The possibility of using polymeric selective membranes as protective agents and intelligent coatings on the surface of monumental stones and other artistic materials is today becoming an attractive perspective [1]. Membranes can regulate the transport of different gases or liquids under appropriate driving forces. New materials or the functionalization of the existing ones can extend the possible applications of the systems to specific case of interest. For example, polymeric membranes can realize a selective transport of the aggressive species, such as CO_2 and SO_2 , in vapour or liquid phase, from the ambient to the surface of the stone materials which must be protected. The

Table 1
Principal mechanisms and effects of stone degradation

	Causes of degradation	Mechanism	Degrading effects
PHYSICAL	Water	Solubilization of calcareous materials	– Loss of cohesion in marble granules – Encrustation by recrystallization
	Water	Stress from freezing/thawing	– Loss of granule cohesion – Cracking – Breakage of encrustation and fragments
CHEMICAL	Atmospheric CO ₂ in water	Transformation of calcium carbonate into soluble bicarbonate	– Solubilization of marble – Loss of granule cohesion – Encrustation by recrystallization
	SO ₂ from atmospheric pollutants, in water	Formation of calcium sulphate (Gypsum)	– Degradation of surface strata, formation of more soluble gypsum
	Acid organic substances from smog (NO _x , etc. ...)	Chemical attack of stone	– Black encrustation – Loss of cohesion in surface strata – Formation of soluble salts

possibility of realizing optimal environmental situations is attractive.

In most cases water has an important role in the phenomena which induce the deterioration of ancient monuments, particularly when these are made of porous lithoid materials. In fact the accumulation of rainwater on the walls of the structure, its penetration into material pores by capillary action, water vapor condensation, caused by temperature variations as well as interior heating systems are the principle source of aggression of monumental buildings and monuments. Rainwater, therefore, not only represents humidity, but also corrosive attack by the dissolved acids it contains [2]. In the first minutes of its action, the rain holds a high concentration of aggressive species and works as a carrier of conduction and contact of these with the exposed surfaces [3–5]. The solubility of calcium carbonate, very low in water containing small concentrations of calcium ions increases in their absence and especially in the presence of dissolved carbon dioxide. Rainwater, in absence of pollutants, is capable of dissolving calcium carbonate slowly, but efficiently in a long period, thus causing stone decay when the salt is the ligand [6]. This same decay process however is strongly accelerated by atmospheric pollutants produced by industrial activities and urban settlements.

Pollutants which are causing stone decay are those of acidic nature such as sulphuric acid, sulphur dioxide, carbon dioxide and nitrogen oxides. Calcium carbonate reacts giving products such as calcium sulphate, calcium bicarbonate or nitrate which are soluble enough to be eliminated in solution. In Table 1 are listed the principal mechanisms and effects of stone degradation [7].

The properties generally indicated as essential for a protective agent for stone materials are:

- chemical inertia with respect to the stone;
- chemical stability with respect to atmospheric agents;
- stability under effects of light;
- transparency and colorlessness;
- stability under the effects of heat;
- insolubility in water and common organic solvents;
- low volatility;
- air and water vapour permeability;
- treatment reversibility.

Among the solutions proposed up to now, is the possibility to use fluorinated products, [6,8,9], dissolved in highly viscous fluids. These products have proved to be effective and possess all the characteristics required. Among the possible disadvantages there could be the difficulty of extracting them after use. From this point of view their treatment might not be

perfectly reversible. Instead of this, the use of new membranes for the protection of stones as alternatives to the various hydrophobic and hydrophilic chemical products, which generally are adsorbed on the porous surfaces, could avoid possible mechanical damage related to volume variations with temperature or swelling with solvents. Moreover using these membranes as superficial films the treatment will be reversible.

For this purpose we have prepared membranes of an amorphous copolymer PVDF ($\text{CH}_2\text{CF}_2/\text{C}_3\text{F}_6$) in a 79/21 molar ratio and composite membranes, or PDLC, in which a nematic liquid crystal mixture E7 (from BDH, England) is dispersed in the CoPVDF polymer.

Polymer-dispersed liquid crystals (PDLCs) form a relatively new class of materials which have use in many types of displays and other light shutter devices, [10,11]. In their most common form, they consist of micron-size droplets of a low molecular weight nematic liquid crystal dispersed in an organic polymer matrix.

The general feature of liquid crystals, namely long-range orientational order in the absence of long-range order in the arrangement of the centers of molecules, can occur with different spatial arrangement of the particles. Depending on the arrangement of the molecules, three types of liquid crystal are usually distinguished: nematic, smectic, cholesteric. In the case of nematic liquid crystal a definitive order in the direction of the long axis of the molecules is observed for the entire sample: there exists some preferential orientation of molecules, characterized by the axis of nematic order and by the unit vector, \mathbf{n} (director) [12]. The nematic droplets strongly scatter light, and the material has a white opaque appearance. The material becomes transparent in the presence of an electric field which aligns the droplets such that their refractive index nearly matches that of the polymer, substantially reducing the scattering power of the droplets [13]. The characteristics of polymer/liquid crystal systems as novel material for preparation of permselective membranes have been studied in recent years [14–17]. We have studied the permeability and selectivity of pure and modified CoPVDF membranes as function of several gases (O_2 , N_2 , CO_2); tests of water passage in liquid phase and tests of water absorption in vapour phase have been carried out on samples of stone covered with the membranes.

Both systems, pure and modified CoPVDF membranes, show total resistance to the liquid water pas-

sage. They can be used to control the humidity present in the stone matrix to realize a direct protection of the stone surface and to control the biodeterioration phenomenon, realizing the appropriate environmental conditions on the stone surface.

The PDLCs are applicable to thermocontrol gas permeation systems. Their permeability behaviour as a function of the percentage of liquid crystal within the polymeric matrix has been studied.

The possibility of also modifying their transparency by applying electrical field, might become an interesting additional property in respect of the application suggested in this paper.

2. Experimental

Poly(1,1-difluoroethene), or PVDF, is a polymer having a crystalline structure which can be modified by adding several compounds in variable quantity. We have studied an amorphous copolymer PVDF ($\text{CH}_2\text{CF}_2/\text{C}_3\text{F}_6$) in a 79/21 molar ratio. It is an elastomer with a high molecular weight (3.5×10^5). The main feature of this material is its transparency: this peculiarity is due to the copolymer/solvent ratio. The chemical structure and the main characteristics of the copolymer used are shown in Fig. 1. The polymer selectivity toward different gases has been studied.

Tests of water passage in the liquid phase, through the CoPVDF membrane, as a function of applied pressure and thickness of the membrane have been carried out. To this purpose an ultrafiltration cell was used, consisting of a bedplate, provided with a porous support on which the membrane was been placed, and an upper chamber connected to a pressure generator. The pressures used were: a) 0.5, b) 1, c) 1.5 and d) 2 bar. The

Co-PVDF Polymer

Formula $(\text{CH}_2\text{CF}_2/\text{C}_3\text{F}_6)$

Molar Ratio : 1,1-Difluoroethylene/Exafluoropropene (79/21 w/w)

Molecular Weight: $3,5 \times 10^5$

Solvent: Ethyl Acetate

Co-PVDF/Solvent ratio: 1/10 (w/w)

Fig. 1. The chemical structure and the main characteristics of the copolymer CoPVDF.

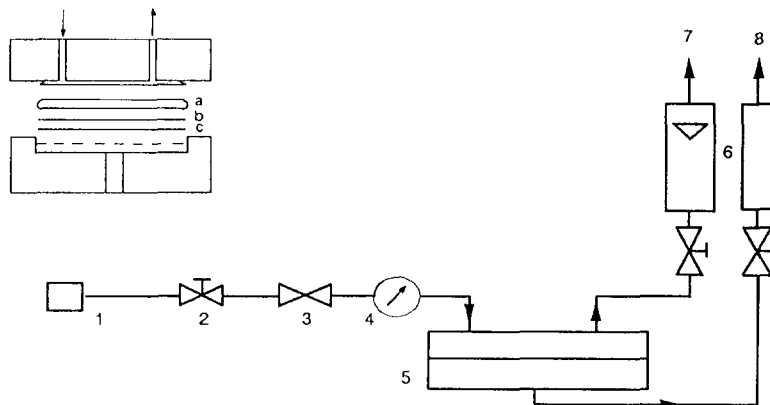


Fig. 2. Experimental apparatus used for liquid water passage through CoPVDF membranes. 1) Feed; 2) regulation valve; 3) security valve; 4) manometer; 5) permeation cell; 6) flowmeters; 7) residue; 8) permeate. Particulars of a permeation cell: a) gasket; b) membrane; c) support.

membranes were: a) 20, b) 15, c) 10 and d) 8 μm thick. The tests were carried out at 298 K for 30 days. A scheme of the experimental apparatus is depicted in Fig. 2.

To determine the capacity of CoPVDF membrane to favour the exchange of water vapor between the external and internal ambient of the same stone samples (coming from the Center of Diagnosis and Conservation of Arezzo, Italy) a series of tests of water absorption in vapour phase has been carried out. The CoPVDF membrane has been tested on *Pietra Serena*, a porous sandstone which has been frequently used to realize balconies, stairs and decorations of Italian monuments.

Changes in sample weight after exposure to water vapor was measured at 30°C. The apparatus comprises a glass vessel, hermetically sealed and divided by a perforated disk in an upper chamber and a lower chamber (Fig. 3). The system was immersed in a thermostated tank. The lower chamber, filled with water, was used as a vapor generator. Stone samples were placed on the perforated disk with one of the surfaces facing the water vapor saturated environment. To eliminate residual humidity, which can be absorbed by the upper surface of the stone sample, and to create a vapour pressure difference, the upper chamber was connected to a vacuum system.

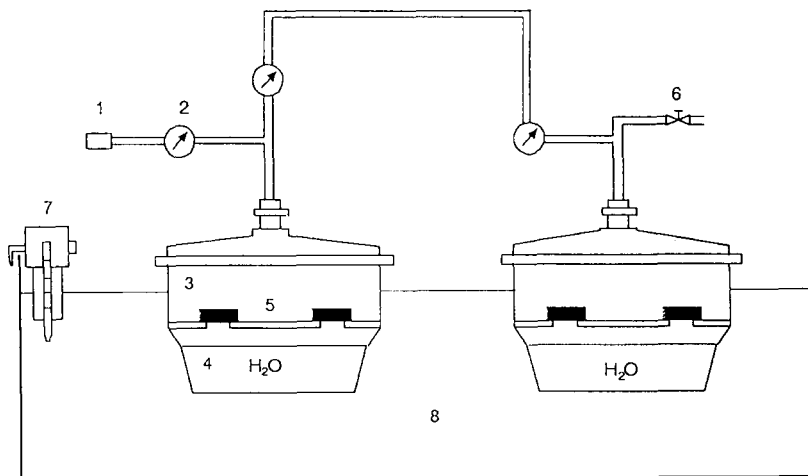
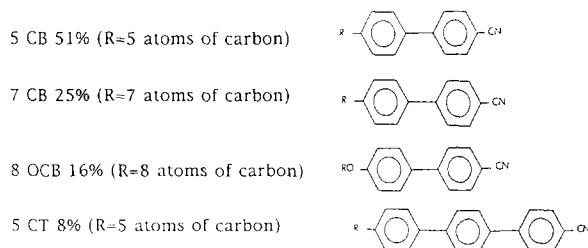


Fig. 3. Experimental system used for water vapour passage through CoPVDF membranes. 1) Vacuum system; 2) manometer; 3) vacuum compartment; 4) water compartment; 5) stone sample; 6) security valve; 7) thermostatic group; 8) thermostatic bath.



CB: cyano-diphenyl; OCB: Alkoxy-cyano-diphenyl; CT: Cyano-triphenyl.

Fig. 4. The main components of E7 with their relative chemical structures.

The main components of E7 with their relative chemical structures are shown in Fig. 4. The PDLCs were prepared by dissolving appropriate quantities of the copolymer and liquid crystal in ethyl acetate solvent (1/10 [v/v]). The solution formed after 24 h of agitation was used to prepare the membranes. Solvent was evaporated under high vacuum for 24 h [18]. The weight % of liquid crystal in the PDLCs was 10%, 20% and 25%. This last percentage represents the most that can be embedded in the copolymer matrix. The thickness of PDLCs was kept between 20 and 50 microns.

Permeation characteristics for oxygen, nitrogen and carbon dioxide gases in the pure membrane and in the PDLCs were investigated by a volumetric method (ASTM 1434-80), in the temperature range from 303 to 328 K and at a pressure of 2 bar. The apparatus and procedure for gas permeation experiments have been described previously [19].

3. Results and discussion

3.1. Characterization of pure membrane and PDLCs

The morphology of each of the membranes was been analyzed by electron microscopy. Figs. 5–7 show the surfaces and the internal sections of pure membrane and of the PDLCs with 10 and 20% of E7 respectively. The observation was carried out by the freeze fracture technique, using liquid nitrogen as the cryogenic fluid.

The surface of CoPVDF membrane appears smooth and dense (Fig. 5a and 5b). In the PDLC with 10% of E7 (Fig. 6a and 6b) it is apparent that the surface is still dense; in the cross-section, the cavities left by

liquid crystal after the cut can be observed. Holes are approximately one micron in diameter.

In the PDLC with 20% E7 (Fig. 7a and 7b), a homogeneous distribution of holes with average dimensions 1 and 2 microns characterize the surface. The section shows holes whose dimensions are in the range of 1–2 microns lying below the surface.

3.2. Water passage in the liquid and vapour phases through the CoPVDF membrane

Both unprotected and protected *Serena* stone samples were used to determine the quantity of the liquid water absorbed by the stone matrix. In our experiments the samples were exposed to the liquid water source and the stone weight was measured as a function of

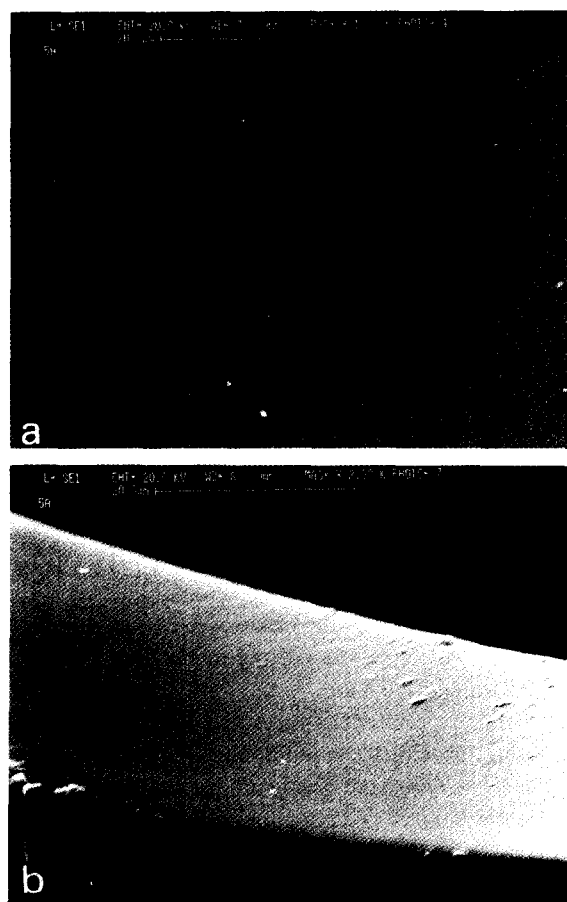


Fig. 5. (a) SEM of the surface of CoPVDF membrane. (b) SEM of the section of CoPVDF membrane.

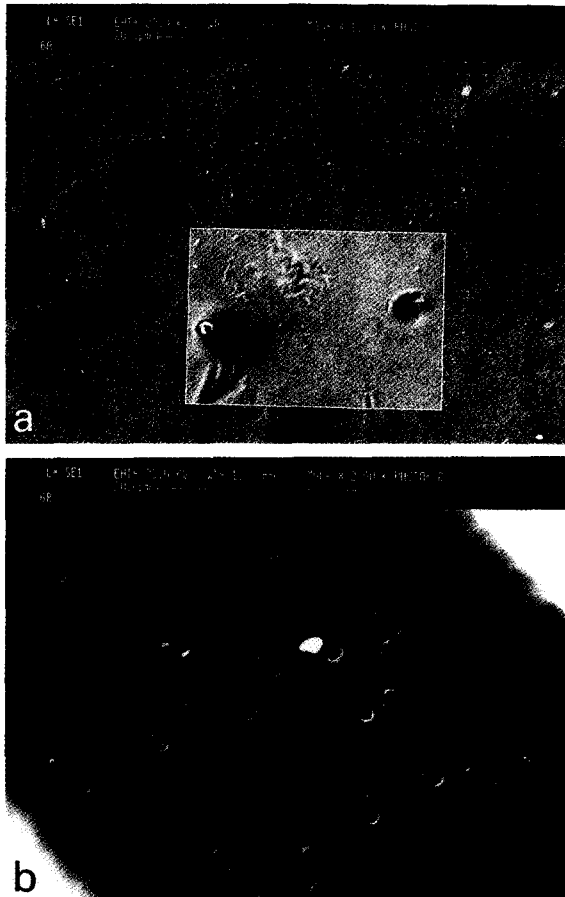


Fig. 6. (a) SEM of the surface of PDLC with 10% of E7. (b) SEM of the section of PDLC with 10% of E7.

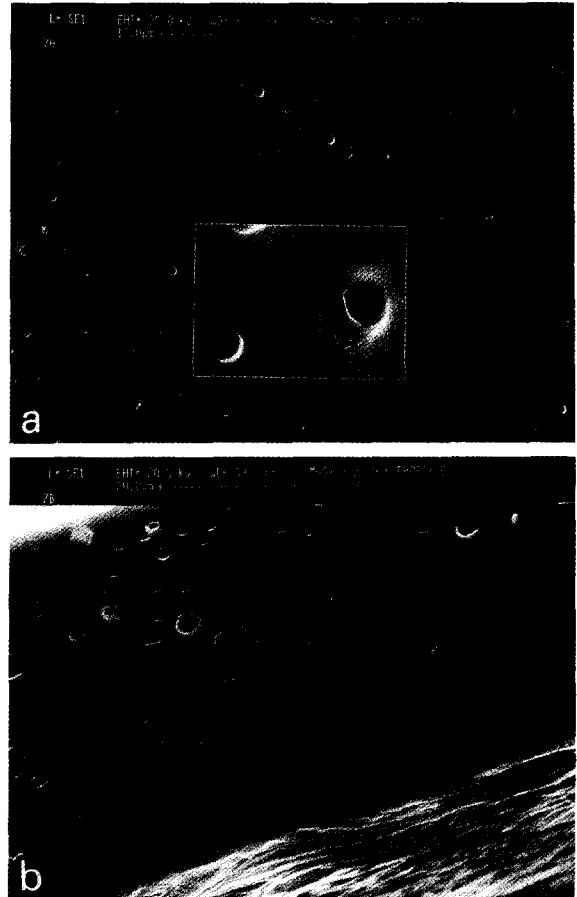


Fig. 7. (a) SEM of the surface of PDLC with 20% of E7. (b) SEM of the section of PDLC with 20% of E7.

time. As reported in Fig. 8, in the case of the protected *Serena* stone there is no liquid water absorption. Some of the stone that was treated with traditional methods, using perfluorinated fluids, has shown higher absorption in liquid water of the order of $7 \mu\text{l}/\text{cm}^2$ in about 25 days [20], compared with the some of the stone that was protected by the membrane.

Several experiments concerning liquid water passage through CoPVDF membranes as a function of thickness and pressure gradient have been carried out. When the *Serena* stone samples are protected, liquid water passage through the pure and composite membranes is not observed, independently of the applied pressure and of the membrane thickness.

The capacity of pure membrane to reduce water vapor absorption and desorption has also been studied.

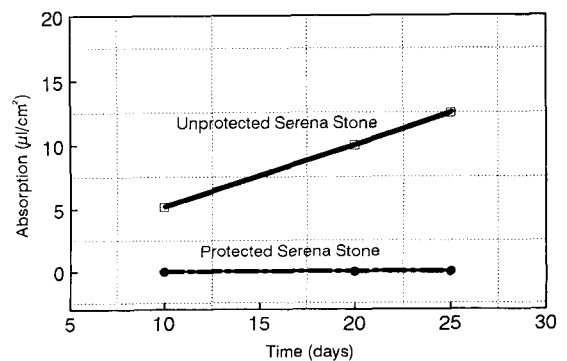


Fig. 8. Liquid water absorbed by unprotected and protected *Serena* stone with CoPVDF membrane. Membrane thickness = $15 \mu\text{m}$; $T = 25^\circ\text{C}$.

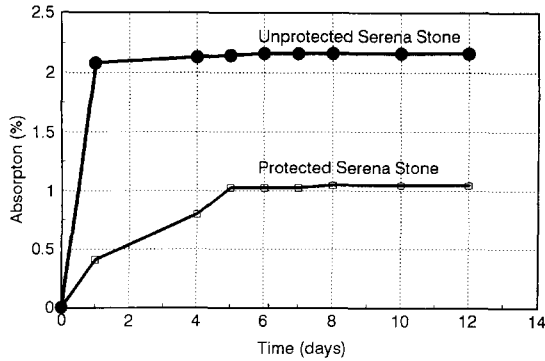


Fig. 9. Water vapour absorbed by unprotected and protected *Serena stone* with CoPVDF membrane. Membrane thickness = 15 μm ; $T = 30^\circ\text{C}$; $A = 15.85 \text{ cm}^2$.

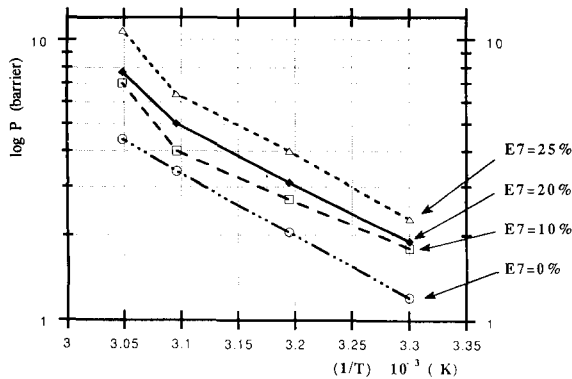


Fig. 10. Arrhenius plots of permeability coefficients for oxygen gas in composite membrane and in pure membrane.

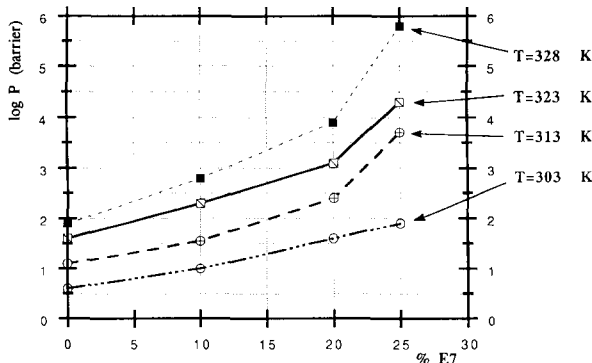


Fig. 11. Plots of $P(\text{N}_2)$ vs. E7 for CoPVDF membranes at different temperatures.

Serena stone samples have been used to determine water vapor absorbed in the absence or the presence of the pure CoPVDF membrane. Experimental procedure

involved the measurement of the weight increase of the stone sample, as a function of time, after exposure of the stone to the water vapour source. As shown in Fig. 9, in the case of the protected *Serena stone* sample, there was a significant decrease of the water vapour absorbed.

3.3. Permselectivity in the pure and composite membranes

Fig. 10 shows Arrhenius plots of permeability coefficients, P , for oxygen gas in the PDLCs and in the pure membrane. When the temperature is increased, except for the pure membrane, a jump in the permeability coefficient near the phase transition N-I (nematic-isotropic) of the liquid crystal is observed; a similar type of behaviour has been already discussed by Kajiyama et al. [16]. Generally over the whole temperature range studied the permeability of all membranes show a linear increase and its values in the PDLCs are greater than those in the pure membrane. The results are valid for all gases studied. At higher temperatures the membrane suffer mechanical damages and the permeability value cannot be measured.

Fig. 11 shows plots of $\log P$ against the percentage (%) of E7 in the PDLCs for nitrogen gas. By increasing the percentage of liquid crystal, the magnitude of permeability in the CoPVDF membranes increases for all examined gases.

These results confirm the influence of the liquid crystal on the permeability of these membranes. As shown in Fig. 12, by increasing the temperature value, the selectivity of $P(\text{O}_2/\text{N}_2)$ of the pure membrane

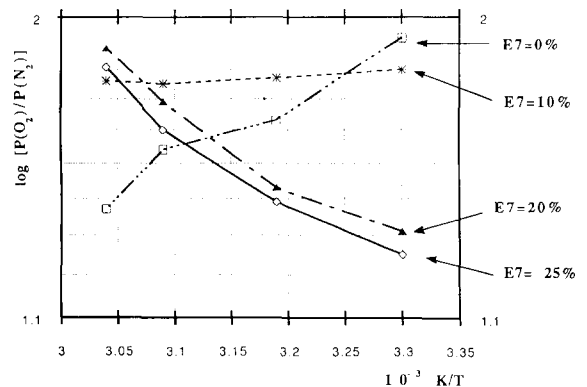


Fig. 12. Plots of $[P(\text{O}_2)/P(\text{N}_2)]$ vs. $1/T$ for CoPVDF membranes.

decreases; it remains constant in the presence of small percentages of the liquid crystal, and when the percentages of liquid crystal becomes sufficiently high, it increases. Similar behaviour is observed for the selectivity of $P(\text{CO}_2/\text{N}_2)$. This trend is in contrast to the behaviour of polymeric membranes for gas separation, where the value of $P(\text{O}_2/\text{N}_2)$ generally decreases with an increase of the temperature.

4. Conclusions

The experimental results have shown the possibility to protect the stone surfaces from liquid water penetration by applying the CoPVDF and PDLC membranes and to reduce and control the water vapour absorption. The membrane permeabilities and selectivities for gases might be modified by embedded liquid crystal in the polymeric phase. The changes observed have to be attributed specifically to the liquid crystal properties.

The results obtained represent only a preliminary approach to developing films to be used for conservative purposes of stone objects.

5. List of symbols

A	area of membrane for permeation (cm^2)
P	gas permeability (10^{-10} cm^3 (STP) $\text{cm}^2/\text{cm sec cmHg}$)
L	membrane thickness (μm)

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References

- [1] E. Drioli et al., Proc. of the EEC China Workshop on preservation of Cultural Heritages, 1992, p. 9–18.
- [2] G.P. Guidetti, Causes of degradation of stone exposed to open air and methods of restoration, P. Parrini (Ed.), Science and Conservation, Arcadia, Milano, 1986, pp. 35–40.
- [3] V. Di Battista, Il degrado delle materie, tecnologia del recupero edilizio, Unione tipografico-Ed. Torinese, 7 (1989) 280.
- [4] P. Parrini et al., *Acqua e Aria*, 4 (1983) 397.
- [5] L. Caglioti et al., Proc. of the EEC China Workshop on preservation of Cultural Heritages, 1992, p. 126.
- [6] F. Piacenti, Proc. of the EEC China Workshop on preservation of Cultural Heritages, 1992, p. 183.
- [7] A. Pasetti, The organic chemistry of fluorine in the protection and conservation of lithoid materials, Science and Conservation, Arcadia, 1986.
- [8] E. Zendri et al., Impiego di polimeri fluorurati per la conservazione di intonaci, Atti del Convegno di Studi su Superfici dell'Architettura: Le Finiture, Bressanone, 1990, p. 647.
- [9] L. Caglioti et al., The conservation of stone and lithoid materials. Proc. of the EEC China Workshop on Preservation of Cultural Heritages, 1990, p. 126.
- [10] J.W. Doane et al., *Mol. Cryst. Liq. Cryst.*, 65 (1988) 511.
- [11] P.S. Drzaic, *J. Appl. Phys.*, 60 (1986) 2142.
- [12] A.L. Tsykalo, Thermophysical properties of liquid crystals, Part I, Gordon and Breach, NY, 1991, Chap. 1, p. 7.
- [13] J.W. Doane, Proc. of the SID, Vol. 32/2, 1991.
- [14] T. Kajiyama et al., Novel polymer liquid crystal composite membrane with unique permselective characteristics, *J. Membrane Sci.*, 36 (1988) 243.
- [15] T. Kajiyama et al., Characterization and gas permeation of polycarbonate/liquid crystal composite membrane, *J. Membrane Sci.*, 11 (1982) 39.
- [16] T. Kajiyama et al., Permselective characteristics of polymer/liquid crystal composite membrane, *J. Appl. Polym. Sci.*, 41 (1985) 327.
- [17] T. Kajiyama et al., Membrane structure and permeation properties of poly(vinylchloride)/liquid crystal composite membrane, *J. Appl. Polym. Sci.*, 29 (1984) 3955.
- [18] B.G. Wu et al., *J. Appl. Phys.*, 62 (1987) 3925.
- [19] E. Drioli et al., Gas separation and purification, 5 (1991) 252.
- [20] E. Drioli et al., Sistemi a membrana per la conservazione dei Beni Culturali, *Acqua e Aria*, 4 (1994) 321.