J. Coat. Technol. Res., 11 (4) 661–664, 2014
DOI 10.1007/s11998-014-9585-8

BRIEF COMMUNICATION

Water permeability of quarry stone superficially modified by plasma polymerization of hexamethyldisiloxane at atmospheric pressure

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Abstract The surface of quarry stone was modified with a thin film of plasma-polymerized hexamethyldisiloxane (PPHMDSO) deposited at atmospheric pressure. The surface of the treated stone turned hydrophobic as shown by water contact angle measurements. FTIR characterization showed CH_3 and Si-CH_3 bands characteristic of HDMSO functional groups. Finally, the water absorption of untreated and PPHMDSO-modified stones was studied. In both cases, the water absorption profile was consistent with Fickian diffusion but the treated stone absorbed 8 times less water than the untreated stone.

Keywords Quarry stone, Plasma polymerization, Polyhexamethyldisiloxane, Water repellent

Introduction

Buildings and historical monuments suffer constant deterioration due to biological attacks as well as physicochemical phenomena which occur naturally in a humid environment.[1,2] In particular, quarry stone with hydrophilic characteristics absorbs humidity by means of a capillary process when exposed to high relative humidity in the environment or when submerged in water. Water absorption is a major problem with respect to maintenance of monuments and buildings for two reasons: First, water functions as the medium for the introduction of microorganisms and bacteria that damage or corrode the stone.[3] Second, the stone is susceptible to cracking due to water expansion if the water within the stone freezes as a result of low environmental temperatures.[4] Ethyl silicate compounds are used to arrest these phenomena and to strengthen the matrix of the stone.[5] Halting the deterioration of quarry stone is complicated due to the morphology, roughness, and porosity of the stone. Additional considerations in the case of historical monuments and buildings are the size and geometry of the stone.

Treatment of the stone by coating with a variety of compounds has been proposed to diminish water absorption by functionalizing the surface with water-repellent chemical groups.[6] These treatments are generally applied in aerosol form. Because of the manner in which they are applied, the reported treatments have two important drawbacks: the depth of penetration of the treatment is limited and the adherence of the compounds to the stone is not very strong. Thus, the stone will need to be retreated frequently.

We propose an alternative method for treatment of stone in historic buildings: plasma polymerization. Plasma polymerization has been used, for example, to treat the surface of polymers to modify the wettability of their surface.[7] In general, plasma polymerization is performed in enclosed reactors at low pressures which would not be applicable to the treatment of buildings. Plasma polymerization at atmospheric pressure, however, could be used for this application. In this work, we demonstrate the surface treatment of quarry stone by plasma polymerization. The plasma was formed from HDMSO, which has been previously reported to form hydrophobic surfaces on other substrates by plasma polymerization.[8] The surface of the stone was

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characterized by water contact angle and FTIR, and a comparison was made between untreated and treated stone to determine their water uptake.

Experimental methods and materials

Plasma polymerization

Figure 1 shows a diagram of the plasma polymerization reactor. The reactor consists of a Pyrex glass tube measuring 250 mm in length and 90 mm in exterior diameter. A small glass tube of 7 mm in external diameter and 40 mm in length extends through the center of the main tube. Hexamethyldisiloxane (Sigma-Aldrich) was introduced into the reactor via the small tube. Both ends of the reactor have stainless steel caps with three access ports each. Square stainless steel electrodes measuring 40 x 40 mm were introduced through the central ports of the caps. The electrodes were coated with glass slides to obtain a more homogenized discharge of the plasma and connected to a Cesar 1310-RF power source. The two remaining ports of one cap were sealed. The two ports of the other cap were connected to a Pirani gauge to monitor the pressure inside the reactor and to a vacuum pump.

A quarry stone sample 5 mm thick with a surface of 40 x 40 mm was first cleaned thoroughly with acetone (Sigma-Aldrich, reagent grade) to remove any impurities, kept in an oven for 3 h at 100°C to eliminate humidity, and then placed inside the reactor just below the electrodes (Fig. 1). Three KBr pellets (Sigma-Aldrich, 99%) were also placed inside the discharge tube, one on each extreme and one beside the QS substrate.

The reactor was evacuated to a pressure of 10 Torr and the power source was turned on. The polymerization was initiated by allowing monomer into the reactor and setting the power source to 50 W power and frequency of 13.5 MHz. The vacuum line was closed and the pressure was allowed to increase up to atmospheric pressure. After 30 min, the polymerization was terminated by turning the power source off and closing the monomer inlet.

Once the reaction was finished, the material adhering to the sides of the reactor was scraped and deposited in Petri dishes for later analysis.

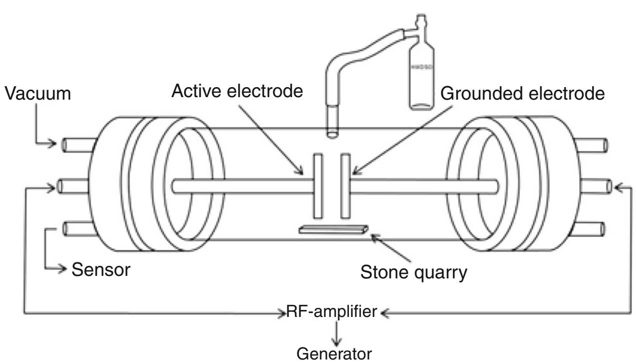

Fig. 1: Plasma polymerization set-up

Characterization

The quarry stone substrate was characterized by measuring the water contact angle. An F480 FUJIFILM camera with 16 MP and a 10× zoom was used to photograph a drop of distilled water deposited on the surface of the modified stone. ImageJ software was used to measure the contact angle.

The KBr pellets that were placed in the reactor alongside the QS sample were analyzed by IR spectrophotometry (Perkin-Elmer 2000) in a wavelength range of 400–4000 cm^{-1}. The measurements consisted of 32 scans.

To study the water absorption in quarry stone with and without PPHMDSO modification, samples were immersed in water and the gain in mass was measured as a function of immersion time.

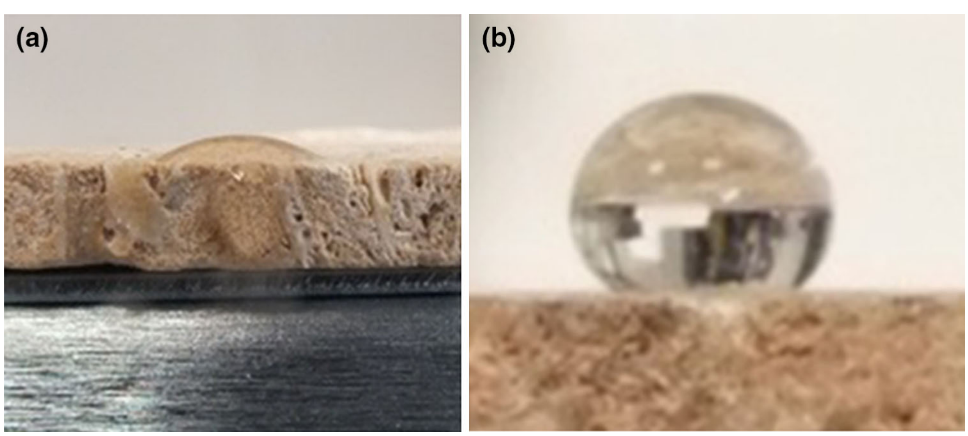

Fig. 2: Water drops on untreated (a) quarry stone and (b) PPHMDSO-treated stone

Results and discussion

Quarry stone samples were treated by plasma polymerization of HMDSO. The modified samples were similar in appearance to untreated samples. The samples were analyzed by water contact angle and FTIR and their water absorption capacity with time was measured.

PPHMDSO treatment changed the surface characteristics. Figure 2 shows pictures of water drops on the surface of untreated and PPHMDSO-treated quarry stone samples. While the untreated sample was wet by the drop and had a contact angle of approximately 20°, the treated sample showed hydrophobic character with a contact angle of 130 ± 1°. This same average contact angle was measured on the KBr pellets coated with PPHMDSO.

Figure 3 shows the FTIR spectrum of PPHMDSO deposited on one of the KBr pellets. The observed bands can be assigned to vibrations of methyl silane, methyl, and Si-O groups. Details of the band assignment are shown in Table 1.[9]

The water absorption properties of unmodified and PPHMDSO-modified quarry stone were characterized by immersing samples in water and measuring the mass of absorbed water as a function of time. The untreated and PPHMDSO-treated samples had the same dimensions and weighted 17.583 and 17.488 g, respectively. As can be seen in Fig. 4, both samples absorbed water up to a saturation point. The untreated sample saturated after 120 min and absorbed 4.3 g of water; in contrast, the PPHMDSO-treated sample saturated after 90 min and absorbed 0.5 g of water.

Figure 5 shows plots of fraction of total absorbed water as a function of the square root of time for both untreated and PPHMDSO-treated samples. A linear relationship is observed for both samples, consistent with a Fickian diffusion process. The data for the first 6 min were fitted with straight lines to determine whether there were significant differences in effective diffusion constants between the two samples. Only the first 6 min were chosen given that at longer times the

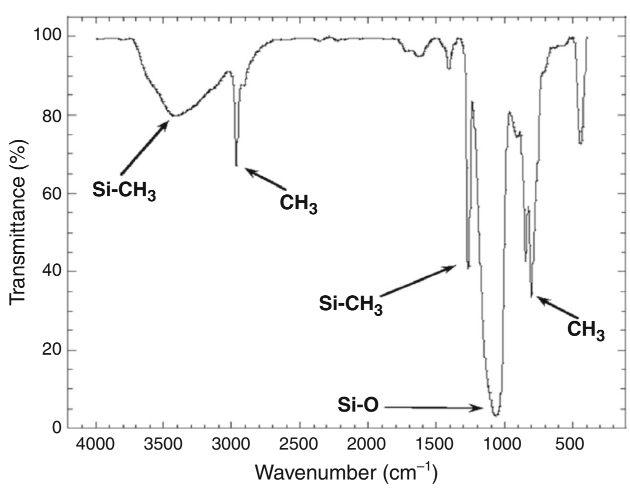

Fig. 3: FTIR spectrum of PPHMDSO

Table 1: FTIR band assignment

Wavenumber/(cm^{-1})	FTIR assignment
3440	Si-CH_3
2980–2850	CH_3, CH_2
1260	Si-(CH_3)
1200–1000	SiO_x, Si-O-Si
900–750	CH_3

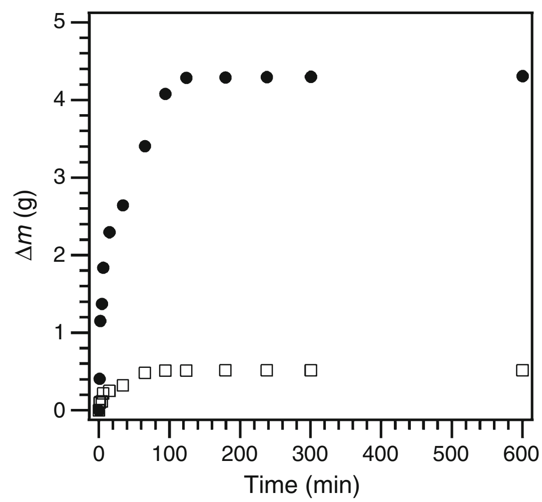

Fig. 4: Absorbed water as a function of immersion time of untreated (filled circles) and PPHMDSO-treated (empty squares) quarry stone

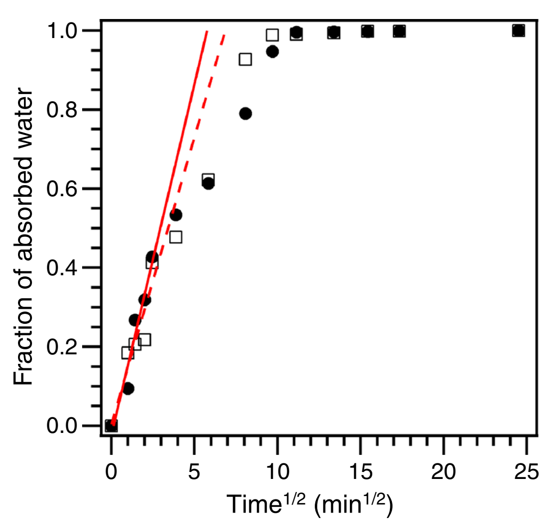

Fig. 5: Fraction of absorbed water as a function of the square root of time for the untreated sample (filled circles) and PPHMDSO-treated sample (empty squares). Linear fits for the untreated (solid line) and PPHMDSO-treated (dashed line) samples are also shown

diffusion fronts from the different faces of the samples meet and the time dependence of absorption is no longer a simple $t^{1/2}$ relationship. The slopes of the lines were 0.177 ± 0.024 min$^{-1/2}$ for the untreated sample and 0.145 ± 0.030 min$^{-1/2}$ for the PPHMDSO-treated sample; the difference is, thus, not significant. This slope is a function of the effective diffusion coefficient which includes the valid fraction and the tortuosity of the pores.

Conclusions

The surface modification of quarry stone has been demonstrated. By depositing a film of plasma-polymerized hexamethyldisiloxane, the surface of the stone is modified as shown by water contact angle and FTIR measurements. Both measurements confirm that the surface turns hydrophobic after treatment. The treatment reduces the amount of water absorbed by 800%. The hydrophobic character of the treated surface is likely due to a combination of methyl groups on the surface and its roughness.

While this work was performed on small samples of stone in a tubular reactor, the development of atmospheric plasma jets[8] should make it possible to apply this type of treatment directly onto monuments and buildings. More research is under way to understand the structure of the deposited film and its stability.

Acknowledgments The authors thank the partial support from Universidad Autónoma de la Ciudad de México (UACM) through project PI-2011-FM08 CONVENTION UACM/OAG/ADI/002/2011 and from the Instituto de Ciencia y Tecnología del Distrito Federal (ICYT-DF) through projects PIUTE 10-63, ICyTDF 276/2010, and ICyTDF-PICSA11-14/2011.

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