

On the desiccant capacity of the mesoporous RF-xerogels

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Abstract

Resorcinol-formaldehyde xerogels are ideal desiccant materials since the high concentration of hydroxyl groups on their surfaces confers on them a high hydrophilicity, which adsorbs moisture from their surroundings and their large porosity provides them with a high water sorption capacity. In this study, the porosity of organic xerogels was tailored by adjusting the proportion of methanol in the precursor solution in order to optimize their desiccant capability. It was found that, although an increase in microporosity improves the performance of the desiccant, mesoporosity is a more important property for this application. Organic xerogels are excellent desiccants which are able to adsorb more than 80 % of their own weight in moisture and function efficiently for more than 3000 h, when their porosity is optimized. This is a great improvement on the commonly used silica gels that become saturated after only 150 h and can only adsorb a maximum of 40 wt % of their own weight in moisture. Moreover, RF xerogels have the advantage that they are organic materials resistant to acid attack and this allows them to be used in processes where conventional inorganic desiccants would rapidly deteriorate.

Keywords: water sorption; desiccant materials; xerogels; hydrophilic materials

1. Introduction

Resorcinol-formaldehyde (RF) gels have been the most widely studied nanoporous organic gels in recent years [1-3]. However, other precursors can be used to produce materials with similar properties [4-9]. The synthesis process of these polymers consists of three steps: gelation, curing and drying. Depending on the type of drying method used in the synthesis process, (i.e., supercritical drying, freeze-drying or evaporative drying), they are classified as aerogels, cryogels or xerogels, respectively [10, 11]. In this study, microwave radiation was used as heating source to synthesize the xerogels described, as it is a simple, fast and cost-effective method to fabricate RF-xerogels in just one step using only one device [12].

The widely recognized advantage of RF xerogels is that it is possible to obtain materials whose porosity can be designed for a specific application by adjusting the variables used during the synthesis process (i.e., the pH of the precursor solution, dilution ratio, RF molar ratio, etc.) [13-16]. This versatility, in combination with the fact that they are light and cheap to produce, makes them suitable for a wide range of applications [17-21].

As already pointed out in a previous study, organic xerogels can be used as desiccant materials [22]. Any desiccant material, whose behaviour is determined by surface interactions and not by chemical reactions [23-25], requires two main properties to ensure its effectiveness [26]: i) hydrophilicity, i.e., its high affinity towards water and ii) a good sorption capacity, i.e., an ability to retain a large volume of water. In the case of RF xerogels, the high concentration of hydroxyl groups on their surfaces provides them

with a high hydrophilicity that attracts surrounding moisture through hydrogen bonding, and their large porosity gives them their high water sorption capacity. Their hydrophilicity and suitability for use as desiccant materials have been demonstrated in a previous work [22]. However, in that study only two samples were evaluated and compared with a silica gel, a mesoporous xerogel and a macroporous RF xerogel with pore sizes of 10 and 2100 nm, respectively. There is a huge difference in pore size between 10 and 2100 nm, and although pore size would seem to be the determinant factor for the performance of a desiccant, mesopores being more effective than others, there is still a need for pore-size optimization. Therefore, further studies on the influence of mesopore size on the desiccant behaviour of RF xerogels are required, as optimization of the mesopores is essential in light of the increasing use of desiccant materials for different applications in recent years [25, 27-29]. Moreover, the optimization of desiccant performance in combination with the chemical resistance of these RF xerogels (i.e. in acid or basic media), their light weight and their production in just one-step (without the need for any post-treatment or a large number of steps in the production line), make these materials highly cost-effective and competitive for scaling up.

Accordingly, in this work the influence of porous properties, in the mesopore range, on the water adsorption capacity of RF xerogels is studied in order to optimize their effectiveness as light-weight organic desiccants.

2. Experimental

2.1. Synthesis of organic xerogels

Organic xerogels were obtained by a process described in detail elsewhere [22]. Briefly, resorcinol (R), and formaldehyde (F) were mixed at a R/F molar ratio of 0.3. Water was added at a dilution ratio of 5, and the pH of the precursor solutions was adjusted to 5 using a 0.1 M NaOH solution (Titripac, Merck). As previously reported, the methanol (MeOH) content of formaldehyde solutions plays a determinant role in the formation of the porosity [14]. For this reason, formaldehyde solutions with: 2, 4, 13, 20, 30 and 40 % of MeOH were used in order to obtain different porosities. As the MeOH content is the only difference between the samples, the percentage of methanol is used in the nomenclature preceded by OX in reference to the organic xerogel.

2.2. Sample characterization

Before characterization, the samples were outgassed (*Micromeritics VacPrep 0.61*) at 0.1 mbar and 120 °C overnight in order to remove any humidity and other physisorbed gases.

2.2.1. Porous properties

The porosity of the samples was characterized by means of nitrogen adsorption-desorption isotherms and mercury porosimetry.

The nitrogen adsorption-desorption isotherms were measured at -196°C in a Tristar 3020 (Micromeritics) device. S_{BET} , micropore volume and pore size distribution were determined from the N₂ adsorption branch, by applying the Brunauer-Emmett-Teller equation, Dubinin-Raduskevich equation and DFT method, respectively. Total pore volume was estimated from the amount of nitrogen adsorbed at $p/p^0=0.99$.

Total pore volume and pore size were determined by means of mercury porosimetry, using an AutoPore IV 9500 (Micromeritics), which is able to measure from atmospheric pressure up to 228 MPa. In this study, the lowest limit of mesopores detectable by this apparatus was 5.5 nm. In accordance with the findings of previous studies [10], no alterations in the macro and mesoporosity were observed during the carbonization process (Figure S1a). Therefore, the organic xerogels were thermally treated under an inert atmosphere (700°C, 2 h) before mercury porosimetry characterization in order to avoid compression problems arising from the low mechanical resistance of these materials [30]. Figure S1 in the supplementary material shows the problems of mercury porosimetry characterization of the organic samples due to their poor mechanical properties.

The bulk density and percentage of porosity of all the samples studied were determined by means of a Geopyc 1360 (Micromeritics) densitometer. A chamber with an internal diameter of 12.7 mm and a strength of 28 N over 20 cycles with conversion factor of 0.1284 (cm³ mm⁻¹) was employed. The chamber was filled with 0.8 g of Dryflow and a sample volume of ca. 50 % of the total volume.

2.2.2. Moisture adsorption capacity

For measuring the overall capacity of water vapour adsorption and kinetics, samples with a 2-3 mm particle size were kept in a sealed vessel in conditions of 100% humidity at 25°C. Weight changes were recorded until a constant value was obtained.

On the other hand, water vapour adsorption-desorption isotherms were also evaluated by a volumetric method at 25°C using a Hydrosorb 1000 multigas instrument (Quantachrome). These isotherms were repeated five times for each sample in order to

evaluate its regeneration capacity and the potential influence on moisture adsorption of the re-used desiccants. Samples were outgassed at 100°C under vacuum for 3 hours in the same analysis tube between subsequent water vapour isotherms.

2.2.3. Microscopy

A Zeiss DSM 942 scanning electron microscope was used to obtain micrographs of the RF xerogels. The samples were attached to an aluminium tap using conductive double-sided adhesive tape. An EDT Everhart-Thornley secondary electron detector, programmed to operate at an accelerating voltage of 25 kV, was employed for all the characterizations.

2.2.4. FTIR analysis

Fourier transform infrared spectroscopy (FTIR) was applied to evaluate the surface chemistry of the RF xerogels. A Nicolet FTIR 8700 fitted with a DTGS detector was employed. The data were recorded between 4000-400 cm^{-1} , over 64 scans at a resolution of 4 cm^{-1} .

3. Results and Discussion

In a previous work [22] it was observed that xerogels of large pore size (macropores of ca. 2100 nm) show a poorer water adsorption capacity than those with a narrow mesoporosity (ca. 10 nm). Nevertheless, there are many possible pore sizes between these two options, and given that optimal water adsorption capability seems to be in the mesopore range, the search for a good desiccant should be based on finding the optimal mesopore size.

Table 1 shows the porous properties of RF xerogels synthesized with formaldehyde solutions with different concentrations of methanol. It can be observed that just by varying the methanol content mesopore materials with pore sizes of 8, 22 and 51 nm for samples OX-20, OX-13 and OX-4, respectively, can be obtained as well as a macroporous sample with narrow macropores centred at 79 nm (OX-2). Thus, the lower the concentration of methanol used, the higher the total pore volume and pore size achieved with the result that the density of the materials is reduced and their porosity is increased. The role of the methanol in the formaldehyde solution is to serve as a stabilizer, i.e. to prevent the formaldehyde molecules from precipitating. However, the methanol also acts as a retardant of the polymerization reaction between formaldehyde and resorcinol, which delays the crosslinking step and causes an increase in the size of the nodules (Figure 1a), generating wider pore inter-clusters and therefore less dense materials. As the methanol content increases, the nodules formed during the polymerization also decrease (Figures 1b and 1c) together with the pore size, resulting in denser materials.

It should also be mentioned that an excess of methanol during the synthesis of RF xerogels may result in such a weak structure that it may collapse during the drying step. This is the case of sample OX-40, which shows no porous properties (see Table 1).

Previous studies suggest that the methanol concentration has an influence only on meso and/or macroporosity, but not on micropore volume [14]. However, the nitrogen adsorption-desorption isotherms in Figure 2 show that the samples synthesized with very high concentrations of methanol experience an increase in volume adsorbed at low relative pressures, which indicates an increase in micropore volume and therefore, in the

BET surface area (see Table 1), except for the sample with an excess of methanol (OX-40) that shows no N₂ adsorption. This effect on microporosity seems to be greater when larger concentrations of methanol are used. For example, an increase in methanol content of 11 wt% from OX-2 to OX-13 entails an increase of 92 m² g⁻¹ in S_{BET} (Table 1). However, an increase of only 7 wt% of methanol from OX-13 to OX-20 also leads to an increase in S_{BET} of 91 m² g⁻¹. This could be due to the fact that the higher the concentration of methanol in the precursor mixture, the higher the concentration of residual methanol in the polymer that does not take part in the polymerization reaction. This residual compound may affect the drying step process, causing defects in the polymeric structure and in an increase in microporosity and S_{BET}. On the other hand, an excess of methanol may result in such a weak structure that collapses, like OX-40. It is worth to be noted that the total pore volume determined by N₂ adsorption isotherms is underrated for samples with macroporosity (i.e. OX-2 and OX-4) as it is not the proper technique for these kind of pore characterization. On the other hand, samples with narrow mesoporosity may be underrated by the mercury porosimetry because this technique only characterizes pores bigger than 5.5 nm, and samples such as OX-20 and OX-30 have a considerable micropore volume (Table 1) and mesopores lower than 5 nm (Figure S2). Therefore, the combination of both techniques is mandatory for a complete porous properties characterization of series of samples with very different porosity.

In spite of all of the variations in the porosities of the samples synthesized with different methanol contents, the surface chemistry of the samples is almost identical in all cases. In Figure 3, the FTIR spectra of just two RF xerogels randomly selected are shown for purposes of clarity (all the samples studied show analogous spectra). It can be observed

that the samples have similar functional groups. Both groups of spectra show two bands fixed at 2900 and 1400 cm^{-1} which correspond to aliphatic stretching and deformation vibrations, respectively. The stretching vibration from the aromatic ring of resorcinol is fixed at 1600 cm^{-1} . Moreover, the bands at 1100 and 1200 cm^{-1} correspond to methylene ether bridges formed during the polymerization. The wide band between 3600 and 3000 cm^{-1} is associated to O-H stretching vibrations from the phenolic groups of the resorcinol. These functional groups are the cause of the hydrophilicity of these materials since water molecules from the air are attracted by their surfaces through hydrogen bonding. Therefore, as the surface chemistry is the same in all the samples studied, any difference in their water sorption capacity must be caused by differences in their porous properties.

Regarding the desiccant capability of these materials, Figure 4 shows that water adsorption performance at the beginning of the experiment is the same for all the samples, if they are exposed to the same humidity conditions (i.e. 100%). This agrees with the fact that all the samples have the same surface chemistry (Figure 3), and therefore the same water affinity. It can be inferred therefore that, at the beginning of the experiment the porous properties, which differ significantly between samples, have no influence. However, as moisture adsorption takes place over the surface of the adsorbent, the role of the porous properties becomes more relevant. It is clear that samples with wider pores (i.e. 79 and 51 nm from OX-2 and OX-4, respectively), caused by introducing a lower methanol content, prove to be poorer desiccants because they become saturated even at very low percentages of moisture adsorption (ca. 20 wt%). It can be therefore affirmed that a good desiccant is characterized by its mesopore content and not by its macroporosity. Samples OX-13 and OX-20 show a greater water

adsorption capacity, and the smaller the mesopore size is, the more water they adsorb (75 wt% and 83 % for 22 and 8 nm, respectively). According to these results therefore, the water adsorption capacity is not favoured by a greater pore volume or greater percentage of porosity, but by the mesopore size. The sample with a pore size of ca. 8 nm (OX-20) seems to exhibit the highest adsorption capacity, although its pore volume is nearly 3 times lower than that of OX-13 (0.35 vs 0.98 cm^3 g^{-1} for OX-20 vs OX-13, respectively). However, this enhancement in desiccant performance could also be due to the micropore volume, as sample OX-20 also presents a higher S_{BET} (350 vs 261 m^2 g^{-1} for OX-20 vs OX-13).

The S_{BET} (Table 1) and water adsorption data in Figure 4, indicate that the microporosity has no influence if the samples have wide pores (i.e. macropores). Thus, samples OX-2 and OX-4 have different S_{BET} values (169 and 204 m^2 g^{-1} , respectively), but their adsorption capacities (Figure 4) are almost the same. However, if these samples are compared with OX-13 and OX-20, which have surface areas of 261 and 350 m^2 g^{-1} , it can be seen that the higher the microporosity is (i.e. the higher the S_{BET}) the greater the water adsorption capacity.

In order to determine the effect of microporosity on the desiccant performance an extra sample was synthesized and compared with the OX series. As mentioned before, all the RF xerogels have similar chemical compositions and so their surface chemistry cannot be considered a determinant variable in the water adsorption process. It is also well known that one of the main advantages of RF xerogels is that their porosity can be tailored by modifying the synthesis conditions. Therefore, a sample (OX-30) with the same surface chemistry and same mesoporosity as OX-20 was synthesized so that the

only difference was in their microporosities. The porous characteristics and water adsorption performance of the OX-30 sample are shown in Table 1 and in Figure 4, respectively. It can be observed that the adsorption profile for the OX-13, OX-20 and OX-30 samples is very similar up to 500 h. At this stage the different microporosities of the samples have no influence at all on adsorption capacity. However, over longer periods of time the adsorption profiles of OX-20 and OX-30 increase more quickly than those of OX-13 due to the narrow mesoporosities of the former samples. Therefore, mesopores ca. 8 nm are preferable for this application. The adsorption profiles of OX-20 and OX-30 are very similar up to 1200 h of experimentation, due to their similar mesoporosities. At this point sample OX-20 shows a higher adsorption capacity than OX-30, even though its S_{BET} is smaller.

It is apparent that, although microporosity is important for the water adsorption, it is not the most important parameter. An increase in microporosity does not imply an increase in water adsorption capacity (see comparison of OX-20 profile to that of OX-30 in Figure 4). Like surface chemistry it is important for desiccant performance but it is not the most important parameter (see the OX-20 profile compared to the OX-2 profile in Figure 4). It is the presence of feeder pores in the mesoporosity range that is the most important parameter for optimal desiccant performance.

This implies that, although the micropore volume is important for this type of materials, it is the size and volume of the mesopores that make RF xerogels useful for water adsorption purposes. It is also worth pointing out that sample OX-20, with mesopores of ca. 8 nm, adsorbs more than 80 % of its own weight in moisture and up to 20 % is adsorbed during the first 48 h. As one might expect, the rate of adsorption slows down

with time as the surface becomes covered with water molecules; nevertheless it works effectively for more than 3000 h.

For comparative purposes, a new commercial silica gel from Sigma-Aldrich with a 2-6 mm particle size (SG-760), commonly used as desiccant material, was purchased. As the rest of the samples used in this work, this material was not previously used but outgassed, as described in the experimental section, before to carry out any experiment. The porous properties of this reference gel were also determined by N₂ adsorption-desorption isotherms (Figure S3). This material which is predominantly microporous has a pore volume of 0.42 cm³ g⁻¹, a narrow mesopore size of 3 nm, and a S_{BET} of 760 m² g⁻¹ (see Table 1). The water adsorption capacity of this reference gel was also evaluated in the same conditions as the series of RF xerogels (Figure 4). The results show that the commercial desiccant adsorbs less than 40 wt% and becomes saturated after 200 h of experimentation. It is clear that it is not the high microporosity of this sample that gives it its high water adsorption capacity, which suggests that microporosity is not the determinant factor here for producing an effective desiccant. However, it has to be taken into account that in this case the reference gel has a different chemistry to the RF xerogels, and therefore only a tentative comparison of the water adsorption process can be made.

The regeneration capacity of sample OX-20 was tested by saturating and regenerating the sample for 5 consecutive cycles, in the volumetric equipment mentioned in section 2.2.2. Given that part of the water retained in the porous structure of the sample cannot be desorbed by simply decreasing the pressure (see desorption branch in Figure 5), the sample was heated for regeneration at 100 °C for 3 hour between cycles. The

adsorption-desorption isotherms corresponding to cycles 1 and 5 are shown in Figure 5. As it can be observed, OX-20 preserves virtually intact its adsorption capacity after these 5 cycles. Therefore, it seems reasonable to assume that the optimised RF-xerogels have a good regeneration capacity.

4. Conclusions

Organic xerogels have demonstrated to be excellent desiccant materials which are able to adsorb more than 80 % of their own weight in moisture, up to 20 % of which is adsorbed during the first 48 h. In addition, they can work efficiently for more than 3000 h, once their porosity has been optimized. Although it is recognized that surface chemistry and microporosity are important features for this application, the key property for RF xerogels to function as an efficient desiccant material is mesopore size (i.e. pores ca. 8 nm). Moreover, the use of these organic materials as desiccants have other advantages such as their light weight and chemical resistance that make RF xerogels ideal for use in water removal processes.

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Table 1. Porous properties of the RF xerogels studied and the silica gel used as reference.

Sample	Mercury porosimetry		Densitometer		N ₂ adsorption-desorption isotherms		
	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Bulk density (g cm ³)	Porosity (%)	S _{BET} (m ² g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Total pore volume (cm ³ g ⁻¹)
OX-2	2.07	79	0.30	79	169	0.07	0.38
OX-4	1.53	51	0.39	72	204	0.09	0.59
OX-13	0.98	22	0.48	66	261	0.10	0.88
OX-20	0.35	8	0.73	48	350	0.15	0.58
OX-30	0.33	7	0.70	50	600	0.23	0.72
OX-40	0	0	1.10	18	28	0.01	0.02
SG-760	n.a.	n.a.	1.21	42	760	0.28	0.42

Figure captions

Fig.1. SEM images showing the decrease in nodule size when the methanol content is increased for: a) OX-2, b) OX-13 and c) OX-20

Fig.2. N₂ adsorption-desorption isotherms of the samples synthesized with different concentrations of methanol

Fig. 3. FTIR spectra of two RF xerogels: OX-2 (top trace) and OX-20 (bottom trace)

Fig. 4. Moisture adsorption isotherms at 25 °C, atmospheric pressure and 100 % humidity for organic xerogels with different pore sizes and the silica gel used as reference.

Fig. 5. Water adsorption-desorption isotherms of sample OX-20 (pristine and after 5 cycles of adsorption/regeneration).

Fig. 1

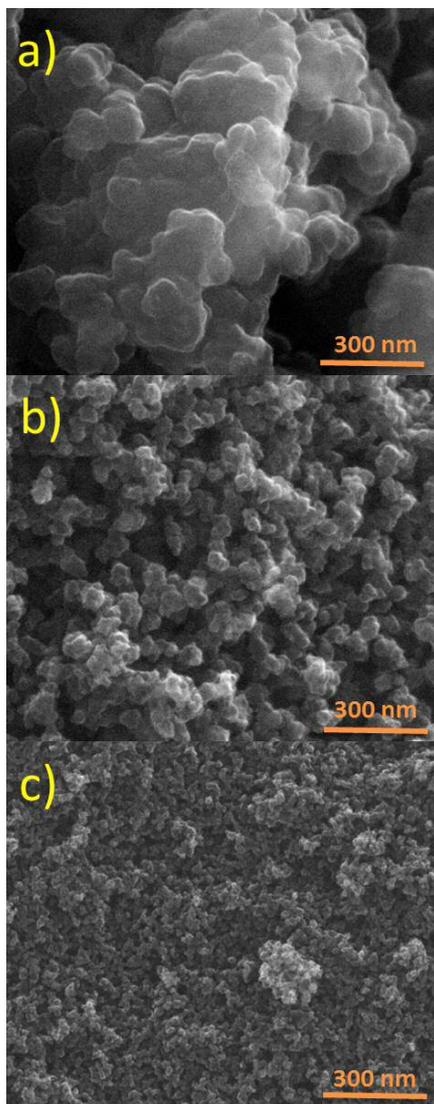


Fig. 2

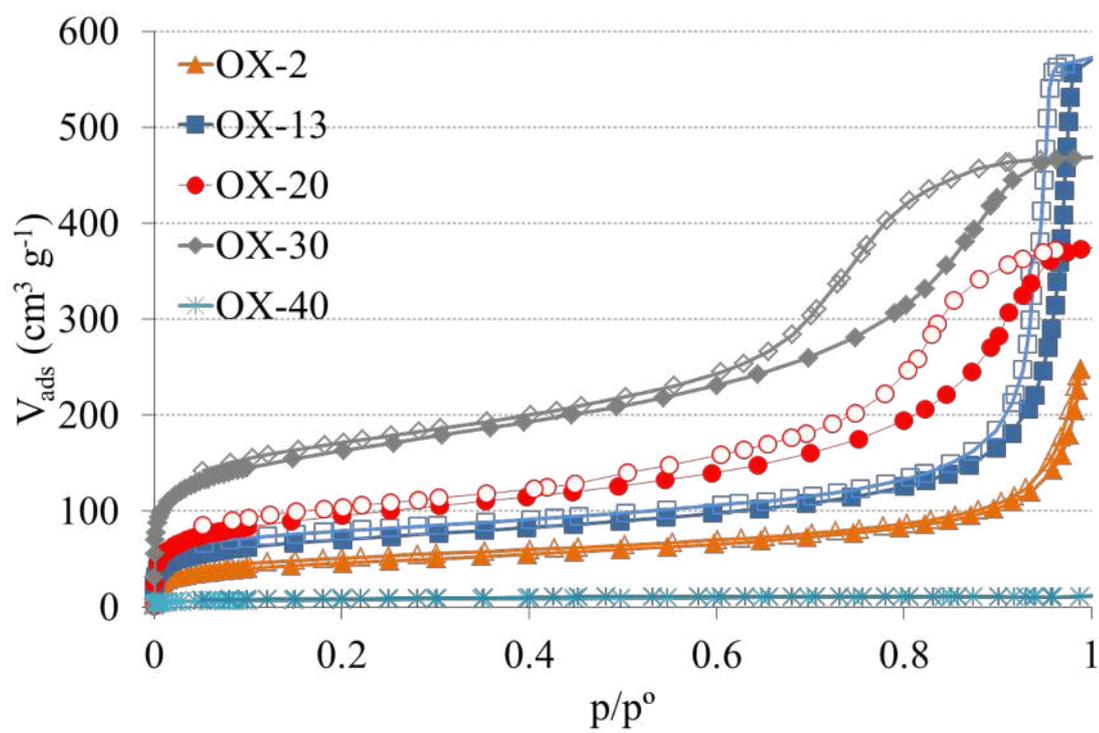


Fig. 3

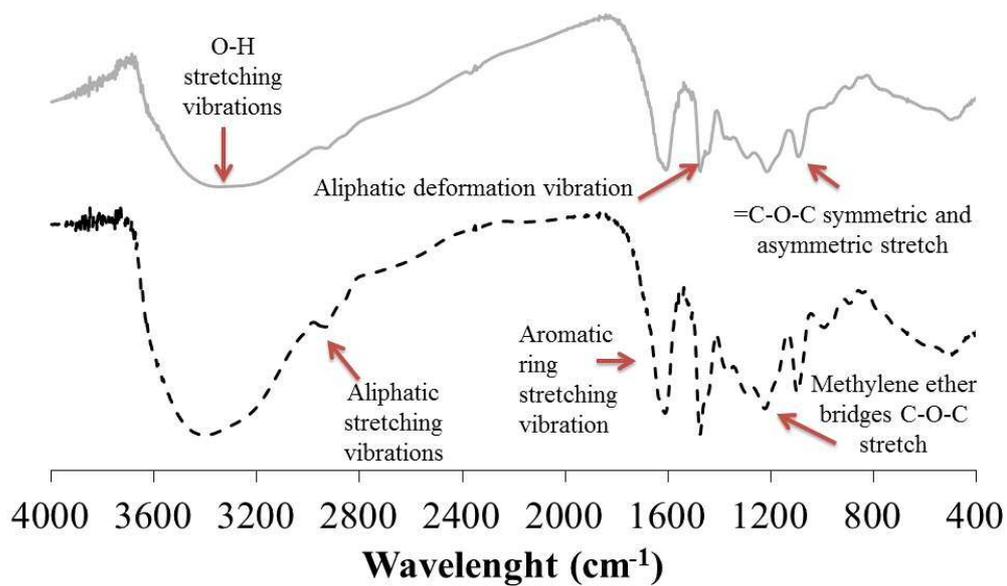


Fig.4

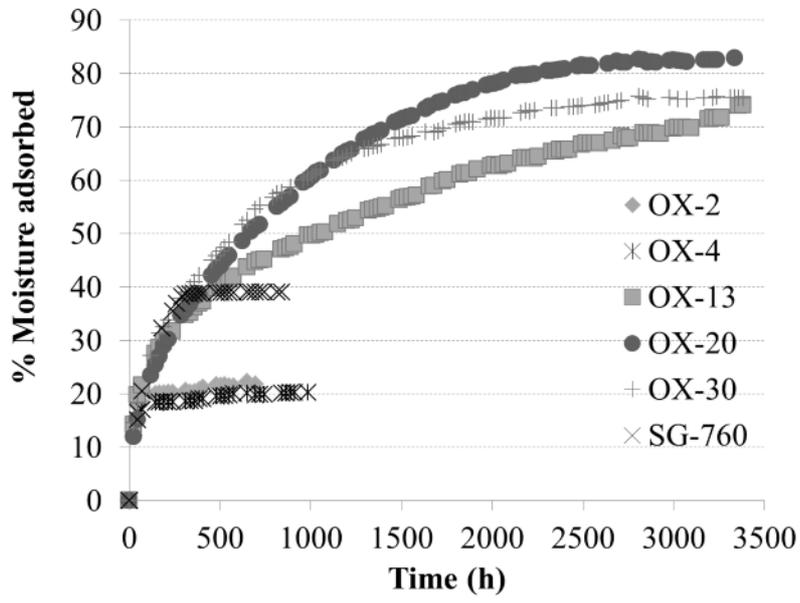


Fig.5

