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Hybrid Polycaprolactone/Silica Porous Membranes Produced by Sol-Gel

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Summary: Hybrid porous membranes of polycaprolactone (PCL) and silica were obtained by a two stage procedure. First a porous PCL membrane was produced by freeze extraction technique and then a sol-gel reaction was used to form a uniform silica coating on the pore walls. Sol-gel reaction was performed at low pH with tetraethylorthosilicate (TEOS) as the precursor of silica. In this work we analyze the influence of several clue parameters on the silica film formation and in turn on the properties of the hybrid material. Water:TEOS molar ratio and drying protocol were considered in this study.

Keywords: hybrid composite; PCL; polycaprolactone; porous membrane; sol-gel reaction; TEOS; tetraethyorthosilicate

Introduction

Poly(ε-caprolactone) (PCL) is a hydrophobic, semicrystalline linear polyester well known for its biocompatibility and biodegradability. The good solubility and processability of PCL, its low melting point (59–64°C) and the exceptional blend-compatibility has stimulated extensive research into its potential application in the biomedical field and especially for tissue engineering applications.[1,2] PCL is characterized by a rather slow degradation appearing as a material with suitable behavior for bone and cartilage tissue engineering.[3] Nevertheless, in order to fulfill the requirements of the above applications its mechanical performance needs to be improved.

Blending with other biomaterials or mixing with inorganic particles in order to produce composites appears as an appealing route for tailoring its properties. For example blending with polylactic acid (PLA),[4] chitosan,[5,6] polyvinylpyrrolidone (PVP)[7] or Poly(glycerol sebacate) (PGS)[8] could allow the modification of degradation behavior of scaffolds as well as the mechanical properties by varying the components content. Furthermore, the mechanical and bioactive characteristics (e.g osteoconduction, cell prolifiration) could be enhanced by the reinforcement with inorganic particles like bioglass particles,[9] phosphate glasses,[10] hydroxyapatite,[11,12] mesoporous silica[13] and silica nanoparticles.[14] All the above examples refer to the reinforcement of the polymeric organic phase by incorporating already prepared inorganic particles. In this work a different strategy was followed which is based on the *in situ* synthesis of the inorganic part in the presence of already prepared porous membranes by using the highly versatile sol-gel method.

Sol-gel is an established technique for the production of glasses and ceramics from the liquid phase at room temperature. The major advantages that offers includes the feasibility of the technique which allows the production of a great variety of glasses with different morphologies, the high purity of the products, and the simplicity of the procedure performed at low-temperatures.

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A typical sol-gel procedure[15] could be described by the following stages: mixing of the reactants, gelation, ageing and drying. Initially, the alkoxide which is the precursor of the ceramic, water, alcohol and either acid or basic catalyst are mixed at atmospheric pressure and at temperatures ranging from 10 to 100 °C. Alcohol serves as a miscibility promoter while at the same time reduces the rate of reaction by diluting the reacting alkoxide and water molecules. The above solution is allowed to form a gel: a three-dimensional network is produced as a result of colloidal particles and condensed silica species linkage to each other. During ageing, a stage also known as syneresis, the gel is left over a period of time ranging from hours to days in which the polycondensation continues while the material shrinks and stiffens. Finally, a drying step is followed in which the byproducts (water and alcohol) are removed from the pores.

The reactions taking place could be roughly described by the following:

$$\equiv \mathrm{Si} - \mathrm{OR} + \mathrm{H_2O} \leftrightarrow \equiv \mathrm{Si} - \mathrm{OH} + \mathrm{ROH} \quad \text{(hydrolysis)} \tag{1}$$

$$\equiv \mathrm{Si} - \mathrm{OR} + \mathrm{HO} - \mathrm{Si} \equiv \;\leftrightarrow\; \equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv + \mathrm{ROH} \quad \text{(alcohol condensation)} \tag{2}$$

$$\equiv \mathrm{Si} - \mathrm{OH} + \mathrm{HO} - \mathrm{Si} \equiv \;\leftrightarrow\; \equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv + \mathrm{H_2O} \quad \text{(water condensation)} \tag{3}$$

Where R is an alkyl group and in the case of using TEOS as the silica precursor R: C_2H_5. During the hydrolysis reaction the alkoxide groups of TEOS are replaced by hydroxyl groups. In the condensation reactions the silanol groups produce siloxane bonds. Under most conditions condensation begins before hydrolysis is complete. The above reactions imply that ideally the stoichiometric water to TEOS ratio in order to have complete hydrolysis and condensation is 2. Among the processing parameters the pH of the starting solution has a strong influence on the final morphology by modifying the rates of hydrolysis and condensation.[16] Basic conditions lead to particulate and highly branched species whereas reaction performed in acidic media produces more polymer-like structures.

The sol-gel process performed in acidic conditions was chosen in this work with the aim of producing a continuous phase of silica covering the walls of the pores of PCL membranes. The low temperature synthesis characterizing the sol-gel technique allowed the in-situ production of the silica network in the presence of the polymeric organic phase. PCL-silica membranes were prepared by a two-step procedure. Initially, microporous membranes of PCL were produced by the freeze-extraction method and then the starting solution containing TEOS as the precursor of silica was introduced inside the pores of the membranes. The silica phase was produced by sol-gel reactions taking place inside the pores of the membranes. Critical processing parameters as the $r = \text{water/TEOS}$ ratio was varied from understoichiometric ($r = 1{,}6$) to a value implying a high excess of water ($r = 8$). Furthermore, different processing conditions namely the time of ageing (from 2h to 24h) and the usage of vacuum for drying was also employed. The influence of the above processing parameters in the composition and the mechanical properties of the prepared membranes as well as on dissolution properties of the silica network were studied.

Materials and Methods

PCL Membranes Prepared by Freeze Extraction

PCL microporous membranes were prepared following the freeze extraction technique.[17] Solutions of polycaprolactone (Sigma Aldrich, Mw = 70 000–90 000 (GPC)) in 1,4-dioxane (Scharlab, reagent grade) at a concentration of 10% (W/V) were stirred until its complete dissolution at room temperature (RT). The solution was poured into Teflon crystallizers in order to obtain membranes with 1-2 mm thick membranes. Teflon crystallizers were quickly immersed in liquid nitrogen for 3-4 min until the solution becomes opaque and white. Then, membranes were covered with cold ethanol and they were stored at −20°C. Ethanol was changed 2 times each day during 3 days to dissolve dioxane. Membranes were dried at room temperature, RT, in vacuum desiccators for 48h. Finally, membranes were cut into appropriate shape.

Sol-Gel Reaction

Sol-gel reaction was performed in acid medium with tetraethylorthosilicate (TEOS, Sigma-Aldrich, reagent grade 98%) as a precursor. The molar composition of the sol was TEOS: water: ethanol: HCl (10% V/V in water) 1: x: 1: 0.0185, where x was 1.6, 2, 4 or 8 in the different samples.

Solutions were stirred at RT for 1h and then were introduced into the porous PCL membranes (previousy subjected to high vacuum for 5min to extract air from the pores) and leaving samples immersed into TEOS solution 15 min at RT. All samples were superficially rinsed with water:ethanol 2:1 (V/V) before drying. The hybrid materials are designated as PCL-SI rX, with X corresponding to the water/TEOS ratio.

The protocol of drying was modified in order to study its influence in the final coating morphology and properties. Samples with sol molar ratio TEOS: water: ethanol: HCl 1: 1.6: 1: 0.0185, were prepared with four different ageing treatments: 2h, 6h or 24h at room conditions and 30 min in vacuum at RT and designated from now on as PCL-SI r1.6 24h, PCL-SI r1.6 2h, PCL-SI r1.6 6h, PCL-SI r1.6 and PCL-SI r1.6 30min vac, respectively. Then, in all cases, drying was performed at 40°C for 24h. Finally, samples were kept into desiccators until their characterization.

Materials Characterization

Microstructure was assessed by means of Scanning Electron Microscopy (Jeol JSM-5410), cryofracturing samples after their immersion in liquid nitrogen. Copper sample-holders were used and samples were sputtered with a gold layer. An accelerating voltage of 10kV was used. Silica phase distribution was assessed by Energy Dispersive X-ray Spectroscopy (EDS, Oxford Instruments). Samples for EDS elemental analysis were sputter-coated with carbon.

Porosity was measured by a gravimetric method. Dry samples were weighted before and after their immersion in ethanol under vacuum conditions. Porosity, ϕ, was calculated as shows Eq. 4. Briefly, it is the ratio of the weight of the volume pores to the total volume of the sample assuming negligible the mass of ethanol absorbed by the bulk material.

$$\phi = \frac{V_{pores}}{V_{pores} + V_{mat}} = \frac{m_{et}/\rho_{et}}{m_{et}/\rho_{et} + m_{mat}/\rho_{mat}} \tag{4}$$

m_{et} is the mass of ethanol absorbed by the membrane and m_{mat} is the mass of the dry sample; ρ_{et} is the density of ethanol and ρ_{mat} is the density of bulk PCL in pure PCL membranes ($\rho_{PCL} = 1.145\ g/cm^3$).[18] In the hybrids the density of the silica phase ρ_{SiO2} inside the pores was calculated with Eq. 5, by using the bulk material density (ρ_{hyb}) measured by immersion in ethanol with the technique based on Archimedes' principle.

$$\frac{1}{\rho_{hyb}} = \frac{1 - w_{si}}{\rho_{PCL}} + \frac{w_{si}}{\rho_{Si}} \tag{5}$$

Where w_{Si} is weight fraction of silica in the hybrid.

The thermal properties of samples were studied by thermogravimetric analysis (TGA) using a SDT-Q600 (TA-Instruments) equipment in nitrogen atmosphere with a constant heating rate of 10°C/min from room temperature to 650°C. Simultaneously with the changes in the mass of the sample, the heat flow was recorded during the heating scan.

Indentation tests were performed in a Seiko Extar 7ss6000 (Seiko Instruments) using a 0.785 mm^2 flat ended cylindrical indenter on dry samples. Ramp forces at 0.05 N/min for all samples were applied up to a force of 1N.

The weight loss of membranes due to silica dissolution was assessed by weighting after immersion in distilled water (pH 7.4) at 37°C. The weight loss was recorded after 1, 3 and 6 days while water was exchanged every day.

Results and Discussion

Microstructure

Freeze extraction produces a membrane with a network of well interconnected pores with sizes in the order of few microns

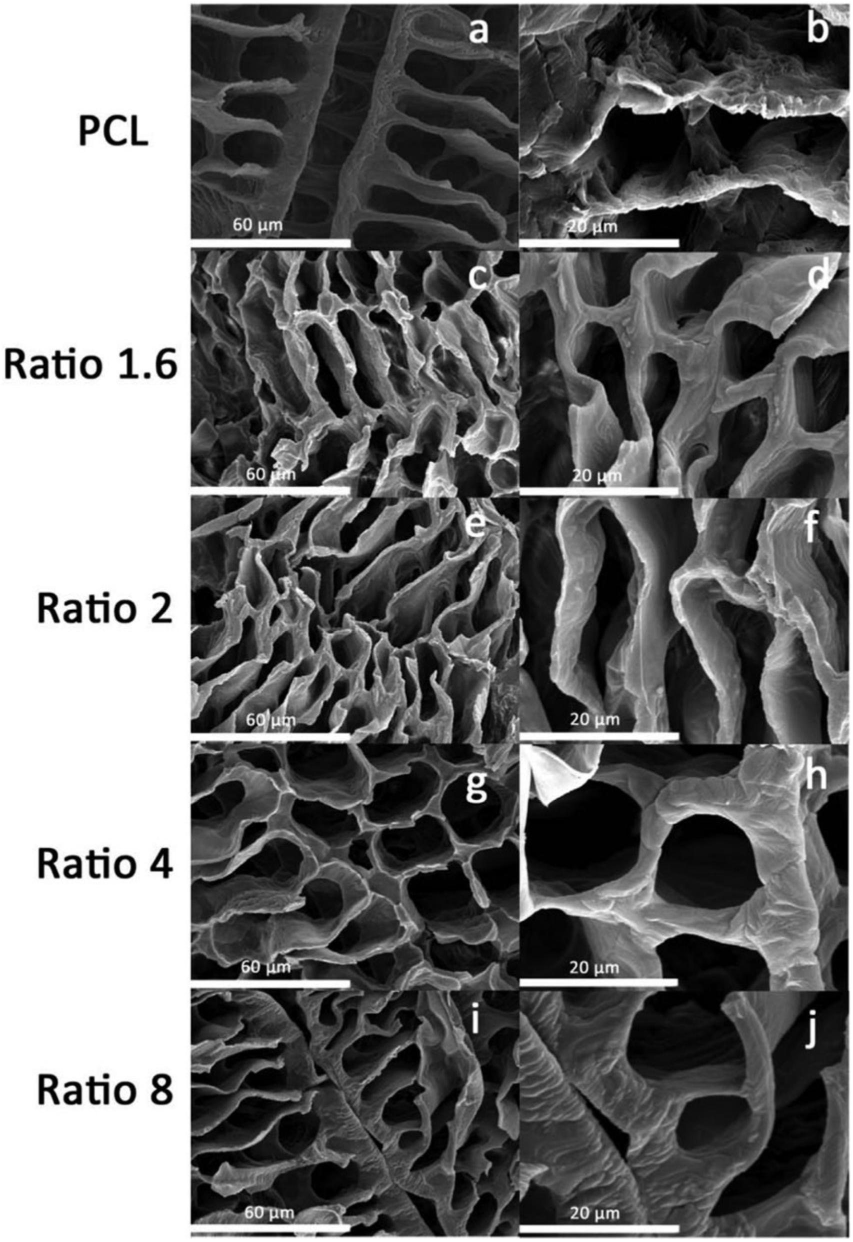

Figure 1.
SEM images showing the different coatings formed on pore walls of PCL membranes by changing water:TEOS molar ratio (1.6, 2, 4 and 8).

(Figure 1a), Figure 1b shows at a higher magnification the roughness of the pore walls. Pore interconnectivity allows that the silica precursor solution penetrates in the whole sample filling all the pores. It was shown in previous papers that sol-gel reaction taking place while the sol is confined in the pores of a polymer could yield a variety of silica phase micro or nanostructures depending on the capacity of the precursor to penetrate into the polymer matrix and on the catalyst used. Thus, sol-gel reaction performed into a microporous membrane of poly(hydroxyethyl acrylate) yields a non-porous composite with a silica phase consisting in interconnected nano and micro-domains[19] because silica is in part formed into the nanopores of the hydrogel and in part in the macropores of the membrane, and silica interconnectivity collapses any remaining empty spaces. When silica is formed into the pores of a polycaprolactone membrane the polymer is not swollen by the precursor solution and silica is formed as a coating of the pore walls if sol-gel reaction is performed at low pH or as dispersed microparticles loosely adhered to each other or the pore walls if performed at high pH.[20]

In this work we have used an acid catalyzer to ensure the formation of a coating silica layer as shown in Figures 1 and 2. It has been shown that the formation of silica film coating a surface is highly influenced by the flexibility of silica network when reaction progresses.[21] The water/TEOS ratio determines the extent of hydrolisis at the beginning of the condensation of silica network. In our work this ratio ranged from well below the stoichiometric ratio to a high water excess. In all cases a continuous layer of silica is formed on the PCL surfaces. In fact in Figure 1 the appearance of the electron microscopy picture is similar to that of the original PCL membrane. The increase of weight of the sample after the sol-gel reaction (Table 1) probes the presence of silica phase.

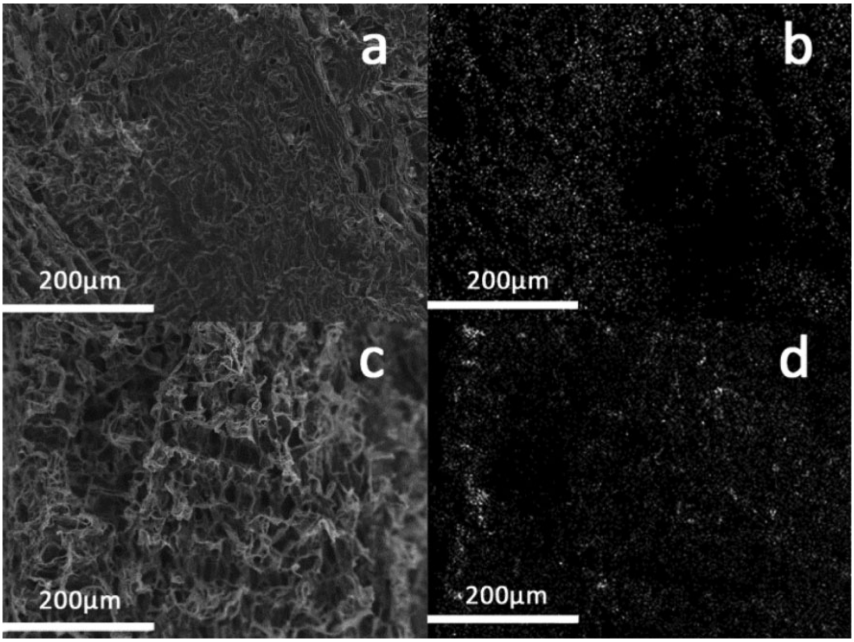

Figure 2.
SEM micrographs and EDS mapping of the surface (a and b) and cross-section (c and d) for the PCL-SI r1.6 membrane.

Table 1.
Results for the porosity and silica content obtained by gravimetric techniques and TGA.

sample	Silica Content[a] %	Silica density g/cm^3	Porosity %	Silica Residue[b] %
PCL	0	0	82 ± 2	0
PCL-SI r1.6	53	1.80	53 ± 2	41.3
PCL-SI r2	46	1.72	63 ± 2	40.8
PCL-SI r4	45	1.55	64 ± 2	31.0
PCL-SI r8	30	1.54	65 ± 2	23.1
PCL-SI r1.6 6h	52	1.76	58 ± 2	42,7
PCL-SI r1.6 2h	53	1.66	61 ± 2	43,6
PCL-SI r1.6 30min vac	52	1.69	59 ± 2	43.6

[a] Calculated from the difference of weight before and after sol-gel reaction.
[b] Residue from TGA.

The homogeneity of the silica phase was also confirmed by EDS mapping in both the surface and the cross section of the samples. Figures 2a and 2b present SEM micrographs corresponding to the surface and cross section of PCL-SI r1.6 membrane while Figure 2b and 2d depicts the spatial distribution of silica atoms of the same areas respectively. The ratio of oxygen to silica atoms was evaluated giving a value of 2.82 ± 1.08 at the surface and 3.51 ± 0.61 at the cross section. The theoretical expected O/Si atomic ratio for silica (SiO2) would be 2, nevertheless, the obtained value is slightly higher because of the presence of oxygen atoms in PCL chain. On the other hand, after calcination of the sample in air atmosphere at 800°C with complete elimination of the polymeric component, the sample is still coherent (result not shown).

The porosity of the hybrid membranes is much smaller than that of pure PCL, what shows that a thick coating has been formed on the pore walls, reducing the volume of the pores (Table 1). The freeze extraction method performed with the immediate freezing at −80°C of the initial solution of PCL with 10%v.v in dioxane yielded to PCL membranes with a porosity of 82%. After the completion of sol-gel reactions the lowest porosity is obtained for the PCL-SI r1.6 and the highest for PCL-SI r8 with values of 52 and 65% respectively. Interestingly, the membranes with r = 2, r = 4 and r = 8 present values of porosity very close to each other, namely 63, 64 and 65% respectively. Furthermore, the density of the silica phase decreases by increasing water content.

Drying protocol does not affect neither silica content or membrane porosity (Table 1) nor the morphology of silica coating of PCL surfaces (Figure 3). A uniform and continuous layer is obtained in all the samples. An increase of the density of the silica phase is observed when the time of ageing is increased indicating that when more time is given for the network formation a more close-packed structure is obtained. The above significantly influences also the mechanical properties, as we will see below what informs about the different nanostructure of the silica film formed.

Thermal Properties

The TGA thermogram and the weight derivative (DTA) curves of pure PCL and PCL-SI membranes prepared with various processing parameters are presented in Figure 4. An initial weight loss at around 100°C could be seen in the thermograms of all samples except in that of pure PCL. The above weight loss is associated with the evaporation of water bound or trapped in the membranes. It is well known that PCL is a highly hydrophobic polymer[22,23] so it is reasonable not to observe a weight loss at that temperature range in the thermogram corresponding to pure PCL. On the contrary all the samples containing silica present a 3 ÷ 5% weight loss due to water evaporation. Silica presents a hydrophilic character due to

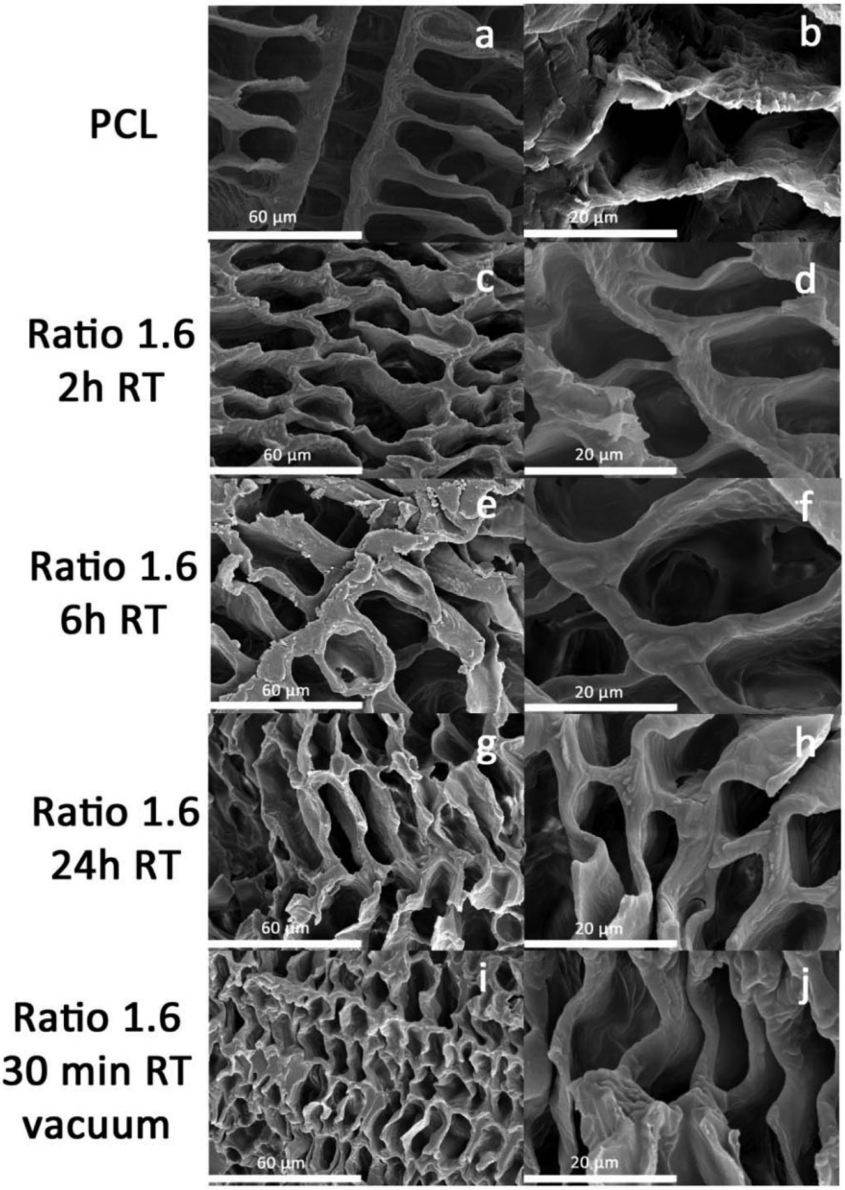

Figure 3.
SEM images of the different coatings formed on pore walls of PCL membranes by changing the drying step (2h RT, 6h RT, 24h RT and 30 min RT using vacuum) being water:TEOS molar ratio 1.6. In all cases ageing was performed at 40°C for 24h.

the remaining silanol groups (Si-OH) which are always present in its surface. Previous studies have shown that the binding sites of silica prepared by sol-gel are already occupied by water molecules at a relative humidity level of 20% being the equilibrium water content around 10%.[24] The above result is in accordance with the observed weight loss up to 100°C in TGA analysis taking into consideration only the hydrophilic inorganic part of the membranes.

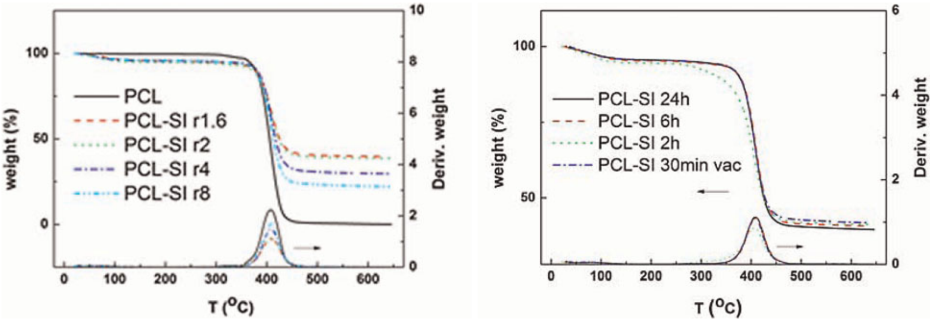

Figure 4.
TGA and DTG curves of pure PCL and PCL-SI prepared with different water/TEOS ratios (a) and with r = 1.6 but different ageing times.

By increasing the temperature the thermal degradation of the organic part occurs. All samples present similar degradation profile in one step which is depicted by only one peak in the DTA signal and is located around 408°C independently of the silica preparation procedure. The above behavior is typical for the thermal degradation of pure PCL.[25] The starting solution of the sol-gel process is not expected to be absorbed by the polymer bulk and on the other hand it should not react chemically with PCL pore wall surfaces. Rather, silica phase appears as a coating of the inside walls of the pores and thus not affecting the thermal properties of the organic phase. The latter observation holds true also for the melting temperature of the organic part of the samples which was followed by measuring the heat flow simultaneously with the weight changes during the heating scan (results not shown). The melting temperature obtained from the endothermic peaks of heat flow thermograms was around 65°C for all the samples, a typical value for PCL membranes.[26] TGA performed in nitrogen atmosphere allows also the compositional analysis of the samples. As can be seen from the curve corresponding to pure PCL no residue is observed at the end of the temperature scan up to 650°C. The above allows us determining the fraction of the inorganic part of the hybrids associated with the silica being inert up to the final temperature. The results are reported in Table 1 showing that the silica part in the membranes ranges from 23 to 43%. The values are smaller than those determined by the weight increase of the membrane in sol-gel reaction because non-reacted side groups of TEOS are lost during TGA scans. An increase of silica content with the decrease of water/TEOS ratio could be observed. Furthermore, the time of ageing and the use of vacuum at the ageing and drying procedure do not seem to affect the final silica content which in the case of the materials with water/TEOS ratio equal to 1.6 is about 42%. The latter indicates that the parameter that is critical for the final composition is the water/TEOS ratio. By increasing r and therefore the water content, the starting solution containing the silica precursor is more diluted. Consequently, introducing a more dilute solution of higher r into the PCL membranes, less quantity of the silica precursor enters inside the pores to form the silica phase after the completion of the sol-gel reaction. McDonagh et al[27] has shown that the film thickness of dip coated silica films employing sol-gel reactions at acidic conditions increases with water/precursor ratio. Even though in our case it is not possible to estimate the thickness of the silica layer covering the pore walls the decrease of silica content upon increasing water content would suggest a decrease of silica thickness meaning that the dissolution of silica precursor upon increase of water content is more crucial for the final structure.

Mechanical Behavior

Mechanical behavior was studied by employing indentation tests on both the surface and the cross-section of the prepared membranes. A cylindrical flat-ended indenter with a contact surface much smaller than the samples was used. In this type of measurements where a controlled time-dependent compression force is applied the obtained force-penetration curves allow the evaluation of the material Compliance.[28,29] Following the analysis of Hayes[30] with the procedure described in ref[19] the creep compliance of a sample with thickness h intended by a stiff flat-ended cylindrical indenter with radius α could be evaluated from the load (F) - penetration (w) curve through the Eq. (6):

$$J(t) = \frac{4ak}{(1-\nu)\left[\frac{dF}{dt}\right]}\frac{dw}{dt} \tag{6}$$

where k is a non-dimensional parameter which depends on the ratio, α/h, and the Poisson coefficient of the material, ν. The k values used for the calculations were obtained from ref.[30] by assuming $\nu = 0.4$.[19] Figure 5 depicts the force-penetration curves during a loading-unloading cycle up to a maximum force of 1N for the materials prepared with different water/TEOS ratio and processing parameters. The results of the analysis using Eq. 6 as well as the penetration for each sample at the maximum load are shown in Table 2. Higher compliance and deeper penetration is observed for the pure PCL as expected for a porous structure made from a flexible polymer. At room temperature PCL is in the rubbery state characterized by a low tensile strength (≈23MPa) and an extremely high elongation at break (>700%).[31] When silica is incorporated both the compliance and the penetration depth decreases significantly. As a general trend the stiffness of the membranes increases with the decrease of the water/TEOS ratio. This is more evident if one compares the values of compliance and maximum penetration depths of the samples prepared with r = 1.6 and r = 8 both for the measurements corresponding to indentation on the surface as well as on the cross section. The above variations in stiffness could be explained in terms of the differences in the content of the stiff

Table 2.
Results from indentation tests analysis for the membranes with different water/TEOS ratio.

sample	penetration at 1N μm	J m²/N
PCL cross section	577	$2.43 \cdot 10^{-6}$
PCL-SI r1,6 cross section	163	$0,.1 \cdot 10^{-6}$
PCL-SI r2 cross section	210	$0.87 \cdot 10^{-6}$
PCL-SI r4 cross section	197	$0.62 \cdot 10^{-6}$
PCL-SI r8 cross section	204	$1.12 \cdot 10^{-6}$
PCL surface	354	$1.50 \cdot 10^{-6}$
PCL-SI r1,6 surface	46	$0.16 \cdot 10^{-6}$
PCL-SI r2 surface	106	$0.24 \cdot 10^{-6}$
PCL-SI r4 surface	115	$0.34 \cdot 10^{-6}$
PCL-SI r8 surface	230	$1.06 \cdot 10^{-6}$

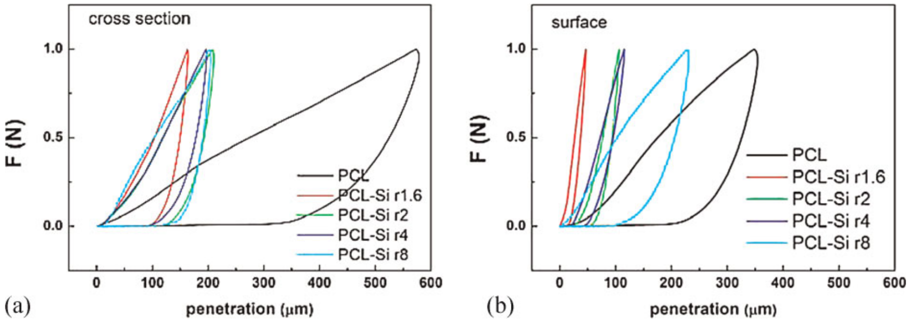

Figure 5.
Force-penetration curves obtained in indentation tests on the cross section (a) and surface (b) of pure PCL and PCL-SI porous membranes prepared with various r:water/TEOS ratios.

Table 3.
Results from indentation tests analysis for the membranes with water/TEOS ratio 1.6 using various preparation parameters.

sample	penetration at 1N µm	J m^2/N
PCL SI r1.6 24h	163	$0.51 \cdot 10^{-6}$
PCL SI r1.6 6h	178	$0.73 \cdot 10^{-6}$
PCL SI r1.6 2h	218	$0.87 \cdot 10^{-6}$
PCL SI r.6 30min vac	131	$0.52 \cdot 10^{-6}$

inorganic phase as well as of the stiffness of the silica network itself. As shown earlier in the compositional analysis from TGA, the content of silica decreases with water/TEOS ratio. Consequently the mechanical reinforcement of the membranes by the silica incorporation is higher when lower r ratios are used for the synthesis of silica inside the pores of PCL membranes. Figure 6 shows the force-penetration curves on the cross-section of the membranes prepared by varying the parameters of the drying procedure while the evaluated Compliance values are reported in Table 3. Higher penetration depth is observed when shorter time of drying is used.

The different nanostructures and perfection of the silica network formed can be revealed by its solubility. Weight loss of samples immersed in water for up to six days are listed in Table 4. Results are expressed as the fraction of silica lost with respect to the silica mass contained in the sample. Significant differences were found for samples prepared with varying water/TEOS ratios. As this ratio increases silica formed becomes more soluble what can be explained by the higher hydrolisis at the beginning of condensation reaction, in this conditions a stiffer network is rapidly formed and the lack of mobility leaves a more porous and imperfect structure.

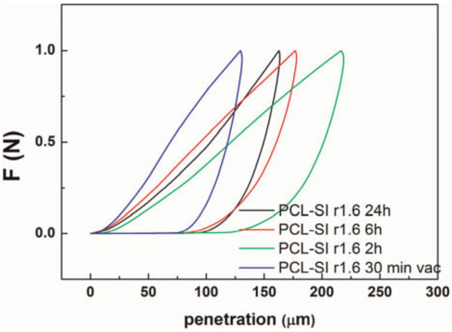

Figure 6.
Force-displacement curves from indentation tests on the cross section of PCL-SI 1.6 porous membranes prepared with various processing parameters.

Table 4.
Weight loss of the silica phase of the membranes after immersion in water.

sample	After 1day %	After 3days %	After 6days %
PCL	0	0	0
PCL-SI r1.6	3 ± 1	5 ± 1	8 ± 2
PCL-SI r2	1 ± 1	5 ± 1	7 ± 2
PCL-SI r4	1 ± 1	4 ± 1	11 ± 2
PCL-SI r8	2 ± 1	5 ± 1	15
PCL-SI r1.6 6h	1 ± 1	2 ± 1	5 ± 2
PCL-SI r1.6 2h	2 ± 1	2 ± 1	6 ± 2
PCL-SI r1.6 30min vac	2 ± 1	2 ± 1	5 ± 2

Conclusion

PCL microporous membranes were reinforced with an inorganic silica using sol-gel. Firstly, PCL membranes with a porosity of 82% were obtained by the freeze extraction method. In a second stage the silica inorganic part was synthesized inside the pores of the membranes by sol-gel reactions performed in acidic conditions and using TEOS as the precursor. The water to TEOS ratio, r, was varied as well as the drying protocol and the influence on composition, morphology, thermal and mechanical properties was studied. SEM analysis revealed the microstructure of the obtained hybrids composed by a continuous silica phase covering the pore walls for all the prepared membranes. TGA was used to study the influence on thermal properties and to evaluate the composition. The silica content decreased from 41.3 to 23.1 wt % by increasing the water content. The variations in the inorganic content influenced also the mechanical properties as probed by indentation tests on both the surface and the cross section. The stiffness was increased upon decreasing water content in the initial sol-gel solution. Finally, slower solution of the inorganic part in water was observed for the membranes with lower r. The above findings suggest that the variation of the processing parameters of sol-gel and especially the water content provides a practical tool for tailoring the microstructure, the mechanical properties and the release profile of silica in hybrid porous membranes, the latter being in a co-continuous phase with the organic polymer.

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