

High porosity polyethylene aerogels

Christophe Daniel, Simona Longo, Gaetano Guerra*

Dipartimento di Chimica e Biologia e Unità INSTM, Università degli Studi di Salerno

Via Giovanni Paolo II, 132- 84084 Fisciano (SA), Italy

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ABSTRACT

Monolithic aerogels of high molecular weight polyethylene ($M_w = 3 \times 10^6 - 6 \times 10^6$ g/mol) have been prepared by solvent extraction with supercritical carbon dioxide from thermoreversible gels prepared in decalin. These low density and highly porous aerogels present an apparent porosity up to 90%. The aerogel morphology observed by scanning electron microscopy (SEM) is characterized by spherulitic structures being interconnected by fibers. The X-ray diffraction experiments show that PE aerogels are highly crystalline with a degree of crystallinity of c.a. 80% and PE chains being packed into the typical orthorhombic unit cell. The combined SEM and N_2 sorption investigations show that PE aerogels are essentially macroporous with a small amount of mesopores. The oil-sorption performance of polyethylene aerogels has been also evaluated in this study in order to assess a possible use of these materials for oil spillage recovery and results show that aerogel macropores allow a very fast sorption kinetics with a 100% oil weight uptake obtained in less than 1 min. **Polyolefins J (2015) 2: 49-55**

Keywords: polyethylene; thermoreversible gels; aerogels; supercritical carbon dioxide; oil spillage recovery.

INTRODUCTION

Porous polymers have received an increased level of research interest because of their potential to merge the properties of both porous materials and polymers. Porous materials with different structural characteristics such as pore size and geometry, void fraction, surface area can be obtained depending on the preparation technique [1].

The most common preparation process of polyolefin

porous materials is foaming which leads to pores (or cells) with size typically in the range of 1 μm to hundreds of μm [2-4]. Polyethylene and polypropylene with porous structures have been also prepared through crystallization of swollen polymer in supercritical conditions but the mechanical properties of the resulting material are low since the crystals are weakly connected with each other [5-7]. This problem can eventually be overcome by cross-linking the polymer [8].

* Corresponding Author - E-mail: gguerra@unisa.it

Another alternative process to obtain robust polymeric materials with high porosity is based on the gelation of a polymer in a solvent followed by solvent removal with a supercritical fluid (usually carbon dioxide). This type of material generally called aerogel differs from the foams by the dimensions of the pores which are a few nm to a few tens of nm wide.

The advantage of using supercritical CO₂ drying is the absence of surface tension. During the extraction process, a supercritical solution is formed between supercritical CO₂ and liquid solvent and is, thus, possible to extract the solvent without collapsing the structure.

The first examples of polymeric aerogels were based on highly cross-linked polymers (mainly resorcinol-formaldehyde [9] and melamine-formaldehyde [10] aerogels), but recently it has also been shown that uncrosslinked polymeric aerogels can be also obtained by CO₂ extraction of organo gels where the gel three-dimensional network is due to crystalline regions instead of covalent bonds. In particular, aerogels with crystalline phases have been obtained using various regular synthetic polymers such as syndiotactic polystyrene (s-PS) [11-13], poly(vinylidene fluoride) [14], poly(vinylidene fluoride-co-hexafluoropropylene) [15] and isotactic poly(4-methyl-pentene-1) (i-P4MP1) [16].

It is worth adding that the mechanical properties of the gel and the possibility to obtain robust monolithic aerogels strongly depend on the morphology of the crystalline phases obtained in the gel. Thus, stable physical polymeric aerogels generally present a fibrillar morphology as observed, for instance for s-PS [11, 12] and i-P4MP1 [16]. On the other hand, crystallization of polymer in solutions which leads to spherulitic or other globular morphologies such as poly(2,6-dimethyl-1,4-phenylene oxide) produces unstable gels, which are crushed as a consequence of drying and thus lead to powder samples rather than stable monolith aerogels [17]. In these cases, aerogels can still be obtained by blending with a polymer forming a fibrillar 3D network in the gel such as s-PS [17-18].

Depending on the polymer concentration, the crystallization of PE in organic solvent usually leads to lamellar single crystals or crystalline spherulites which do not give rise to gel formation in dilute and semi-dilute polymer solutions. However, it has been observed

that gelation of PE in solvents such as decalin or p-xylene can occur under special conditions [19-22]. In particular, it has been shown that the gelation of PE can be obtained by stirring PE/solvent solutions for PE with a molecular weight larger than $M_w = 1.5 \times 10^6$ [22].

In this contribution, the preparation of highly porous monolithic polyethylene aerogels is reported for the first time. The preparation method is based on the formation in PE/decalin gels (and in the derived aerogels) of some fibrils ensuring the formation of a 3D network between PE crystalline spherulites allowing the obtaining of monolithic aerogels after complete solvent extraction with supercritical carbon dioxide. These aerogels are characterized by a high degree of crystallinity and an apparent porosity higher than 90%. The sorption properties of PE aerogels have been also investigated and the results concerning the sorption of nitrogen at 77 K and of white mineral oil will be presented.

EXPERIMENTAL

Materials and sample preparation

The polyethylene used in this study was purchased from Sigma Aldrich and presents weight-average molecular mass $M_w = 3 \times 10^6 - 6 \times 10^6$ g/mol. Decalin and di-t-butyl-p-cresol anti-oxidant were also purchased from Sigma Aldrich and used as received.

PE gel samples were prepared by heating at 160°C under stirring a 10 wt% solution of PE and decalin containing 0.5 wt% of di-t-butyl-p-cresol anti-oxidant in hermetically sealed test tubes until complete dissolution of the polymer and the appearance of a transparent and homogeneous solution. During stirring at 160°C an increase of the solution apparent viscosity occurred, leading to a stop of the stirring magnet rotation. Then the mixture was cooled down to room temperature where gelation occurred.

Aerogel samples were then obtained by treating native gels in a SFX 200 supercritical carbon dioxide extractor (ISCO Inc.) using the following conditions: T = 40°C, P = 200 bar and extraction time t = 240 min.

For monolithic aerogels with a regular shape (i.e. spherical or cylindrical) the total porosity, including

macroporosity, mesoporosity and microporosity, can be estimated from the volume/mass ratio of the aerogel.

Then the percentage of porosity P of the aerogel samples can be expressed as:

$$P = 100 \left(1 - \frac{\rho_{\text{app}}}{\rho_{\text{pol}}} \right) \quad (1)$$

where ρ_{pol} is the density of the polymer matrix (e.g., equal to 0.9 g/cm^3) and ρ_{app} is the aerogel apparent density calculated from the mass/volume ratio of the monolithic aerogels.

Characterization techniques

Wide-angle X-ray diffraction (WAXD)

X-ray diffraction patterns were obtained on a Bruker D8 Advance automatic diffractometer operating with a nickel-filtered $\text{CuK}\alpha$ radiation. The degree of crystallinity of powders and films was obtained from the X-ray diffraction data, by applying the standard procedure of resolving the diffraction pattern into two areas corresponding to the contributions of the crystalline and amorphous fractions.

Scanning electron microscopy (SEM)

The internal morphology of the monolithic aerogels was characterized by means of a scanning electron microscope (SEM, Zeiss Evo50 equipped with an Oxford energy dispersive X-ray detector). Samples were prepared by fracturing small pieces of the monoliths in order to gain access to the internal part of the speci-

men. Low energy was used (5 keV) in order to obtain the highest possible surface resolution. Before imaging, all the specimens were coated with gold using a VCR high resolution indirect ion-beam sputtering system. The samples were coated depositing approximately 20 nm of gold. The coating procedure was necessary in order to prevent surface charging during the measurement and to increase the image resolution.

Porosimetry

Surface area was obtained by N_2 adsorption measurements carried out at 77 K with a Micromeritics ASAP 2020 instrument. Before the adsorption measurement, PE aerogels and PE commercial powder were degassed at 40°C under vacuum for 24 h. The surface area values were calculated using the Brunauer-Emmet-Teller (BET) method in the range $0.05\text{--}0.2 P/P_0$.

RESULTS AND DISCUSSIONS

In Figure 1 are reported the photographs of a piece of gel of PE prepared in decalin at $C_{\text{pol}} = 10 \text{ wt}\%$ before and after solvent extraction with supercritical carbon dioxide.

We can observe that the shape and the dimensions remain substantially unchanged during solvent extraction and a monolithic aerogel with a total pore volume of c.a. $11 \text{ cm}^3/\text{g}$ and a percentage of porosity of 90% is obtained.

Typical scanning electron microscopy (SEM) im-

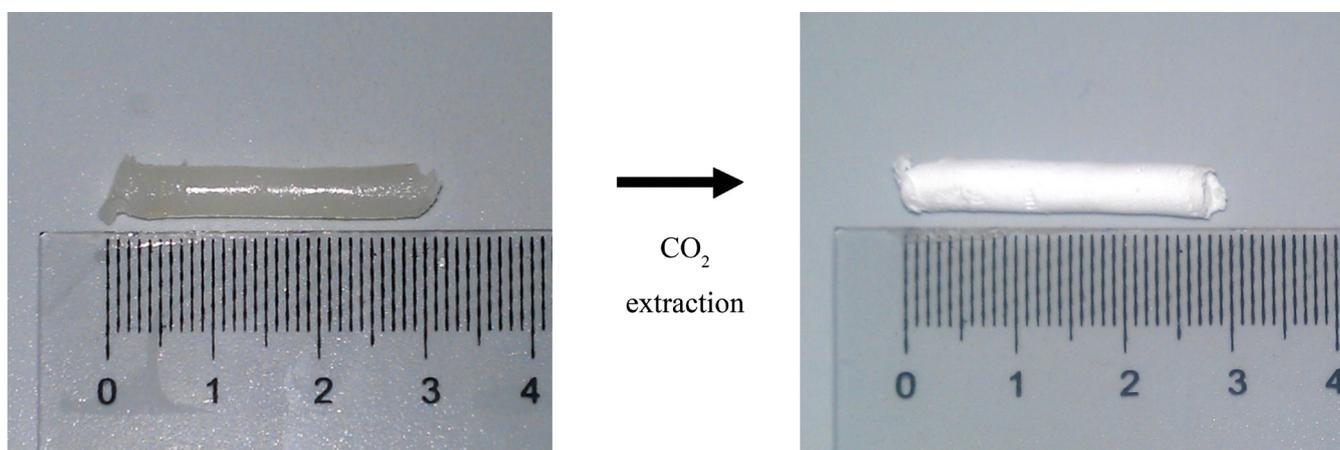


Figure 1. Photographs of a piece of PE gel prepared in decalin at $C_{\text{pol}} = 10 \text{ wt}\%$, before and after complete solvent extraction via supercritical carbon dioxide (units of the ruler are cm).

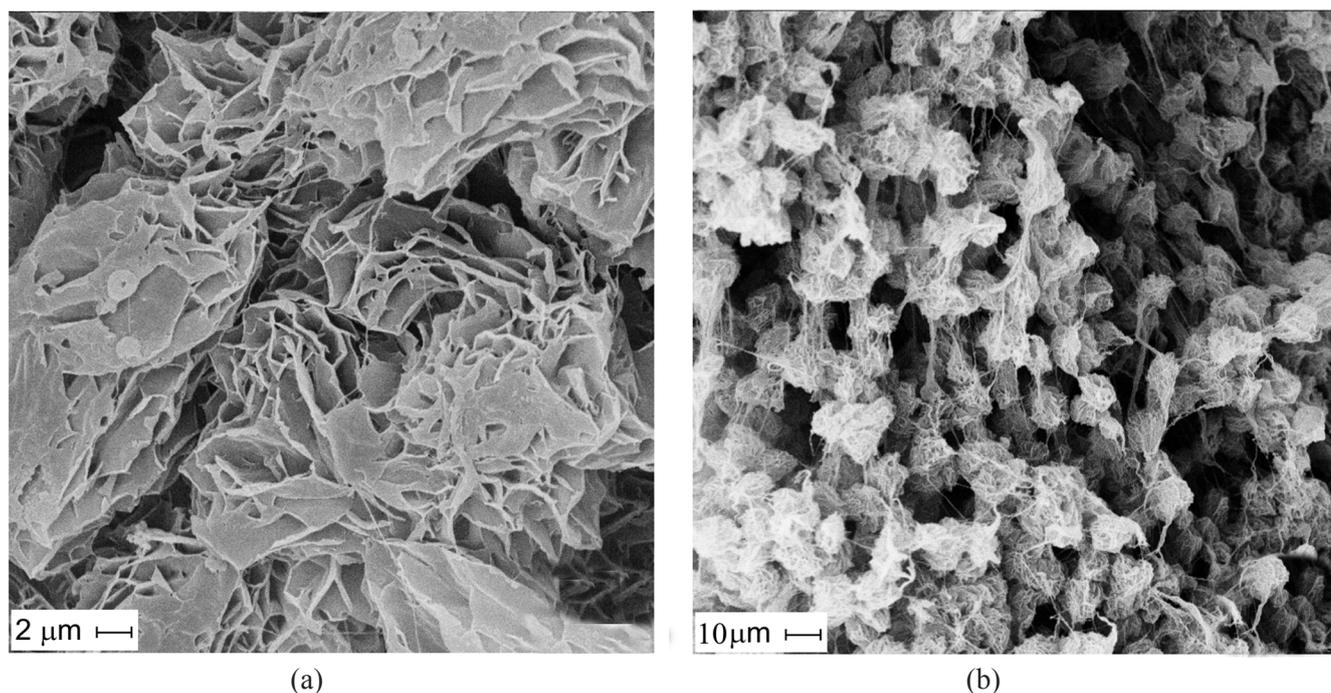


Figure 2. SEM images of a polyethylene aerogel with porosity $P = 90\%$ obtained from a gel prepared in decalin with $C_{\text{pol}} = 10$ wt %, after complete solvent extraction by SC-CO_2 .

ages of the aerogel are reported in Figure 2. As can clearly be seen in Figure 2A, a lamellar morphology with the formation of spherulites is obtained in the aerogel. However, the SEM image of Figure 2B clearly shows the presence of fibrils between the spherulites ensuring the formation of a 3D network and the obtaining of a monolithic sample.

In Figure 3 are reported the X-ray diffraction patterns of the commercial starting PE powder and of the PE aerogel.

The diffraction patterns of the commercial starting PE powder and of the PE aerogel display the typical (110) and (200) reflections of the orthorhombic polyethylene unit cell at $2\theta = 21.4^\circ$ and 23.7° , respectively. It is also worth noting that the amorphous halo of the PE aerogel is significantly lower than the commercial PE powder. This indicates that the aerogel presents a higher degree of crystallinity compared to the starting PE powder. The degree of crystallinity of the samples was evaluated from the X-ray diffraction data applying the standard procedure of resolving the diffraction pattern into two areas corresponding to the contributions of the crystalline and amorphous fractions for the 2θ range $11\text{--}28^\circ$. For the PE aerogel, the observed degree of crystallinity is $X_c = 80\%$, while for the commercial PE powder $X_c = 60\%$.

According to IUPAC classification [23] pores are divided into three families according to their diameter

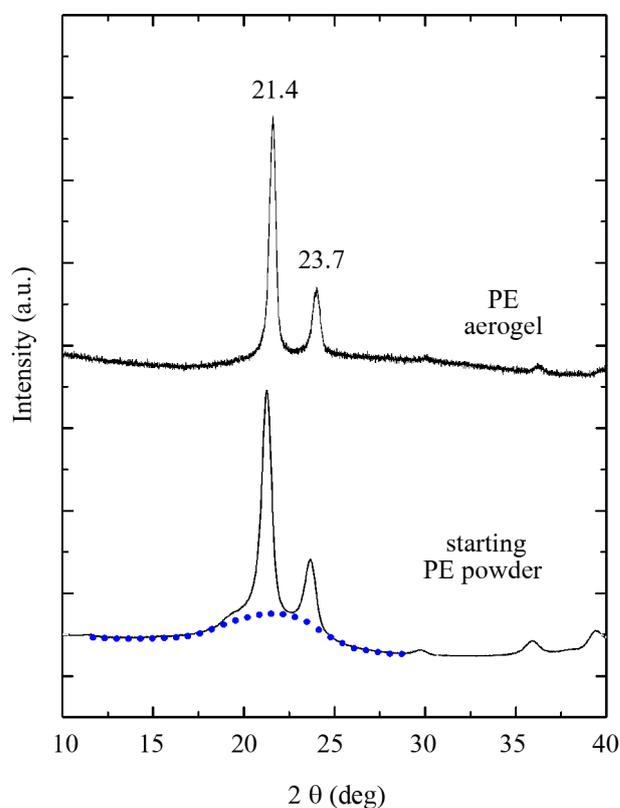


Figure 3. X-ray diffraction of commercial starting PE powder and PE aerogel.

size (ϕ): micropores ($\phi < 2\text{ nm}$), mesopores ($2\text{ nm} < \phi < 50\text{ nm}$) and macropores ($\phi > 50\text{ nm}$).

SEM measurements (Figure 2) have clearly shown the large amount of macropores in the PE aerogels and in order to investigate the porosity characteristics of these materials in the smaller mesopore and micropore range nitrogen physisorption at 77K was carried out.

The N_2 sorption isotherms (where the sorption is expressed as cm^3 of nitrogen in normal conditions per gram of polymer) of the PE aerogel and commercial PE powder used for the aerogel preparation are compared in Figure 4.

The pore volume calculated as volume of the liquid N_2 at $P/P_0 \approx 0.98$ is equal to $V_{\text{totN}_2} = 0.25\text{ cm}^3/\text{g}$ and differs greatly from the aerogel total pore volume determined from the apparent porosity ($V_{\text{tot}} = 11\text{ cm}^3/\text{g}$). The difference between the total pore volume and the V_{totN_2} value represents an estimate of the macropore volume. These values indicate that mesoporosity represents only a small fraction of the total porosity (i.e., less than 3%). This result is in agreement with the SEM micrographs of Figure 2 that show the strong macroporous nature of the aerogel.

The shape of the aerogel isotherm, associated to the presence of hysteresis, suggests a type IV isotherm with the presence of big mesopores. Moreover, the high adsorbed-gas volume indicates a prevalent mesoporous nature of the aerogel. This was confirmed by the estimated microporous surface area $S_{\text{micro}} = 8\text{ m}^2/\text{g}$ which is much smaller than the total surface area $S_{\text{tot}} =$

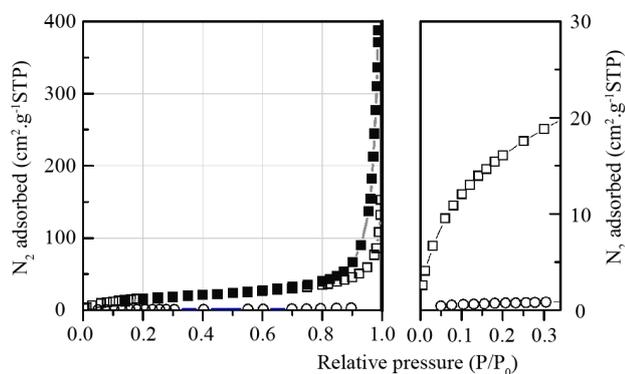


Figure 4. Left: volumetric N_2 adsorption-desorption isotherms at 77 K in the 0-0.99 P/P_0 range of a PE aerogel (\blacksquare, \square) and PE commercial powder (\circ). For the aerogel, the empty and filled scatters refer to the adsorption and desorption branches, respectively. Right: volumetric N_2 adsorption isotherms in the 0-0.3 P/P_0 range of a PE aerogel (\square) and PE commercial powder (\circ).

$66\text{ m}^2/\text{g}$ (i.e. c.a. 12%).

As expected, the PE commercial powder presents a much lower nitrogen sorption capacity and the total surface area is minor than $3\text{ m}^2/\text{g}$.

The mineral oil sorption capacity of PE aerogels was determined in order to assess a possible use of these aerogels for oil spillage recovery.

In Figure 5 is reported the sorption kinetics of a PE aerogel with a porosity of 90% soaked at room temperature in white mineral oil.

The presence of the macropores allows a very fast sorption kinetics and in less than one minute the oil uptake already reaches 100% of the initial aerogel weight. Then the oil sorption kinetics proceeds at a slower rate and an equilibrium weight uptake of 180% is obtained in c.a. 25 min.

In absence of aerogel shrinkage or swelling, the theoretical weight uptake limit corresponding to the filling of all the aerogel pores can be easily calculated from the aerogel porosity [24]. For the 90% porosity aerogel considered here, the maximum theoretical weight uptake of white mineral oil is c.a. 800%.

The oil equilibrium weight uptake in the PE aerogel is much lower than the theoretical value and is also lower than the 500-650% uptake range been previously reported for syndiotactic polystyrene monolithic aerogels with similar porosity [25]. As no shrinkage was observed during the oil sorption, the much lower sorption uptake observed with the PE aerogel may be explained by the presence of spherulites in the aerogel which may prevent the diffusion of the oil between the lamellae.

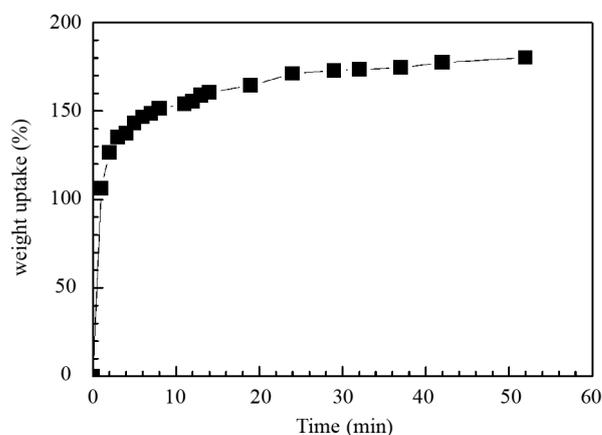


Figure 5. Sorption kinetics at room temperature of white mineral oil in a PE aerogel with a porosity of 90%.

CONCLUSIONS

In this contribution, the preparation of polyethylene monolithic aerogels obtained by solvent extraction with supercritical carbon dioxide from gels in decalin has been reported. These highly crystalline aerogels are characterized by spherulitic structures connected by fibrils which allow the obtaining of robust monolithic aerogels. The Combined SEM observations and N₂ physisorption measurements show that the PE aerogels obtained with this process are essentially macroporous with a small amount of mesopores. The presence of the macropores allows a fast sorption of mineral oil with an equilibrium uptake of 180 weight% which is much lower than that of other polyolefin aerogels [24, 25] or commercially available nonwoven commercial polypropylene sorbents [26].

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SYMBOLS AND ABBREVIATIONS

BET = Brunauer-Emmet-Teller method

SEM = scanning electron microscopy

s-PS = syndiotactic Polystyrene

i-P4MP1: isotactic poly(4-methyl-pentene-1)

PE= polyethylene

ρ_{pol} = density of the polymer matrix

ρ_{app} = apparent density calculated

(ϕ) = diameter size

SC-CO₂ = supercritical carbon dioxide