Superhydrophobic and Breathable Resorcinol-Formaldehyde Xerogels

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ABSTRACT. A new macroporous, waterproof and breathable material has been synthesized. The synthesis of these materials consists in a modified version of the classical resorcinol-formaldehyde (RF) xerogels synthesis. This new process includes a further treatment, after the gelation-curing-drying process, with methanol at 240 °C in order to passivate the hydrophilic phenolic groups of the surface of the RF xerogel. It was found that the treatment time strongly depends on the pore size of the xerogels. After reaching this threshold time, the hydrophilic materials become superhydrophobic. It is postulated that the exohedral inner surface of the porous xerogels, different from most porous materials, is responsible for this behavior. Although the materials exhibit a superhydrophobic behavior against liquid water and maintain its waterproofness for a long period of time, they are able to adsorb/desorb water vapor, which makes them also breathable.

KEYWORDS: xerogels; hydrophobicity; surface chemistry; passivation

1. Introduction

Waterproof and breathable materials or composites are essential in a number of processes and commodities, including protective clothing, sports apparel, and membrane contactors.[1-6] For all these applications, materials are required to combine conflicting properties such as avoiding liquid water to penetrate and allowing the vapor water to pass through at the same time. In any case, the combination of waterproofness and breathability is essentially a size discrimination issue. Thus, a waterproof and breathable material (or laminate) should be able to repel water droplets normally exceeding 10^5 nm in diameter (i.e., 0.1 mm) and to let through water molecules in the vapor phase with ca. 0.4 nm in diameter. The transport properties of water and moisture through a given material will determine its final performance in this type of applications.[2, 7]

So far, two successful approaches, in terms of commercial products, have been developed to cope with this sieving effect, namely porous and hydrophilic membranes/coatings.[1, 8] Hydrophilic membranes are virtually non-porous materials through which the water molecules diffuse following an anomalous mechanism.[1, 9] This type of membranes/coatings are based on copolymers of poly(ethylene oxide), poly(vinyl alcohol), polyurethane, etc. On the other hand, porous membranes are made of hydrophobic materials with an adequate porous texture to both withstand penetration by liquid water and maximize the transfer of water vapor molecules.[1, 2, 7] Polymers used for these porous membranes include polyolefins, polyurethanes and poly(tetrafluoroethylene), amongst others. Porosity in these materials can be attained either during the polymer synthesis or by using post-treatments such as mechanical frothing or fibrillation.[1, 10]

In addition to these two well-established methodologies, research in the field is still much in progress. Different approaches try to overcome drawbacks such as materials cost,[10-12] durability,[12-14] and a finer control of the porous structure in the case of porous membranes/coatings. Regarding this last subject, it is generally accepted that pore diameters in the 10^2 - 10^4 nm interval are required for effective waterproofness and breathability.[15] Still, the control of the porosity of the hydrophobic polymers is very imperfect due to the limitations of the conventional processing. Alternatives include new polymeric formulations,[15, 16] and the use of more exotic polymer processing technologies such as electrospinning.[17-19]

Organic gels in general, and resorcinol/formaldehyde (RF) resins in particular, are polymeric systems that show tremendous versatility in terms of developing tailored porous textures. Since the seminal work of Pekala,[20] a number of works have detailed the effect of different synthesis variables on the final three-dimensional structure of the RF gels,[21-26] which in turn determines the porosity of the materials. As a consequence, RF gels are nowadays synthesized with pore sizes and volumes adapted to the requirements of a given application. Furthermore, the use of microwave radiation to assist the synthesis of RF xerogels has dramatically shorten the production times, hence the costs.[27] The tight control of the porosity of the RF xerogels would make them an ideal candidate polymer for waterproof/breathable applications. However, the surface chemistry of the organic xerogels is rich in phenolic groups, which provides them with a high hydrophilicity. This property, which in conjunction with their textural properties allows these materials to be used as desiccant materials,[28] will not favor the water repellency required for this new application. Thus, to fulfil requirements of water repellency a passivating post-treatment of the RF xerogel surfaces would be eventually required.

There already exist several procedures for chemically modifying a micro-/nanostructured surface to give rise to low-surface energy materials (fluorinated substrates, coating mesh films, etc),[29-35] as well as methods to impart roughness to hydrophobic solid surfaces such as crystallization control,[36] phase separation,[37] electrochemical deposition,[38] and chemical vapour deposition.[39, 40] Hydrophilic silica gels, which also have surfaces rich on hydroxyl groups resembling that of RF xerogels, have been turned into hydrophobic materials by grafting methylsilane compounds on their surface.[30, 41, 42] However, the use of silane compounds to this aim has not been considered a suitable procedure due to the possible hydrolysis reactions that could likely take place at ambient conditions, which would limit the range of final applications of the resulting materials. A much more attractive alternative of surface passivation of surface hydroxyl groups has been described in a previous work, in which surface methoxylation was carried out using methanol vapor.[43]

In this work, a similar one-step methoxylation reaction of the phenolic groups of RF xerogels has been carried out. The resulting methoxylated xerogels are superhydrophobic materials that, at the same time, absorb and desorb significant quantities of water vapor. The process was studied using different RF xerogels with average pore sizes covering a wide range of macroporosity (from 70-6000 nm) in order to explore the potential of this material in waterproof, breathable applications. Possible porosity alterations after the treatment were evaluated as well as the durability of the treatment over time.

2. Experimental

2.1. Materials

Resorcinol (Indspec, 99.6 wt. %), formaldehyde (Química S.A.U., aqueous solution with 37 wt. % formaldehyde and 0.7 wt. % methanol), deionized water, methanol (AnalaR Normapur, 99%) and sodium hydroxide solutions made up from solid NaOH, (AnalaR Normapur, 99.9 %).

2.2. Synthesis of RF-xerogels

Resorcinol-formaldehyde xerogels were prepared according to Pekala's method described elsewhere.^{22,40} Briefly, solid resorcinol was dissolved by magnetic stirring in deionized water until total solution. At the same time the formaldehyde is mixed with the methanol in another glass baker. Both solutions were mixed and stirred to ensure homogeneity. The pH of the resulting solution was modified by dropping NaOH in order to achieve the desired final pH. The proportion of each reagent depends on the variables selected in order to give rise each textural properties which was previously designed (Table 1). Each precursor solution was placed in a microwave oven for 10000 seconds (2 h and 47 min) in order to induce gelation and curing to take place. The final material was dried until a loss of mass of 50 % weight was achieved.

Sample	pH	D	R/F	% MeOH
OX-6000	5.0	8	0.7	0.7
OX-2000	5.5	8	0.7	0.7
OX-500	3.1	5.6	0.5	12.5
OX-150	3.3	5.6	0.5	12.5
OX-70	3.3	5.7	0.1	12.5

Table 1. Experimental variables used in the preparation of the organic xerogels (pH of the precursor solution; molar ratio of the total solvent to reactants, D; molar ratio resorcinol/formaldehyde and percentage of methanol in the formaldehyde solution).

2.3. Surface modification

Each RF-xerogel was grinded and sieved under $< 212\ \mu\text{m}$ and finally heated at $100\ ^\circ\text{C}$ overnight to eliminate completely the residual moisture and unreacted compounds. The hydrophilic RF-xerogel was placed inside a quartz reactor. A nitrogen flow of $100\ \text{mL min}^{-1}$ was bubbled in liquid methanol at $80\ ^\circ\text{C}$ in a vessel flask and introduced in the reactor at $240\ ^\circ\text{C}$. Different dwelling times were carried out to study the effect of the time of treatment on the wetting properties of the resulting materials. Prior testing, methoxylated RF samples were heated in an oven for 1 h at $80\ ^\circ\text{C}$ to remove residual methanol.

2.4. Sample characterization

Most of the measured sample properties were repeated at least three times and the final value is presented as the average with the standard deviation.

Pore size and volume were determined by means of mercury porosimetry (*AutoPore IV 9500*, *Micromeritics*) from atmospheric pressure up to 228 MPa. That pressure ensures pores of 5.5 nm as the minimum pore size detectable by the equipment. The surface tension and contact angle values for Hg in all the characterizations were $0.485\ \text{N m}^{-1}$ and 130° , respectively. Prior to these analyses, samples were outgassed (*Micromeritics VacPrep 0.61*) at 0.1 mbar and $120\ ^\circ\text{C}$ overnight.

The morphology was observed by means of scanning electron microscopy (SEM). Prior to this characterization, the xerogels were carbonized at $700\ ^\circ\text{C}$ under nitrogen atmosphere ($100\ \text{mL min}^{-1}$) for 2 h. The morphology of the sample do not change notably by the carbonisation process, but the electrical conductivity of the samples increases and so the SEM image quality is improved notably²¹.

In order to determine the wettability of each sample, contact angle measurements were performed using a Krüss 62/G40 optical tensiometer. To this end, a water droplet (ca. 6 mm of diameter) was placed on the surface of a pellet of the RF-xerogels with a glass micrometric syringe. Pellets of 10 mm diameter were obtained by comprising sample powders ($< 212 \mu\text{m}$ particle size) using a pressure of 10 Tons for 25 s.

Fourier transform infrared spectroscopy (FTIR) was carried out in a Nicolet FTIR 8700 (Thermo Scientific) spectrometer fitted with a DTGS (deuterated triglycine sulphate) detector. The data were recorded between $4000\text{--}400 \text{ cm}^{-1}$, over 64 scans at a resolution of 4 cm^{-1} . Determination of C, H and N was carried out in a LECO CHNS-932 analyzer. The oxygen content was determined using a LECO VTF-900 analyzer.

Temperature programmed desorption (TPD) experiments were performed by thermogravimetry (DSC Q600 TA Instruments) coupled with a mass spectrometer (ThermoStar Pfeiffer). The sample was heated in the thermobalance at 5°C min^{-1} up to 300°C , whilst the m/z signals (from 1 to 50) were registered in the mass spectrometer.

Moisture absorption capacity of each sample was tested by exposing them to saturated (100 % relative humidity) air at 25°C . Controlled amounts (200 mg) of RF xerogels were placed in 2 cm diameter glass vials. Weight changes were recorded until a constant mass was obtained. Thermogravimetric analysis was performed in order to corroborate these results by means of a TA instrument DSC Q600 analyzer. Changes in the weight of each sample were recorded in the temperature range of 25 to 350°C under nitrogen flow of 20 ml min^{-1} and at a heating rate of $10^\circ\text{C min}^{-1}$.

3. Results and Discussion

The nanostructure of RF-xerogels is composed of packed quasi-spherical nodules, with small holes between them that constitute the porosity of these materials. Moreover, the size of these nodules, and therefore the size of the pores, can be pre-set, by selecting the appropriate synthesis conditions.²⁰ As an example of this, Figure 1 shows how different conditions of preparation (see Table 1) determine the nanometric structure of the OX-70, OX-500 and OX-2000 samples used in this study.

Figure 1. SEM images of carbonized RF-xerogels: OX-70, OX-500 and OX-2000 (from left to right). Carbonized samples were used to increase de electrical conductivity and so have better SEM pictures. Nevertheless, the structure of the organic xerogels is virtually identical except by some minimum shrinking of the nodules after carbonization.

The main porous characteristics of the different RF-xerogels are summarized in Table 2. Results show that it is possible to obtain RF xerogels with different pore size in the range of macropores (i.e. from ca. 70 to 6000 nm) and with a relatively narrow pore size distribution (Figure 2). Obviously, the pore volume increases with the pore size, with values for the sample OX-6000 almost doubling that for OX-70 (i.e., 2 vs 1 cm³ g⁻¹, Table 2). As a consequence, samples with higher pore size present a lower bulk density. The porosity of all the samples ranges between 50-70% (Table 2).

Sample	Pore volume (± 0.05 , $\text{cm}^3 \text{g}^{-1}$)	Average pore size (± 1 , nm)	Bulk density (± 0.01 , g cm^{-3})	Porosity (± 2 , %)
OX-6000	2.01	6260	0.34	69
OX-2000	2.17	2292	0.33	70
OX-500	1.57	522	0.42	65
OX-150	1.56	172	0.43	66
OX-70	1.04	65	0.45	47

Table 2. Selected textural properties, determined by Hg porosimetry, of the RF-xerogels.

Figure 2. Pore size distribution, obtained by mercury porosimetry, of the RF-xerogels. (Points correspond to experimental data, but lines are drawn as guides to the eyes).

Regarding the surface chemistry of these materials, it is well established that the surface of the RF-xerogels is covered with some dangling phenolic groups (see Figure 3).⁴¹ The passivating mechanism that would transform those hydrophilic sites into hydrophobic is also depicted in Figure 3. According to the methoxylation reaction shown in Figure 3, hydrophobic methyl ether groups will decorate the passivated surface of the treated RF xerogels. The contact angle

measurements carried out on the passivated RF-xerogels corroborate this, i.e., all the materials except OX-70 eventually become superhydrophobic (i.e. contact angle $> 150^\circ$, Figure 4). Moreover, measuring the contact angle on these samples is, most of times, a tough task since the water drops are repelled away from the sample surface (see video in the supplementary material).

Figure 3. Chemical structure of RF-xerogels (top) and passivation of hydrophilic sites of the xerogel surface by the reaction of alcohol condensation between methanol and hydroxyl groups (down).

Figure 4. Behavior of a drop of water over compacted powders of (a) hydrophilic (non-treated) and (b) superhydrophobic (passivated) RF xerogel. (c) Powder suspensions of the superhydrophobic xerogel after vigorous shaking; a bubble of air is clearly standing between liquid and solid phases.

The minimum time of the treatment with methanol required for transforming the RF-xerogels into superhydrophobic materials (SHP) is different for each material. Interestingly, this time increases as decreasing the pore size in a nearly exponentially way (Figure 5). Thus, while ca. 1 h of treatment is enough to passivate the OX-6000 surface and to transform it into SHP-6000, OX-150 needs 27 hours for changing its hydrophilic surface to the superhydrophobic of SPH-150 and OX-70 remains hydrophilic even after 100 hours of treatment.

Figure 5. Minimum time necessary for passivate the RF-xerogels surface transforming it into a superhydrophobic surface (contact angle $> 150^\circ$), as a function of their average pore size. (Points correspond to experimental data, but dotted line is drawn as guide to the eyes).

Given the big differences in size between the molecule of methanol (0.46 nm),⁴² and the mean pore size of these materials (70 - 6000 nm), this strong dependence of the time of passivation

with the size of the pores is, somehow, surprising. There are two facts, however, that could explain it. The first one is related to the particular shape of the pores of the RF-xerogels. As schematized in Figure 6, the internal surface of RF-xerogels has a positive curvature, which differs from most porous materials with cylindrical or slit shaped pores, with a negative or null curvature, respectively.⁴³ This particular porous texture of the RF-xerogels implies that, although the size of the pore may be large enough, pores are connected through bottlenecks formed by the contact points between spheres (see Figure 6). The number of these bottlenecks increases and their size becomes narrower as the clusters are smaller (i.e., the mean pore size of the RF xerogel is smaller), thus hindering the access of the methanol molecules to the inner surface area. The second fact that would account for the increasing difficulty of methanol to passivate the RF-xerogel surfaces as their average pore size decreases is that, as the passivation proceeds, polar hydroxyl groups are being substituted by the nonpolar methyl groups. Since methanol is an amphipathic molecule, the passivation of the hydroxyl groups of the RF-xerogel would turn a polar surface into nonpolar as the reaction proceeds. Nonpolar (dispersive) interactions between the methanol molecules and the passivated surface would increase progressively, thus competing with the main reaction pathway depicted in Figure 3 and slowing down the methoxylation. This phenomenon would become more important in small pores (or in the aforementioned bottlenecks) where methyl groups would be closer to each other.

Figure 6. Different pore models according to the surface curvature on the inner surface or the pore.

Another surprising fact is that after a certain treatment time, the RF-xerogels shift abruptly from hydrophilic to superhydrophobic. Indeed, the treatments with methanol were stopped at different times and contact angle tests carried out (Figure 7). Angles measured were either 0° or 180° . This suggests that there is a threshold in the proportion of passivated phenolic groups above which the RF-xerogels surface repels liquid water completely.

Figure 7. Variation of the contact angle with the time of passivation. (Points correspond to experimental data, but lines are drawn as guides to the eyes).

So far it has been demonstrated that the hydrophilic surfaces of the macroporous RF-xerogels can be made superhydrophobic by a simple passivation with methanol. However, as one of the advantages of RF xerogels is the possibility to design and adjust the porosity for a determined application, it would be necessary to check if this tailored porosity is modified by the methanol treatment. For this purpose, mercury porosimetry was carried out on the passivated samples. Figure 8 shows the plots of cumulative intrusion of Hg vs pore diameter comparing two RF xerogels with very different mean pore size (OX-2000 and OX-150) and their passivated counterparts (SHP-2000 and SHP-150, respectively). The curves of each pair of materials are essentially identical, i.e., the treatment with methanol does not change the pore size distribution of the original OX samples. It should be pointed out that although it is clear that the main steps in the cumulative intrusion plots occur around 150 and 2000 nm for both pair of samples OX-150/SHP-150 and OX-2000/SHP-2000, respectively, the increasing in the intrusion volume observed at the beginning of the analysis (i.e., low pressure conditions corresponding to high pore diameters, Figure 8) should be ascribed to interparticular porosity and/or compressive effects of organic xerogels. In any case, the intrusion profiles are always identical (including all effects) for samples before and after the methanol treatment.

Figure 8. Cumulative intrusion vs pore size obtained by mercury porosimetry of two RF-xerogels before and after the methoxylation reaction.

Changes in the surface chemistry after the passivation treatment have already been advanced and they are expected to take place according to the passivation reaction shown in Figure 3. However, to verify that passivation mechanism and to what extent it takes place: (i) elemental chemical analysis, (ii) FTIR characterization and (iii) Temperature Programmed Desorption (TPD) coupled with mass spectrometry were performed on treated and untreated samples.

Results of the elemental analyses (Table 3) reveals that the SHP-samples contains approximately 2 wt% more carbon than pristine samples and that the H/O and C/O ratios increase after the passivation. This is consistent with the incorporation of methyl groups blocking hydrophilic sites to form methoxy (O-CH_3) groups, considering that the number of atoms of O would remain unaltered during the treatment (Figure 3).

	OX-6000	SHP-6000	OX-150	SHP-150
C (± 0.2 , wt. %)	65.7	67.6	66.1	68.4
H (± 0.2 , wt. %)	4.0	4.0	4.4	4.2

O (± 0.2 , wt. %)	30.3	28.4	29.5	27.4
H/O molar ratio	2.11	2.25	2.34	2.43
C/O molar ratio	2.89	3.17	2.99	3.32

Table 3. Elemental analysis results for two treated and non-treated xerogels and their molar ratios.

The FTIR spectra of samples OX-6000 and SHP-6000 are shown in Figure 9. All bands, which have been already identified in RF xerogels,[28] are also present after the methoxylation. The most notable difference is the decrease of the relative intensity of the broad band at 3600-3000 cm^{-1} (that corresponds to the OH groups) after the passivation treatment. In order to have an estimation of the decrease of the relative intensity of the OH band corresponding to the phenolic groups, the aromatic C=C absorption band centered at 1605 cm^{-1} , which should remain unaltered during the reaction, was taken as reference. Thus, comparing the ratios of these two absorption bands, it can be concluded that the intensity reduction of the OH band after the treatment is ca. 21 % with respect to the band of the original OX-6000 xerogel since the area of the C=C band is 62 for both samples and the area of the O-H band is 420 and 332 for OX-6000 and SHP-6000, respectively. Moreover, SHP-6000 shows an increase of the relative intensities (C=C band at 1605 cm^{-1} as reference) of the bands at 1470 cm^{-1} and 1200 cm^{-1} , which correspond to the aliphatic deformation vibration and the methylene ether bridges C-O-C stretching, respectively [28, 44]. This would confirm the incorporation of CH_3 groups on the surface chemistry of the xerogel after the methoxylation. Beyond this “semi-quantitative” result, it should be noticed that the treatment with methanol passivates only part of the phenolic groups, which, in any case, seems to be enough to make the material superhydrophobic.

Figure 9. FTIR spectra of the RF xerogels before (OX-6000) and after (SHP-6000) the surface modification.

During the TPD analysis by TGA-MS, the m/z 31 corresponding to methoxy groups, was recorded with the increasing temperature. As an example representative of all passivated RF-xerogels, Figure 10 shows the results of the OX-500 and SHP-500 materials. The passivated xerogel exhibits a pronounced peak at temperatures between 50 and 200 °C, with a maximum centered at 120 °C, ascribed to the evolution of the methoxy groups. As expected, this peak does not appear in the original sample. Additional information regarding the thermal stability of the methoxy groups introduced with the passivation treatment can be inferred from this plot. Thus, it

might be expected that the SHP-xerogels would keep their superhydrophobicity, at least, up to 50 °C.

Figure 10. Evolution of methoxy (O-CH₃) groups during TPD analysis for samples OX-500 and SHP-500.

Another question regarding the SHP-materials concerns the stability/reversibility of the methoxylation treatment in terms of the durability of the superhydrophobic property of the passivated samples. In order to find this out, samples of the SPH-xerogels were exposed to an atmosphere saturated with a 100 % of humidity for 40 days, and aliquots of those samples were taken periodically for contact angle measurements. The optical tensiometer shows that the contact angle of all aged samples remained higher than 150° (Table 4). Furthermore, it was found a weight gain in the time, which indicated that the samples were adsorbing moisture from the atmosphere (Table 4). This indicates that the passivated xerogels were able to retain a certain degree of moisture inside its porosity, in spite of their waterproofness. The water vapor

absorption was found to be relatively fast, with most of the moisture absorbed in the first day of exposure (see Table 4).

Days	0	1	10	20	30	40
Moisture uptake (± 2 , wt%)						
SHP-6000	0	13	13	13	14	15
SHP-2000	0	13	17	18	19	19
SHP-500	0	13	15	16	17	18
SHP-150	0	11	11	12	12	13
Contact angle (α)						
SHP-6000	>150°	>150°	>150°	>150°	>150°	>150°
SHP-2000	>150°	>150°	>150°	>150°	>150°	>150°
SHP-500	>150°	>150°	>150°	>150°	>150°	>150°
SHP-150	>150°	>150°	>150°	>150°	>150°	>150°

Table 4. Variations on the moisture uptake and contact angle of the SHP-xerogels during 40 days exposure to 100% relative humidity air

Whether this absorption of moisture is a reversible process or not was also checked by subjecting the soaked samples (after 40 days exposure) to a certain vacuum (10 Pa) at 25 °C and for 24 h and quantifying then the moisture retained (or released). The moisture retained in the different samples was: 1.6 wt% for SHP-6000, 1.7 wt% for SHP-2000, 1.9 wt% for SHP-500 and 2.9 wt% for SHP-150. Additionally, aliquots of the saturated samples were put in a desiccator containing silica gel for 3 days at 25 °C and atmospheric pressure. The moisture retained by the samples after this experiment was: 3.2 wt% for SHP-6000, 3.9 wt% for SHP-2000, 4.0 wt% for SHP-500 and 4.9 wt% for SHP-150. In sum, under the above mentioned conditions the adsorption of moisture by the SHP-xerogels is reversible up to an 80-90%. Therefore, if environmental moisture can enter and leave the sample by simply modifying the pressure or the humidity of the environment, it can be considered that SHP-xerogels are breathable. The effect of the average

pore size on the ability of the SHP samples for absorbing/releasing moisture is only noticeable for low pore size values. Hence, SHP-150 moisture uptake per gram and day is slower than that of SHP-500, but further increase of the pore size from 500 to 6000 nm renders similar values (Table 4).

The mechanism that would explain why the SHP-xerogels are superhydrophobic but, at the same time, breathable is depicted in the sketch of Figure 11.

Figure 11. Proposed mechanism explaining the waterproofing and breathability of the passivated RF-xerogels

As the most external, and most accessible, surface of the material is completely passivated by the treatment with methanol, the liquid water drops are repelled. Furthermore, the diameter of these water drops is, at least, one order of magnitude larger than the pores of the material, which contributes to the superhydrophobicity exhibited against liquid water. On the other hand, water molecules of vapor are, at least, one order of magnitude smaller than the pores of the materials, so they can pass through it. There are, however, some phenolic groups inside the pores that were

not passivated (see Figure 9), so part (ca. 20%) of the moisture is retained inside the pores. Nevertheless, these hydroxyl groups are sufficiently far away from the outer surface to promote the absorption of the liquid water drops.

4. Conclusions

A simple methoxylation treatment transforms highly hydrophilic RF-xerogels into superhydrophobic materials. The treatment time for shifting to superhydrophobic highly depends on the pore size of the material and occurs suddenly, without passing through intermediate states. This is attributed to repulsive/dispersive interactions, magnified by the exohedral shape of the pores, between the nonpolar passivated surface and the methanol. Changes on the surface chemistry of the particles did not affect the porosity of the original xerogels. This is a very important outcome as far as the porosity of this type of materials can be easily controlled during the synthesis, thus opening the possibility of tuning the porosity for a given application. Furthermore, it has been demonstrated that the superhydrophobic xerogels still retain the ability of interchanging water vapor between atmospheres with different vapor activities. This breathable behavior is mainly controlled by the hydrophilic groups that remain unreacted in the inner pore surfaces, with the average pore size being only relevant below 500 nm.

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References

- [1] G.R. Lomax, Breathable polyurethane membranes for textile and related industries, *Journal of Materials Chemistry*, 17 (2007) 2775-2784.
- [2] W. Jeong, S. An, The transport properties of polymer membrane-fabric composites, *Journal of materials science*, 36 (2001) 4797-4803.
- [3] S. Zhao, P.H. Feron, L. Deng, E. Favre, E. Chabanon, S. Yan, J. Hou, V. Chen, H. Qi, Status and progress of membrane contactors in post-combustion carbon capture: A state-of-the-art review of new developments, *Journal of Membrane Science*, 511 (2016) 180-206.
- [4] Z. Fu, K. Li, L. Pu, B. Ge, Z. Chen, Waterproof Breathable Membrane Used as Gas Diffusion Layer in Activated Carbon Air Cathode Microbial Fuel Cells, *Fuel Cells*, 16 (2016) 839-844.
- [5] D. Xing, Y. Tang, X. Mei, B. Liu, Electricity generation of microbial fuel cell with waterproof breathable membrane cathode, *Journal of Power Sources*, 300 (2015) 491-495.
- [6] A. Gugliuzza, E. Drioli, New performance of hydrophobic fluorinated porous membranes exhibiting particulate-like morphology, *Desalination*, 240 (2009) 14-20.
- [7] J. Huang, A new test method for determining water vapor transport properties of polymer membranes, *Polymer testing*, 26 (2007) 685-691.
- [8] Q.B. Meng, S.-I. Lee, C. Nah, Y.-S. Lee, Preparation of waterborne polyurethanes using an amphiphilic diol for breathable waterproof textile coatings, *Progress in Organic Coatings*, 66 (2009) 382-386.
- [9] E.Y. Kim, J.H. Lee, D.J. Lee, Y.H. Lee, J.H. Lee, H.D. Kim, Synthesis and properties of highly hydrophilic waterborne polyurethane-ureas containing various hardener content for waterproof breathable fabrics, *Journal of Applied Polymer Science*, 129 (2013) 1745-1751.
- [10] Y. Li, Z. Zhu, J. Yu, B. Ding, Carbon nanotubes enhanced fluorinated polyurethane macroporous membranes for waterproof and breathable application, *ACS applied materials & interfaces*, 7 (2015) 13538-13546.
- [11] J.B. You, Y. Yoo, M.S. Oh, S.G. Im, Simple and Reliable Method to Incorporate the Janus Property onto Arbitrary Porous Substrates, *ACS applied materials & interfaces*, 6 (2014) 4005-4010.
- [12] J. Sheng, M. Zhang, Y. Xu, J. Yu, B. Ding, Tailoring Water-Resistant and Breathable Performance of Polyacrylonitrile Nanofibrous Membranes Modified by Polydimethylsiloxane, *ACS Applied Materials & Interfaces*, 8 (2016) 27218-27226.
- [13] H. Wang, Y. Xue, J. Ding, L. Feng, X. Wang, T. Lin, Durable, Self-Healing Superhydrophobic and Superoleophobic Surfaces from Fluorinated-Decyl Polyhedral Oligomeric Silsesquioxane and Hydrolyzed Fluorinated Alkyl Silane, *Angewandte Chemie International Edition*, 50 (2011) 11433-11436.
- [14] H. Zhou, H. Wang, H. Niu, A. Gestos, X. Wang, T. Lin, Fluoroalkyl silane modified silicone rubber/nanoparticle composite: a super durable, robust superhydrophobic fabric coating, *Advanced materials*, 24 (2012) 2409-2412.
- [15] W. Zhaohui, G. Zhenya, A study on novel waterproof and moisture-permeable poly (vinylidene fluoride) micropore membrane-coated fabrics, *Journal of applied polymer science*, 79 (2001) 801-807.
- [16] A. Gugliuzza, G. Clarizia, G. Golemme, E. Drioli, New breathable and waterproof coatings for textiles: effect of an aliphatic polyurethane on the formation of PEEK-WC porous membranes, *European Polymer Journal*, 38 (2002) 235-242.

- [17] Y. Li, F. Yang, J. Yu, B. Ding, Hydrophobic fibrous membranes with tunable porous structure for equilibrium of breathable and waterproof performance, *Advanced Materials Interfaces*, 3 (2016).
- [18] F.S. NV, J. Gopinathan, B. Indumathi, S. Thomas, A. Bhattacharyya, Morphology and hydroscopic properties of acrylic/thermoplastic polyurethane core-shell electrospun micro/nano fibrous mats with tunable porosity, *RSC Advances*, 6 (2016) 54286-54292.
- [19] B. Yoon, S. Lee, Designing waterproof breathable materials based on electrospun nanofibers and assessing the performance characteristics, *Fibers and Polymers*, 12 (2011) 57-64.
- [20] R. Pekala, Organic aerogels from the polycondensation of resorcinol with formaldehyde, *Journal of Materials Science*, 24 (1989) 3221-3227.
- [21] N. Rey-Raap, A. Arenillas, J.A. Menéndez, A visual validation of the combined effect of pH and dilution on the porosity of carbon xerogels, *Microporous and Mesoporous Materials*, 223 (2016) 89-93.
- [22] I.D. Alonso-Buenaposada, N. Rey-Raap, E.G. Calvo, J. Angel Menéndez, A. Arenillas, Effect of methanol content in commercial formaldehyde solutions on the porosity of RF carbon xerogels, *Journal of Non-Crystalline Solids*, 426 (2015) 13-18.
- [23] Z. Zapata-Benabithé, C. Moreno-Castilla, F. Carrasco-Marín, Effect of dilution ratio and drying method of resorcinol-formaldehyde carbon gels on their electrocapacitive properties in aqueous and non-aqueous electrolytes, *J Sol Gel Sci Technol*, 75 (2015) 407-412.
- [24] N. Job, C.J. Gommès, R. Pirard, J.-P. Pirard, Effect of the counter-ion of the basification agent on the pore texture of organic and carbon xerogels, *Journal of Non-Crystalline Solids*, 354 (2008) 4698-4701.
- [25] L. Zubizarreta, A. Arenillas, J.J. Pis, Preparation of Ni-doped carbon nanospheres with different surface chemistry and controlled pore structure, *Applied Surface Science*, 254 (2008) 3993-4000.
- [26] J. Choma, K. Jedynak, W. Fahrenholz, J. Ludwinowicz, M. Jaroniec, Microporosity development in phenolic resin-based mesoporous carbons for enhancing CO₂ adsorption at ambient conditions, *Applied Surface Science*, 289 (2014) 592-600.
- [27] E.G. Calvo, E.J. Juárez-Pérez, J.A. Menéndez, A. Arenillas, Fast microwave-assisted synthesis of tailored mesoporous carbon xerogels, *Journal of Colloid and Interface Science*, 357 (2011) 541-547.
- [28] I.D. Alonso-Buenaposada, E.G. Calvo, M.A. Montes-Morán, J. Narciso, J.A. Menéndez, A. Arenillas, Desiccant capability of organic xerogels: Surface chemistry vs porous texture, *Microporous and Mesoporous Materials*, 232 (2016) 70-76.
- [29] M. Hikita, K. Tanaka, T. Nakamura, T. Kajiyama, A. Takahara, Super-Liquid-Repellent Surfaces Prepared by Colloidal Silica Nanoparticles Covered with Fluoroalkyl Groups, *Langmuir*, 21 (2005) 7299-7302.
- [30] A.V. Rao, E. Nilsen, M.-A. Einarsrud, Effect of precursors, methylation agents and solvents on the physicochemical properties of silica aerogels prepared by atmospheric pressure drying method, *Journal of non-crystalline solids*, 296 (2001) 165-171.
- [31] L. Feng, Z. Zhang, Z. Mai, Y. Ma, B. Liu, L. Jiang, D. Zhu, A super-hydrophobic and super-oleophilic coating mesh film for the separation of oil and water, *Angewandte Chemie International Edition*, 43 (2004) 2012-2014.
- [32] H. Guo, M. Ulbricht, The effects of (macro)molecular structure on hydrophilic surface modification of polypropylene membranes via entrapment, *Journal of Colloid and Interface Science*, 350 (2010) 99-109.

- [33] M. Pantoja, J. Abenojar, M.A. Martinez, Influence of the type of solvent on the development of superhydrophobicity from silane-based solution containing nanoparticles, *Applied Surface Science*.
- [34] H. Li, R. Wang, H. Hu, W. Liu, Surface modification of self-healing poly(urea-formaldehyde) microcapsules using silane-coupling agent, *Applied Surface Science*, 255 (2008) 1894-1900.
- [35] H. Tian, T. Yang, Y. Chen, Fabrication and characterization of superhydrophobic thin films based on TEOS/RF hybrid, *Applied Surface Science*, 255 (2009) 4289-4292.
- [36] J. Becerra, G. Sudre, I. Royaud, R. Montserret, B. Verrier, C. Rochas, T. Delair, L. David, Tuning the Hydrophilic/Hydrophobic Balance to Control the Structure of Chitosan Films and Their Protein Release Behavior, *AAPS PharmSciTech*, (2016) 1-14.
- [37] X. Feng, L. Jiang, Design and creation of superwetting/antiwetting surfaces, *Advanced Materials*, 18 (2006) 3063-3078.
- [38] P. Suresh Kumar, J. Sundaramurthy, D. Mangalaraj, D. Nataraj, D. Rajarathnam, M.P. Srinivasan, Enhanced super-hydrophobic and switching behavior of ZnO nanostructured surfaces prepared by simple solution – Immersion successive ionic layer adsorption and reaction process, *Journal of Colloid and Interface Science*, 363 (2011) 51-58.
- [39] C.D. Esplin, A. Bowden, B. Jensen, Super-hydrophobic and Anti-Microbial Surfaces via Carbon Infiltrated-Carbon Nanotubes, (2017).
- [40] T. Supakar, M. Moradiafrapoli, G.F. Christopher, J.O. Marston, Spreading, encapsulation and transition to arrested shapes during drop impact onto hydrophobic powders, *Journal of Colloid and Interface Science*, 468 (2016) 10-20.
- [41] X. Zhang, D. Wang, Preparation and activity of ionic liquid catalysts grafted on hydrophobic silica gel, in: 3rd International Conference on Manufacturing Science and Engineering, ICMSE 2012, Xiamen, 2012, pp. 2621-2624.
- [42] S.H. Li, X.D. Sun, L.-j. Wang, W.-b. Gu, W.-m. Wang, Z.Y. Yang, Y. Wang, J.H. Zhu, Fabricating hydrophobic nanoparticles within mesoporous channel of silica for efficient TSNA removal, *Microporous and Mesoporous Materials*, 237 (2017) 237-245.
- [43] K.-H. Lee, S.-Y. Kim, K.-P. Yoo, Low-density, hydrophobic aerogels, *Journal of Non-Crystalline Solids*, 186 (1995) 18-22.
- [44] J. Coates, Interpretation of infrared spectra, a practical approach, *Encyclopedia of analytical chemistry*, (2000).