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### ► To cite this version:

Fouzia Achchaq, W. Jomaa, Alexandre Godin, Stéphanie Bontemps, Jean-Rodolphe Puiggali. Temperature and moisture effects on the failure mode of highly shrinkable raw catalyst supports. *Procedia Structural Integrity*, 2016, 2, pp.2283-2290. 10.1016/j.prostr.2016.06.286 . hal-02086139

**HAL Id: hal-02086139**

**<https://hal.science/hal-02086139>**

Submitted on 1 Apr 2019

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21st European Conference on Fracture, ECF21, 20-24 June 2016, Catania, Italy

## Temperature and moisture effects on the failure mode of highly shrinkable raw catalyst supports

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### Abstract

Shrinkage implies generally the development of mechanical stresses and then, the formation of cracks. In this work, four formulations of alumina based hydrogels underwent a standard experimental procedure involving drying and mechanical characterizations. The thermo-hydro-mechanical behaviour of such highly shrinkable hydrogels is analysed by determining their specific surface area, calculated from the desorption isotherms. Brazilian test allowed identifying the cracking stress of the four hydrogel formulations, and the ultimate tensile strength as a function of the water content was obtained for each of them. During the drying experiments inside a convective dryer, two formulations of hydrogels displayed a capacity for self-healing. The results showed a real improvement of the strength property due to the self-repair phenomenon when it occurred, proving the importance of taking into account the roles of residual water and of applied temperature conditions in the drying process of the catalyst support production line.

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Peer-review under responsibility of the Scientific Committee of ECF21.

*Keywords:* Raw hydrogels ; rupture stress ; Brazilian test ;

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## 1. Introduction

Studies dealing with heterogeneous catalysts are of a continuous increasing interest so far in numerous application fields such as energy storage/conversion, petrochemical industries, biochemical catalysis and so on. Hence, on the one hand, the properties improvement of both catalyst components and catalyst supports as well as the appropriate methods of their developments are required to face the economic and environmental related issues. On the other hand, the optimization of these properties is important in order to provide the needed reaction rates and to produce the highest catalyst performance possible.

To achieve this last objective, the support texture is one of the key characteristic fostering the active site phase dispersion. Consequently, breakthrough researches aiming to obtain tailored catalyst supports in terms of specific surface area and porosity are conducted. To do so, various base materials can be employed such as alumina, zeolite, metals or carbon-based materials. However, whatever the nature of the material, the greater the specific surface is, the lower the mechanical strength is. For instance, this low mechanical resistance observed leads to 10% of damages during the drying process of the production line in the case of alumina-based catalyst supports.

The Brazilian test, defined by ISRM (1978) and usually performed to study the fracture and toughness of brittle solids such as rocks, ceramics or similar materials has been expanded to various materials; with varied compositions such as multi-material composites or thermal storage materials, and also with varied mechanical properties such as clays, green gels or wet granular materials. For these latter, the usual conditions required to exploit the data of a Brazilian test are not completely respected since the materials do not break as usual *-i.e.* with a clear-cut crack initiation at the centre and its propagation outward of the sample. That is why; some researchers prefer to mention of ‘pseudo’ tensile strength as mentioned in Smith et al. (2012).

In this work, four formulations of raw alumina based hydrogels were mechanically characterized as a function of their moisture contents and of the different drying operating conditions applied. The difference between the obtained results for each formulation are presented and discussed.

### Nomenclature

#### Roman letters

$C$	Brunauer-Emmett-Teller parameter	(a.u)
$P_c$	capillary pressure	(Pa)
$R$	ideal gas constant	(J. mol <sup>-1</sup> . K <sup>-1</sup> )
$T$	temperature	(K)
$V_m$	molar volume of water	(m <sup>3</sup> . mol <sup>-1</sup> )
$S_{BET}$	specific BET surface area	(m <sup>2</sup> /g)
$s$	area of one water molecule on the surface	(m <sup>2</sup> )
$N_A$	Avogadro constant	(mol <sup>-1</sup> )
$n_m$	number of molecules in a single layer	(-)
$F$	applied force	(N)
$D$	sample diameter	(m)
$H$	sample height	(m)

#### Greek letters

$\omega_m$	monolayer capacity	(-)
$a_\omega$	water activity	(-)
$\sigma_R$	ultimate tensile stress	(N/ m <sup>2</sup> )

## 2. Experimental procedure

### 2.1. Raw materials and sample preparation

Four alumina based hydrogels, all of solid cylindrical shape with a diameter slightly inferior to 20 mm after extrusion, were selected for the study. The formulations, given in Table 1, were synthesized by sol-gel process using different nitric acid and neutralization ratios impacting on the size of agglomerates of aggregated crystallites. The raw hydrogels were extruded under vacuum in order to avoid microcrack formation.

Table 1. Nitric acid and neutralization ratios of the studied formulations.

(HNO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> weight ratio) - (NH <sub>4</sub> OH/HNO <sub>3</sub> molar ratio)
6 - 60
1.5 - 60
6 - 20
1.5-20

The extruded samples were polished with SiC papers and measured with a digital caliper in order to ensure the same initial average height of 1.7 cm.

### 2.2. Sample characterization

#### 2.2.1 Desorption isotherms

The hydric behaviour of the raw hydrogels was analysed *via* their desorption isotherms. The standard gravimetric method was carried out for three temperatures: 20, 50 and 80°C and for a water activity comprised within the range [0 - 97%] using appropriate saturated salts. After sampling, the materials were placed in desiccators and their mass decrease with time was monitored using a weight balance (Mettler Toledo). The weighting accuracy is ± 0.3 mg. The equilibrium was assumed to be reached when the mass variation was less than 0.5 mg. The desiccators were maintained under vacuum between each weighting, minimizing the testing time. The temperature was kept constant using an oven.

The initial segment of each obtained desorption isotherm [5 - 40% of water activity] was fitted using the Brunauer-Emmett-Teller model:

$$\omega = \omega_m C a_\omega / (1 - a_\omega) [1 + (C - 1) a_\omega] \quad (1)$$

The specific BET surface area was then calculated for each gel formulation with the following relation by Brunauer et al. (1938):

$$S_{BET} = N_A n_m s \quad (2)$$

Capillary pressure versus vapor saturation was built from the desorption isotherms using the Kelvin law (Newsham et al. (2003)):

$$P_c = \left( - \frac{RT}{V_m} \right) \ln a_\omega \quad (3)$$

### 2.2.2 Brazilian tests

Two drying procedures are applied (detailed in Achchaq et al (2016)): i) smooth operating conditions under uncontrolled atmosphere: at ambient temperature and ambient humidity, ii) harsher operating conditions under controlled atmosphere: inside a convective dryer, allowing different operating conditions: temperature, humidity and air velocity.

Brazilian tests were performed after each procedure of drying. They allowed identifying the rupture stress of the four hydrogel formulations induced by the different operating conditions. The experiments were performed on samples of different initial water contents, at least in triplicate, using a standard loading machine with capacity of 100 kN. The samples were monotonically loaded at room temperature to break at a loading speed of 0.5 mm/min. The ultimate tensile stress as a function of the water content was obtained using relation (4) in order to study the impact of moisture content on the failure mode of the raw hydrogels in both drying procedures.

$$\sigma_R = 2F / \pi DL \quad (4)$$

## 3. Results

### 3.1. Desorption isotherms

The gravimetric method allows ascertaining the desorption capacity as well as revealing the affinity between water vapour and the hydrogel surface. The results being similar for the three temperatures 20, 50 and 80°C, Fig. 1. (a) shows the desorption isotherms of the four formulations of hydrogels obtained at 50°C. The standard deviations are of 4-5% after calculation. All isotherms are fitting the typical type IV (IUPAC classification) and exhibit three distinct areas. From a water activity ranging from 0 to 0.4, a first plateau can be noticed related to the pendular state of water inside the hydrogels. This means that there is still a discontinuous layer of immobile water along the pore walls in spite of the dried surroundings. The second plateau from 0.4 up to 0.85 displays its funicular state *-i.e.* continuous layers of mobile water. Then, the curves increase steeply from a water activity ranging from 0.85 to almost 1. This third area features the drainage process owed to pores filled with capillary water.

The estimations of specific BET surface area obtained at 20, 50 and 80°C are gathered in Fig. 1. (b). At 20 °C, the formulations with an acid ration of 1.5 show the highest values: 376 m<sup>2</sup>/g for 1.5-20 and 347 m<sup>2</sup>/g for 1.5-60, followed by the formulations with an acid ratio of 6 (321 m<sup>2</sup>/g for 6-20 and 300 m<sup>2</sup>/g for 6-60). At 50 °C, all specific BET surface area values decrease with the lowest one for 1.5-60 (196 m<sup>2</sup>/g). Otherwise, the ranking remains the same with 222 m<sup>2</sup>/g for 1.5-20 and approximately 205 m<sup>2</sup>/g for 6-20 and 6-60. No change is observed then at 80 °C. The surface loss is associated with the sticking phenomenon of crystallites during drying (Karouia et al. 2013).

Capillary pressure versus vapor saturation graph was built from the desorption isotherms using the Kelvin law (Fig. 1. (c)). It allows the determination of the air input pressure order of magnitude inside the hydrogels, which is about 1.5x10<sup>7</sup> Pa and concurs with a mean pore access of about 10 nm. This estimation is acquired using the Laplace-Young's equation valid up to a water activity of 0.4 only (Padmaja et al. 2004).

The  $C$  parameter, intervening in the Brunauer-Emmett-Teller model (relation (1)), is related to the desorption heat of the first layer, giving a rough description of the bond rigidity between desorbed water molecules and the surface of hydrogel crystallites. As can be seen in Fig. 1. (d), the highest values for the  $C$  parameter at 20 °C is obtained for the formulations 1.5-60 (24) and 6-20 (21), followed by the formulations 6-60 (17) and 1.5-20 (13). Then, the values decrease down to 9 for 1.5-60 and 8 for 6-20 whereas both 6-60 and 1.5-20 reach the same value (6).

The monolayer capacity  $\omega_m$  describes the amount of water required to form an assumed single and uniform molecular layer on the surface hydrogel. The values obtained in Fig. 1. (e) were determined using the definitions

detailed in Rouquerol et al. (2014). At 20 °C, the highest amount of water is reached by the formulations 1.5-20 and 1.5-60, followed by 6-20 and 6-60. As expected, the values decrease at 50 and 80 °C. Except the formulation 1.5-60 reaching the lowest value ( $\omega_m = 0.0514$ ), the ranking remains the same for the other formulations.

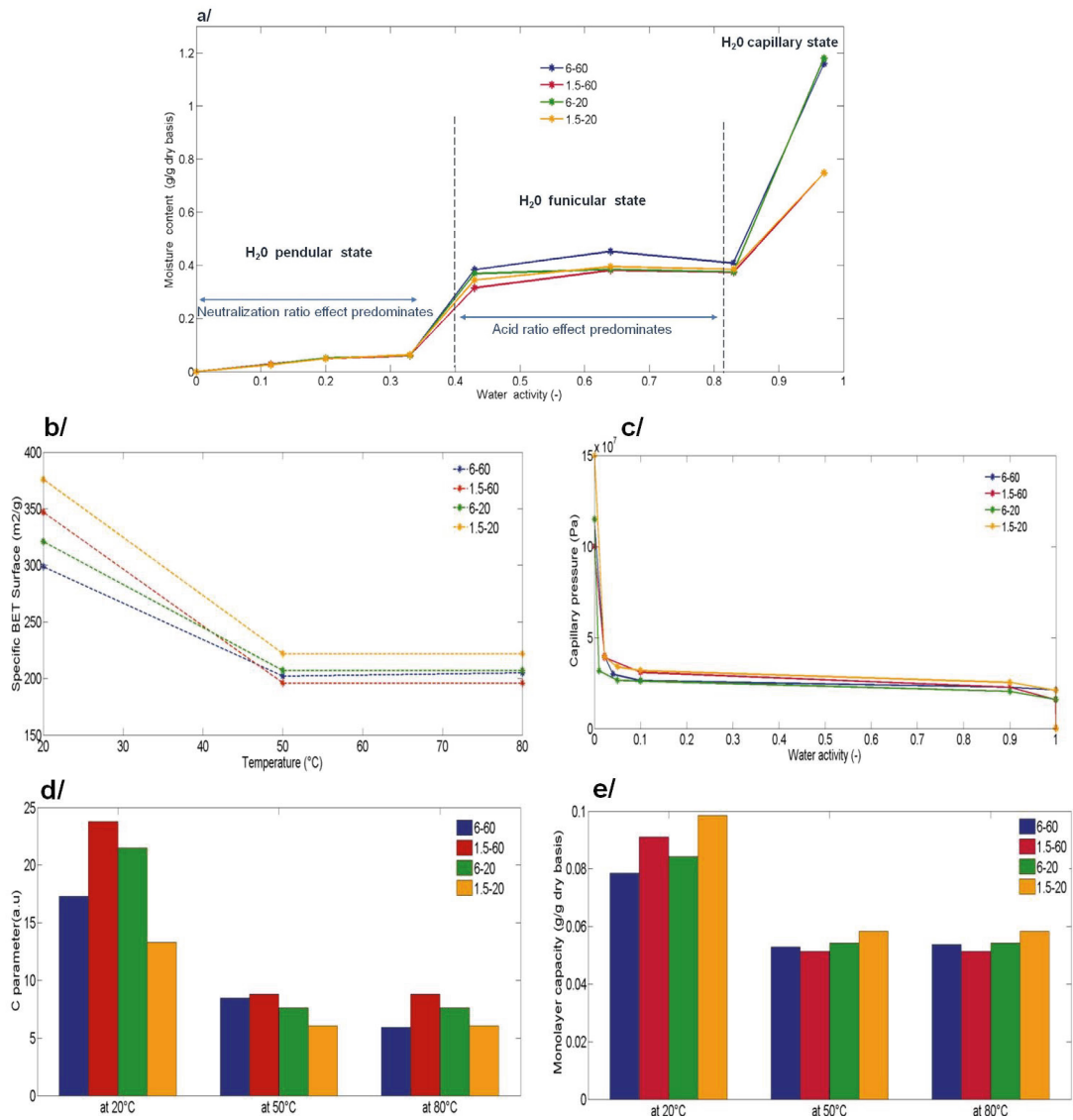


Fig. 1. (a) water desorption isotherms performed between 0 and 97 % of water activity showing how the hydrogels capture water vapor at 50 °C; (b) calculated specific surface area for water activity between 5 and 40 %; (c) calculated capillary pressure using the Kelvin law; (d,e) fitting the desorption isotherms to the Brunauer-Emmett-Teller model giving (d) information regarding the extension of the monolayer and (e) the energy between the first water monolayer and the hydrogel surface

### 3.2. Brazilian tests

During the two drying procedures (see subsection 2.2.2), several macroscopic cracks occurred and influenced the way in which the tests were driven. Hence, careful attention was paid to dispose the samples in order to limit the influence of the cracks as much as possible. The failure mode of each hydrogel formulation at different saturation states were then studied using the Brazilian test.

### 3.2.1 Smooth operating conditions under uncontrolled atmosphere

For the first drying procedure, the Tensile stress vs Displacement curves at saturated state ( $\bar{\omega} = 1.00$  in average) and, at partially saturated state ( $\bar{\omega} = 0.50$  in average) are shown in Fig. 2. At saturated states (Fig. 2. (a)), two extreme modes of failure occurred. The semi-brittle breakage behaviour is observed for the formulations 6-60, 1.5-60 and 1.5-20. The clear-cut crack initiation at the centre, or close to the center, with its propagation outward of the sample is characterized by a sharp peak. However, the first peak did not systematically correspond each time to the crack at the centre. It was then observed after the first peak, which can be more or less well defined as it was often visualized for the formulations 1.5-20 and 6-20. The plastic deformation behaviour is observed for the formulation 6-20, where no peak was noticed until the samples reach finally sufficient low moisture contents. In this case, the 6-20 samples squeezed between the platens like a paste. At partially saturated states, the semi-brittle breakage is observed for all formulations. Nevertheless, careful attention should be paid to identify the right peak corresponding to the crack at the centre. Indeed, the first peak could be sometimes related to a secondary macroscopic crack formation.

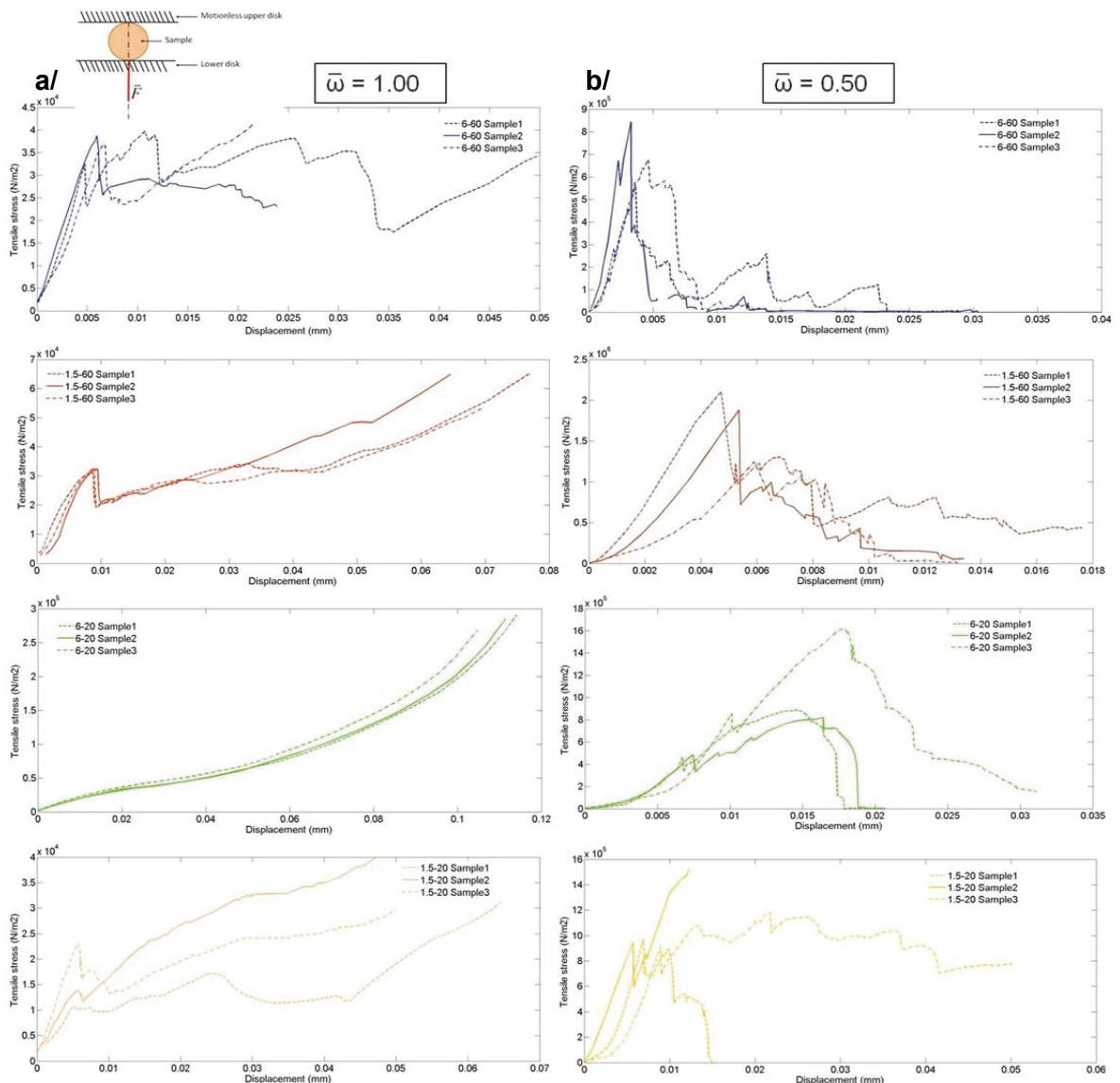


Fig. 2. tensile behaviours of the hydrogels using a loading speed of 0.5 mm/min (a) at their saturated state; (b) at partially saturated water.

The ultimate tensile stress evolution with the moisture content of each hydrogel is then deduced and illustrated in Fig. 3. The trend for all hydrogels follows an exponential law. A dispersion of the experimental points is observed from a moisture content value of 0.55. As all formulations broke for a moisture content value inferior to 0.3, then no Brazilian test was possible.

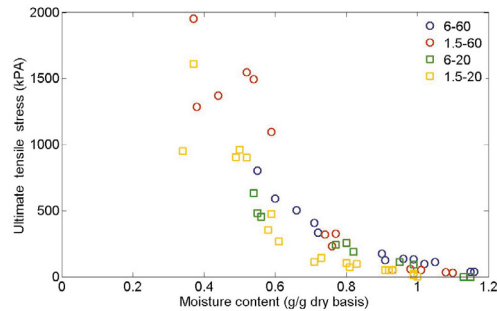


Fig. 3. dependence of the ultimate tensile stress with the moisture contents of hydrogels dried at ambient temperature and ambient humidity.

### 3.2.2 Harsher operating conditions under controlled atmosphere

The formulations with an acid ratio of 6 were totally destroyed at the end of the drying experiments conducted inside the convective dryer. Hence, the previous ultimate tensile stress evolution with the moisture content can only be achieved for the formulations with an acid ratio of 1.5.

The use of the dryer allowed adjusting the operating conditions in terms of temperature [30-70°C] and humidity [8-60%] at a fixed air velocity of 3 m/s. As mentioned in Achchaq et al. (2016), the formulations 1.5-60 and 1.5-20 seemed displaying a self-repair capacity. These latter kept their shape without cracks instead of being completely destroyed for low moisture contents [0.1 - 0.3], as it was the case when applying the smooth operating conditions under uncontrolled atmosphere. Their mechanical resistance is thus improved even if the values of the ultimate tensile stress are decreasing since now, they are no more friable. Finally, the formulation 1.5-60 is unquestionably the most resistant one with a maximum ultimate tensile stress value of around 30% better than that of 1.5-20.

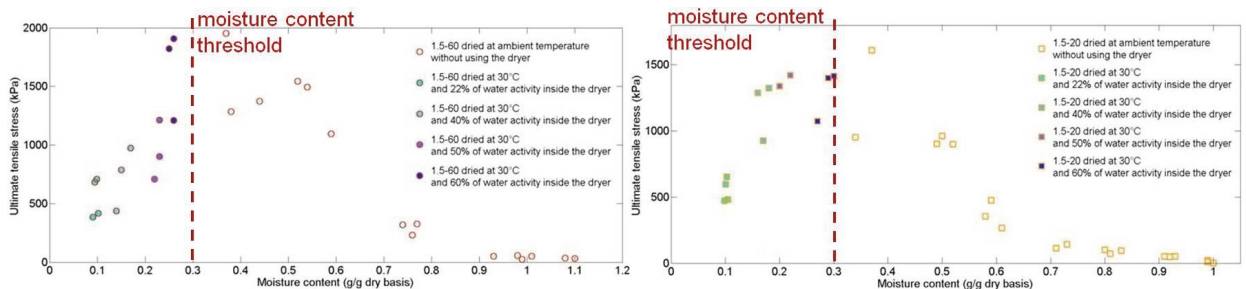


Fig. 4. dependence of the ultimate tensile stress with the moisture contents completed with hydrogels dried inside the convective dryer at the constant temperature 30°C and different humidities: 22, 40, 50 and 60%.

## 4. Discussion and conclusion

In this work, four formulations of raw alumina based hydrogels were characterized as a function of their moisture contents after two drying procedures: smooth operating conditions at uncontrolled atmosphere or harsher ones under controlled atmosphere. The results obtained following the second drying procedure suggest that the formulations with an acid ratio of 1.5 displayed a self-repair capacity inducing their better mechanical resistance. This observation explains why there is, in fact, a partial recovery of the strength property of the formulations with an acid ratio of 1.5.



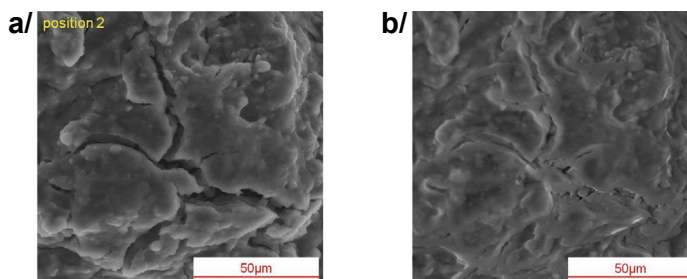


Fig. 4. observations of the 1.5-60 same sample when applying a constant water activity and making the temperature varying from 20 to 60°C (a) with crack and (b) with the same crack self-repaired.

According to the desorption isotherms, the hydrogels with an acid ratio of 6 are more porous than those with an acid ratio of 1.5. The formulations 1.5-60 and 1.5-20 should thus have the highest specific surface area. This is the case except for 1.5-60 from a temperature of 50°C. Indeed, this formulation shows an unexpected value lower than those with an acid ratio of 6. However, its  $C$  parameter has the highest value, which reflecting the highest bond rigidity between water molecules and the crystallites surface. Concerning the formulation 1.5-20, its  $C$  parameter low value is counterbalanced by its highest water monolayer capacity. Knowing that peptization must allow a more efficient particles packing while drying, an acid ratio of 1.5 is better than 6 for these formulations. However then, *a priori* the neutralization ratio and heat intervene for modifying the end organization of agglomerates making a distinction between 1.5-60 and 1.5-20. The moisture content threshold of 0.3 corresponds to the value where the hydrogels undergo both structural and hydric transitions: the samples go from two phases: hydrogel matrix + water to three phases: hydrogel matrix + water + air. Above this value, the continuous layers of mobile water are likely still influencing the acid ratio modifying then, the available porous volume. Below this value, the amount of residual water is of a paramount importance since it fosters the orientation of crystallites. Hence, residual water has a structuring role and acts as a contributor to the mechanical properties. The applied temperature conditions and residual water can then activate the self-repair phenomenon and make the mechanical properties of the final product improve.

### Acknowledgements

The research leading to these results received funding from the European Community's Seventh Framework Programme [FP7/2007-2013] under grant agreement n° 296006. The authors want to warmly thank Karim Djellab for his ESEM pictures as well as for his fruitful exchanges with us.

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