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Surface modification of quarry stone by hexamethyldisiloxane plasma treatment

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The surface of quarry stone was modified by continuous plasma polymerization of hexamethyldisiloxane. The hydrophilic surface of the quarry stone was made hydrophobic and impermeable to water. Three different reaction times were analyzed. All of them resulted in the formation of a homogenous layer on the quarry stone surface. Contact angle and FT-IR analyses show that the hydrophobic character of the surface is due to methyl groups on the surface. The change in the contact angle with temperature and the wetting temperature (T_w) are also discussed. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: plasma polymerization; quarry stone; poly(hexamethyldisiloxane); superficial treatment

INTRODUCTION

Quarry stone is one of the main materials employed in historical and artistic monuments. Owing to the high corrosion rate of quarry stone, the preservation of monuments made from this material is difficult. Many factors such as pollution and the particular climate of a given region affect the erosion rates of quarry stone.[1] Surface treatments on quarry stone monuments help repel water and biological agents.[2] There are many commercial products that can be used to modify the stone surface. Most of these treatments are based on silicone compounds that are dissolved and applied to the surface.[3]

Alkoxysilanes, such as tetraethoxysilane, applied as low viscosity monomers and cured by sol–gel methods, as well as colloidal silicate solutions, are currently used.[4] These may be combined with chemical treatments that make the stone less susceptible to attack by bacteria and fungi. Although these commercial treatments have been successful in protecting the surface of quarry stone monuments, some have the disadvantage of changing the texture as well as the color of the stone. Another disadvantage of these treatments is that their efficiency is diminished when the stone has irregularities or small cracks. Small handicrafts made from quarry stone may also need to be protected since their porous nature promotes environmental attack of the highly hydrophilic surfaces.[5]

The hydrophilic nature of the quarry stone surface can also be modified by means of a plasma surface treatment. It has been demonstrated that plasma polymerization can be used to treat surfaces without affecting the internal characteristics of the material.[6] This process is fast, uniform and cheap.[7,8] Plasma surface treatment can be used to modify the surface characteristics of polymers, metals and ceramics. It not only allows the use of materials already known in new applications, but can also be used to optimize their surface properties. By this method, hydrophobic surfaces can be generated by depositing a very thin fluorocarbon film. When stable surfaces (no diffusion to the bulk is observed) are used, water contact angles greater than 150° are obtained; nevertheless these films show poor mechanical stability.[8] Alternatively, hydrophobic surfaces can be obtained by coating with methyl group-rich compounds, such as hexamethyldisiloxane (HMDS).[9] The plasma polymerization of hexamethyldisiloxane (PPHMDS) has been used to modify the surface of chitosan substrates, changing the hydrophilicity of the surface from highly hydrophilic to hydrophobic.[10]

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In this work, the surface modification of quarry stone by plasma polymerization of HMDS was accomplished to generate stable hydrophobic surfaces. A thin film was deposited on the quarry stone; the film was characterized by FT-IR and the hydrophilic character of the modified quarry stone surface was characterized by contact angle.

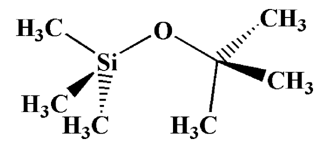

Figure 2. Chemical structure of HMDS.

EXPERIMENTAL

Figure 1 shows a scheme of the plasma reactor used for the surface treatment of quarry stone. The reactor consists of a tubular glass of 20 cm in length and 9 cm of external diameter. The reactor has two flanges and two circular electrodes (6 cm in diameter), made from stainless steel. The electrodes can be displaced along the longitudinal axis of the reactor. Each flange has two access ports. In one of the flanges, one of the access ports is connected to a vacuum system and the other port is connected to pressure gage. The access ports of other flange are used to introduce the monomer and reactive substances. The electrodes are connected to a voltage amplifier (ENI A150) and a radio frequency generator (Wavetek 164). A detailed description of the reactor and its operation can be found elsewhere.[11] HMDS is introduced by creating a pressure difference between the reactor and the monomer container. Before the plasma treatment, the quarry stone was washed with acetone (Aldrich) and was dried in a furnace for 60 min at 100 °C to remove humidity. The stone substrates, 2.5 × 2.5 × 2.5 cm, were placed in the center of the reactor as shown in Fig. 1. During plasma treatment, the power was 30 W, the pressure was maintained at 120 mTorr, RF was set to 13.56 MHz and reaction times of 60, 90 and 180 min were used. The chemical structure of the HMDS monomer is shown in Fig. 2. The monomer was reagent-grade with 99.99% purity (Aldrich).

The characterization of the HMDS layers was done by Fourier transform infrared (FTIR) spectroscopy with a PerkinElmer FTIR-2000 spectrophotometer using 64 scans. The IR data was taken from KBr tablets exposed to the HMDS plasma at same time as quarry stone substrates. The KBr tablets were located next to the quarry stone substrates in the center of the reactor. The polymer film obtained was tested for solubility in acetone and other organic solvents; there was no solubility, and this effect was associated with the crosslinking of the polymer.

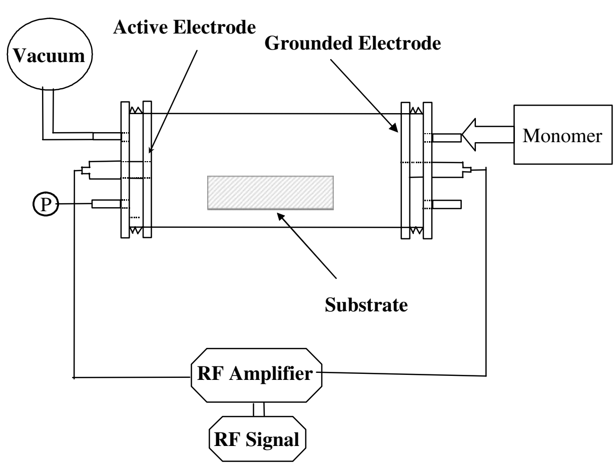

Figure 1. Experimental setup.

In order to characterize the modification of the quarry stone surface, contact angle measurements were performed. The substrates were placed on a leveled support. A drop of each testing liquid was deposited on the substrate, and photographed with a digital camera (Mavica Sony). The digital image was analyzed (NIH Image 1.67) to measure the contact angle. The average of several measurements on both sides of the drop is reported as the contact angle. Contact angles of water, glycerin and ethylene glycol on untreated and treated quarry stone surfaces were measured. The surface tensions of the test liquids are reported in Table 1.[12]

RESULTS AND DISCUSSION

Contact angle analysis

Contact angle measurement on a porous material may be affected by the diffusion of the liquid into the bulk. Therefore, the measured contact angle is an apparent contact angle (ACA). The ACA is a function of the interfacial energy, the size of the pores, the viscosity of the liquid and the normal forces.[13,14]

In Fig. 3 the ACA of quarry stone without treatment is shown. Figure 3(a) shows that there is no ACA between water and untreated quarry stone because water diffuses completely into the bulk of the stone. Glycerin and ethylene glycol form small drops with low contact angles, as can be observed in Fig. 3(b, c). The diffusion of the liquid into the stone can be clearly seen in Fig. 3(a, c). In the case of Fig. 3(b) the diffusion is low.

Table 1. Surface tension of test liquids

	Liquid	Surface tension (mN m^{-1})
1	Water	72.2*
2	Glycerin	65.4*
3	Ethylene-glycol	47.7*

* Source: from Adamson.[12]

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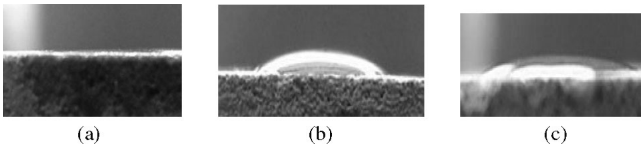

Figure 3. Apparent contact angles of untreated quarry stone: (a) water; (b) glycerin; and (c) ethylene-glycol.

In Fig. 4 contact angles of the treated quarry stone can be appreciated. In the reactive atmosphere of the plasma treatment, a HMDS polymer layer is deposited on the quarry stone surface. As a result, methyl groups cover the surface and give it a hydrophobic character.

Table 2 shows the contact angle values of the different testing liquids obtained after 60, 90 and 180 min of plasma polymerization of HMDS. For 60 and 90 min exposure times the measured contact angles are similar. On the sample treated for 180 min we measured lower water contact angles. In addition, the treated substrates maintained their hydrophobic character after 18 months. These results suggest that quarry stone treated with HMDS plasma will be protected from harmful environmental conditions.

FT-IR analysis

In Fig. 5 the FT-IR spectra of HMDS and plasma polymerized HMDS (PHMDS) after different reaction times can be appreciated. In the HDMS spectrum, the signal corresponding to the characteristic vibration of methyl groups can be seen at 2960 cm^{-1}. The absorption peaks due to the $Si-CH_3$ bond can be identified at 1260 and 855 cm^{-1}. The peaks centered at 1060 and 790 cm^{-1} are attributed to the $-O-Si$ groups.

The spectra of PHMDS after different reaction times show complex absorption bands characteristic of materials synthesized by plasma polymerization.[10] All the spectra show the characteristic peaks of the HMDS monomer; at 2960 cm^{-1} there is a signal in all the spectra, but Fig. 5 shows only the absorptions on 1260, 855, 1060 and 790 cm^{-1}. This is an indication that the monomer chemical structure was mostly conserved in the polymer, but nevertheless the peak at 1060 shows a wide spectrum, which also shows that there may be some combinations like $Si-O-Si$ or $O-CH_3$ as a result of the crosslinking in the polymer. The signal corresponding to the $Si-CH_3$ groups of PHMDS at all reaction times shows high intensity; this indicates that the surface of the quarry stone is rich in methyl groups, thus increasing the hydrophobic character of the surface.

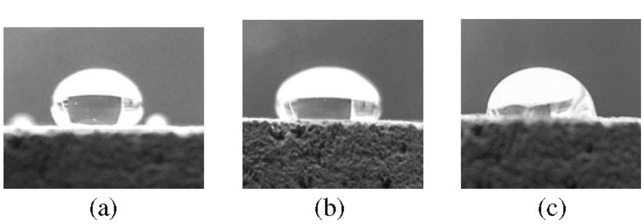

Figure 4. Contact angles of quarry stone treated with HMDS plasma: (a) water; (b) glycerin; and (c) ethylene-glycol.

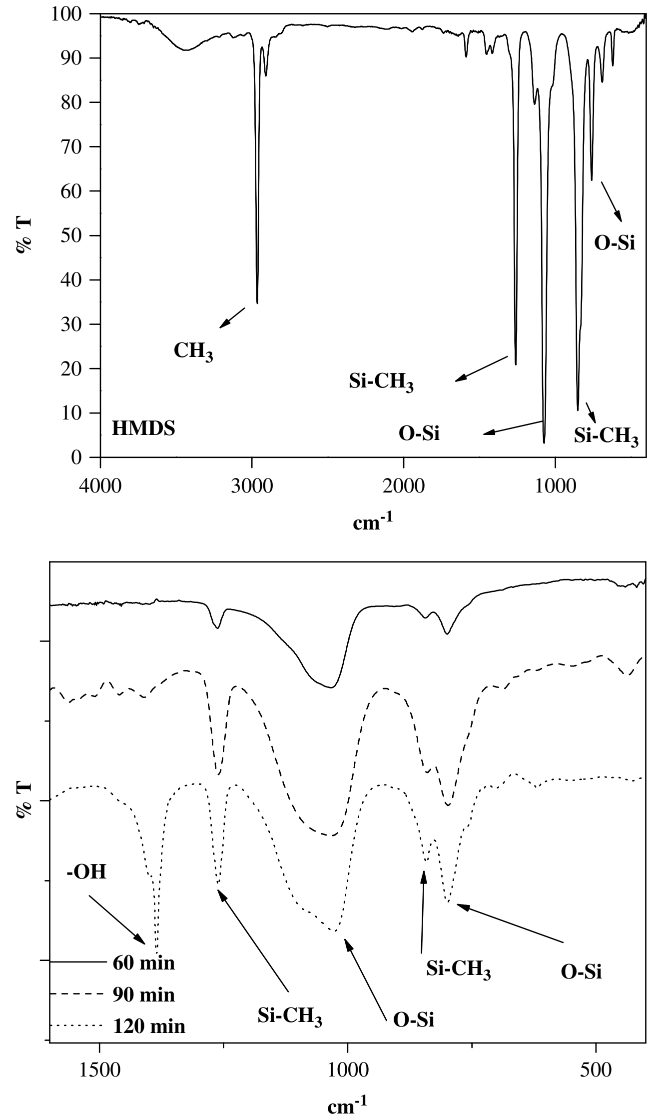

Figure 5. FT-IR spectra of HMDS and PHMDS after treatment times of 60, 90 and 180 min.

The spectrum of 180 min PHDMS shows a strong band at 1390 cm^{-1} which is related to the presence of $O-H$ groups. This can be attributed to free radicals that remained active after the treatment and could react with air at the time that the plasma reactor was opened. The presence of these groups could be responsible for the decrease in water contact angles (Table 2). The contact angle and FT-IR results indicate the formation of a hydrophobic coating on the surface of the quarry stone.

Wetting transition

The change in contact angle on quarry stone substrates treated for 60 min was measured as a function of temperature. The

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Table 2. Contact angles on quarry stone treated with HMDS plasma

Surface	Water	Glycerin	Ethylene-glycol
Quarry stone, QS (ACA)	0.0	33	9
QS-PHDMS, 60 min	122	88	76
QS-PHDMS, 90 min	123	88	76
QS-PHDMS, 180 min	124	110	88
QS-HDMS, 180 min, after 18 months	124	111	86

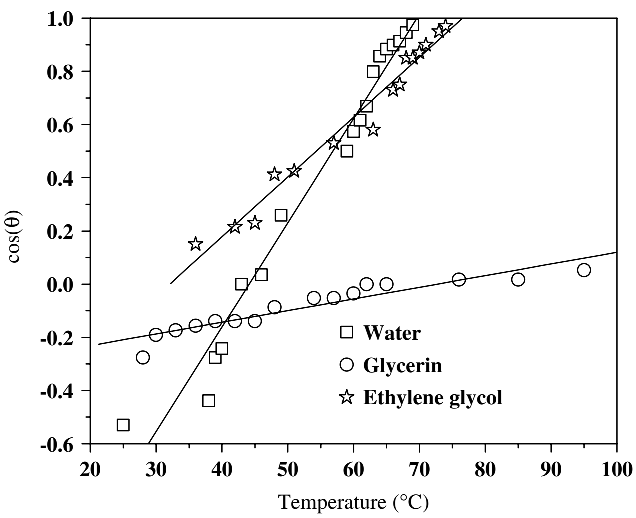

Figure 6. Plot of contact angle of (□) water, (○) glycerin and (*) ethylene glycol as a function of temperature and extrapolation for the determination of wetting temperatures on quarry stone substrates treated for 60 min.

temperature was increased until the testing liquids wet the surface. T_w was obtained by extrapolation in plots of cosine of the contact angle vs temperature. T_w corresponds to the extrapolated temperature at $\cos\theta = 1$.[12,13] Figure 6 shows the plot of contact angle as a function of temperature for the three test liquids. The wetting temperatures of water and ethylene glycol were 68 and 76 °C, respectively. In the case of glycerin there was no wetting transition in the temperature range measured. No absorption into the bulk of the treated quarry stone samples was observed with any of the testing liquids. The PHMDS must therefore form a homogenous layer that does not permit absorption. Longer plasma exposure times result in thicker PHMDS layers so we expect that the impermeability to the liquids will persist up to temperatures higher than 76 °C at all the treatment times used in this study.

CONCLUSIONS

The surface of quarry stone was modified by HMDS plasma polymerization. The modified surface acquired a hydrophobic character. This was demonstrated by the change in its surface activity as measured by contact angle. The change in hydrophilicity was due to the presence of methyl groups on the treated surfaces as the FT-IR analysis showed.

The treated quarry stone surface kept its hydrophobic character at temperatures higher than typical ambient temperatures. When the wetting transition took place, there was no diffusion into the stone due to the formation of an impermeable protecting PHMDS layer. These results suggest that the HMDS plasma treatment used in this work is a possible alternative method for the preservation of quarry stone pieces.

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