Bio-Sintering

Bio-Inspired Hydro-Pressure Consolidation of Silica

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Room-temperature hydro-pressure-driven densification of amorphous silica (nanoparticles and microbeads) is developed. This technique is inspired by biological silicification with reference to dissolution, precipitation, and hardening mechanisms. Cold sintering based on uniaxial pressure is taken as a benchmark. Starting from a green-body relative density of 70%, densification exceeding 99% is achieved by adding distilled water or caustic solution to an amorphous powder under a hydrostatic pressure of 450–600 MPa for 5-30 min. Translucent samples are obtained. Silica microbeads are employed as a model system to define the effect of the sintering parameters: pressure, pH, and soaking time. Densification is attained through a preferential precipitation of a second phase from silica dissolution under hydro-pressure. Precipitation is governed by minimization of the surface energy (Ostwald ripening). Transmission electron microscopy, NMR, thermal gravimetric analysis/differential scanning calorimetry, and Fourier transform infrared spectroscopy reveal the mechanisms of the process and the analogies with biosilicification.

1. Introduction

The natural formation of calcium-based complexes in many living organisms, such as bones, teeth, egg shells, and the invertebrate skeletons, is governed by a process known as biomineralization.^[1] A minority of these processes, as in the case of diatoms and sea sponges, are based on silicon dioxide. The process that incorporates inorganic silicon in living organisms is called biosilicification.^[2,3]

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dioxide is achieved by densification of powders through a thermally activated technique, known as sintering. The initial powder is shaped into a green body, and subsequent heating $(>0.5T_m)$ gives rise to atomic diffusion resulting in minimization of the surface energy. The relatively high melting point of inorganic compounds motivated researchers to focus on low energy consumption methods, e.g., cold sintering process (CSP).^[4,5] The latter relies on the combined effect of temperature (typically below 300 °C) and uniaxial pressure applied to a moisturized powder. A densification >90% for BaTiO₃ was achieved using a uniaxial pressure of 430 MPa and temperature up to 180 °C with a dwell time of 3 h.^[4]

Traditionally, the consolidation of silicon

Biological organisms cannot survive temperatures experienced during CSP or conventional sintering, as the essential

bio-features (proteins, DNA) governing these processes would suffer an obvious thermal degradation.

Here, we report the densification of silicon dioxide particles, achieved through dissolution and rearrangement of silicate species from silica sources, which has some analogies with biosilicification of diatoms. The presence of dissolved silicic acid species (Si(OH)₄) in seawater (around 169 µmol L⁻¹ in the North Pacific Ocean)^[6] is the actual feedstock of silica-based skeleton formation. In this process, the biological mechanisms of transportation and deposition of the silicate species are governed by proteins (long-chain polyamines) contained in specialized cells, forming a honeycomblike structure. The strengthening of the structure is then obtained through polycondensation reaction of deposited species.^[1,7-10] In sea sponges, like desmosponges or hexactinellids, silica is also synthesized by proteins (silicateins) within specialized cells in a lamella-like configuration, called spicules, but in this case, the process is more complex and still not completely understood.^[2,3]

Our work presents an innovative physically driven technique for densification, which tries to emulate, on a simplified level, the intelligent mechanisms behind the process of biosilicification. The newly developed hydro-pressure sintering (HyPS) employs a sealed chamber where powders are pressed along with a suitable liquid. This process is achieved at room temperature, opening up endless possibilities for organic-inorganic integration. As reference materials, we demonstrated HyPS using amorphous silica nanoparticles and microbeads mixed with distilled water or caustic solutions. Learning from the sophisticated bioprocesses in nature might allow intelligent methodologies to grow hybrid organic-inorganic materials, with hierarchical self-organized structures, as in the case of natural metamaterials, known for their unique thermal, electrical, and optical properties.^[11] Full or partial consolidation of particles allows tuning of the above-mentioned properties.







Figure 1. Biosilicification in diatoms. a) Thalassiosira pseudonana diatom (credit to University of Washington). b) Biosilicification mechanisms in the formation of hierarchical silica-based honeycomb-like structure of diatom skeleton.

2. Results and Discussion

2.1. HyPS of Silica Microbeads

The supply of silicates for the formation of diatoms (Figure 1a) is fostered by the hydrostatic pressure (\approx 150 MPa at 100 m) and pH (very variable depending on the geographic zone) of the deep sea as these conditions will influence the solubility limit.^[12,13]

Similarly, in the HyPS process, while the suspension of silica particles is pressed under hydrostatic pressure, the solution is enriched with dissolved silicate species. Under these conditions, we observed an accelerated dissolution of fine particles and a localized rearrangement of the silicates in high surface energy spots, e.g., big particles' surface and contact points between particles. This mechanism, known as Ostwald ripening,^[14–16] is described in detail in Figure S1 and Table S1 in the Supporting Information.

The driving force for Ostwald ripening is the pressureinduced silica dissolution and the minimization of the surface energy where small particles are more unstable than larger ones.^[14] Migration of the silicate species from the dissolved small particles to high surface energy points can happen in the liquid state under relatively high pressure, as demonstrated by the simulation model of hydro-pressurized sodium silicate

conducted by Noritake and Kawamura.^[17] Therefore, the physical dynamics leading to Ostwald ripening are responsible not only for selective dissolution, but also for species transportation and preferential precipitation. A similar scenario applies to specialized proteins belonging to diatoms, i.e., long-chain polyamines (LCPs), contained in specialized intracellular compartments, called silica deposition vesicles (SDVs).^[10] These proteins guide the silica species precursors (silicic acid) toward the periphery of the SDVs and segregate in droplets, leaving behind a core deficient in silica. Consequently, a hexagonal monolayer is formed (stage 1 of deposition in Figure 1b). The silica uptake in SDVs is governed by a Na⁺-dependent transporter protein (termed SIT).^[18] By repeating this process in a structured manner, a honeycomb-like structure is formed (last stage in Figure 1b).^[1,10] The controlled precipitation of silica from a silicic species reservoir (SDV) has some analogies with Ostwald ripening in HyPS. The Ostwald ripening, being a physical mechanism, is not as "intelligent" as in DNA-based organisms, but similarly, it drives a preferential dissolution/precipitation of the silica species.

Following the progression of HyPS, the consolidation mechanisms were divided into four stages (Figure 2a): 1) clustering of the particles, 2) compaction and silica dissolution, 3) preferential precipitation of the second phase, and 4) water evaporation and polycondensation. Figure 2b,c reports evidence in support of the proposed model.







Figure 2. Densification model of HyPS. a) Description of the model: 1—clustering of microbeads, 2—compaction and dissolution, 3—preferential precipitation of the second phase, 4—polycondensation. b) SEM image of a consolidated HyPS sample and neck formation. c) A close-up of a pore, by which the model was built.

Stage 1. Once the particles (MB in Figure 2a) are mixed with the solution, they come together and sediment (clustering in stage 1, Figure 2a). In colloidal chemistry, this condition of clustering and sedimentation is known as unstable suspension.^[19] The rate of aggregation of a suspension is dependent on the pH and zeta potential of the solution.^[20,21] This mechanism occurs immediately after the mixing of the powder and solution, prior to and during application of hydro-pressure.

Stage 2. After application of hydro-pressure, the surface of the particles dissolves, releasing silica species $(Si(OH)_4)$ until saturation of the solution is reached. At this point, the saturated solution (light gray in stage 2, Figure 2a) homogeneously surrounds the compacted powder.

Stage 3. Under the effects of Ostwald ripening, the formation of necks is locally favored by surface energy peaks at the

interparticle contact points (formation of necks in stage 3, Figure 2a). Figure 2b evidences neck formation between two microbeads (MB in stage 3, Figure 2a). The silicate species in HyPS preferentially migrate and precipitate, leaving behind a core phase deficient in silica and possibly porous (analogous to precipitation in SVDs). These species then rearrange and condense to form a second phase rich in silicon (SP in stage 3, Figure 2a). This process spontaneously activates at room temperature when the solution is above its solubility limit (typically ≈ 100 ppm, $\approx 1 \times 10^{-3}$ M).^[3] The rate of species rearrangement through the liquid phase, hence the chemical nature of the SP, strictly depends on the pressure and the soaking time.

Stage 4. As the pressure is released, a further precipitation occurs, due to a sudden decrease of the saturation limit. The sample is then cured and the polycondensation reaction of the



SP progresses (stage 4, Figure 2a). This stage is analogous to the biosintering stage of diatom formation, in which the silica precipitate starts to harden due to the polycondensation reaction. Unlike the segregation process in SDV, which occurs in a few minutes, the biosintering stage takes weeks.^[1,2] In the HyPS process, the polycondensation/curing step can be optimized with respect to temperature and humidity and can last for a week.^[22] The early stage of the reaction consists of a coalescence of monomers and dimers into cyclic species through a chemical conjunction of hydrate groups, with the release of water (polycondensation in Figure 2a). Once the oligomers and cyclic species are formed, the second stage of the condensation process yields the coalescence of these species (polycondensation) to form more intricate and structured networks made of silicon with bridging oxygens (chains and cross-linked network). The process of polycondensation naturally induces a shrinkage, as the size of a silicate monomer (Si(OH)₄) was calculated to be 4.48 Å, whereas the dimension of one silica unit (SiO₂) incorporated in a polycondensed structure is only 3.56 Å.^[2,23] The released water can be entrapped as either physical or chemical water, which evaporates during the curing process. Thermal gravimetric (TGA) and differential scanning calorimetry (DSC) analyses of the dried sample were carried out to detect the presence of any physical water after curing and results are reported in Figure 3. The analysis of the TGA curve revealed an initial weight loss until 150 °C of about 4%, attributed to dehydration of absorbed water, and a second and continuous weight loss from 230 °C until 800 °C due to dehydroxylation of silanol groups (Si-OH).^[24,25] The latter is also confirmed by the endothermic peak in DSC curve (Figure 3),



Figure 3. TGA (black solid line), DTG (red dash line), and DSC (blue dash-dotted line) of HyPS dried silica samples in water, operated until 900 °C through a temperature ramp of 10 °C min⁻¹.

which determines the onset of the dehydration of OH group from silanol.^[25-27] Nevertheless, no peaks related to possible evaporation of internal water were detected, meaning that physical water evaporates during the curing step, most likely due to diffusion of water molecules through the SP from the core to the surface as the polycondensation proceeds. The effectiveness of the polycondensation depends on the ratio between the number of hydrates and silicates in composition, temperature, and pH.^[3,28,29] Due to this process, the SP undergoes a chemical transformation over a period of weeks, which increases its stiffness. The HyPS process applied on silica microbeads allows a densification exceeding 99%, regardless of the process conditions (pressure, type of solvent, soaking time). Details on the relative density assessment of the silica microbead HyPS samples are reported in Figure S2 and Table S2 in the Supporting Information.

An assessment of the chemical nature of the second phase can be provided by transmission electron microscopy (TEM), Fourier transform infrared (FTIR) and NMR spectroscopies performed on the silica microbead HyPS samples. The most significant information is provided by chemical analysis performed through TEM analysis. As depicted in **Figure 4**, the base material has approximately 40–60 at% of silicon–oxygen. The SP (Figure 4) has a variable content of silicon and oxygen, rich in oxygen and depleted in silicon in its core, confirming that Ostwald ripening mechanisms apply. Similar results were attained by Wang et al.,^[30] who performed a line scan energydispersive X-ray analysis (EDX) on biosintered spicules. These authors detected a silicon depletion corresponding to the junction of two spicules, suggesting a similar sintering mechanism.

Figure 5 shows the IR spectra of the silica microbeads as received (black solid line), in comparison to the HyPS sample spectra both immediately after the release of the pressure (red solid line) and after one week of air drying at ambient temperature (blue solid line). The wide absorption band at 800-1200 cm⁻¹ is in common among all the spectra, which is associated with an asymmetric stretching vibration of the Si-O-Si (siloxo bonds).^[31-33] This wide band is normally composed of many peaks, localized around 1200, 1100, 950, 900, and 850 cm⁻¹, related to SiQn silicon networks, where n = 4. 3, 2, 1, and 0, respectively,^[32] which refers to a silicon-based network, with n the number of silicons surrounding a given Si atom.^[32] This absorption band for the HyPS sample before drying has a lower intensity than the other two spectra (thus lower Si-O-Si content), and it is centered in lower wavenumbers, meaning higher presence of poorer interconnected species (SiQ² and SiQ¹). The HyPS sample after drying presents two sharp peaks at 1008 cm⁻¹ (SiQ⁴ and SiQ³) and 949 cm⁻¹ (SiQ²), something not observed in the silica as received, suggesting a lower presence of SiQ⁴ and SiQ³. The higher presence of low connectivity is due to the depletion of silicon in the core of the SP (see TEM in Figure 4). Other chemical insights are provided by the absorption bands in mid-IR (below 750 cm⁻¹). The first series of bands denotes the vibration of possible configurations of cyclic silica species,, i.e., three-membered rings (720–700 cm⁻¹), four-membered rings (\approx 640 cm⁻¹), and six-membered rings (620-600 cm⁻¹).^[34,35] Figure 5 evidences a shift in this absorption band toward the left as the hydro-pressure is applied (red line), suggesting a higher





Figure 4. TEM chemical analysis conducted on a microbead-based HyPS silica sample pressed in water at 450 MPa for 30 min.

presence of three-membered rings, readily formed from the condensation of three Si(OH)₄ species (polycondensation in Figure 2c). Since the orthosilicic acid is chemically unstable at concentrations higher than the solubility limit, these species rearrange in a cyclic ring, immediately after the pressure release, demonstrating that the orthosilicic acid is the product of dissolution. The broad band at 2600–3400 cm⁻¹ in the HyPS sample before and after drying and the peak at 1663 cm⁻¹ are associated with stretching vibration of the -OH group (silanol) and H–O–H bonds (chemical water), respectively.^[31] denoting that after polycondensation (and after drying), molecular water remains entrapped in the silicon network. Finally, a sharp band at ≈790 cm⁻¹ was only detected in the HyPS sample after drving, associated with a symmetric stretching vibration of the Si-O-Si bond,^[32] normally weaker than the asymmetric one ($\approx 1000 \text{ cm}^{-1}$), which might influence the mechanical performance of the HyPS sample. The latter peaks (2600-3400, 1663, and 790 cm⁻¹) are equally prominent in FTIR spectra of biosintered materials (spicules), as reported by Wang et al.^[30] The same peaks do not appear with the same intensity when silica is densified using other methods,^[25] meaning that the presence of water (silanol bonds, physical and chemical water) in both biosilicification and HyPS is a unique signature of the process.



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Figure 5. FTIR spectroscopy conducted on silica microbeads as received (black line) and microbead HyPS sample processed under 450 MPa in water for 5 min before (red line) and after one week of air drying (blue line) in the range of wavelengths between 4000 and 400 cm⁻¹.

The polycondensation reaction in the HyPS process is also confirmed by the ²⁹Si magic angle spinning (MAS) NMR spectroscopic analysis carried out on raw amorphous silica (Figure 6a) and final processed HyPS silica samples (Figure 6b). In raw amorphous silica gel ²⁹Si NMR spectra, three characteristic chemical shifts are evident: the first one falling in the range -92 and -94 ppm representing the SiQ² ambient, the second centered between -102 and -105 ppm attributed to the SiQ3 species, and the last chemical shift between -111 and -113 ppm characteristic of the SiQ⁴ network.^[36-39] The deconvolution of spectra showed a lower amount of SiO² species than SiQ³ and SiQ⁴. Once the HyPS process is carried out, the SiQ⁴ ambient (51.38%) is reduced in favor of SiQ² and SiQ³ increments (2.07% and 46.55%, respectively), due to the silicadeficient nature of the core of the SP. The higher amount of SiQ² ambient is justified by a higher level of hydration of the SP. These results are in good agreement with the TEM and FTIR spectroscopy, and demonstrate a rearrangement of the dissolved species in oligomers and silica rings (SiQ² ambient) as predicted by the model reported above, confirming a polycondensation reaction of the orthosilicic acid species. This suggests some analogies with biosilicification, where the biosintering of the diatoms is carried out by means of polycondensation. For comparison, Figure 6c shows the results from cold sintering of amorphous silica samples processed under 450 MPa at 200 °C kept for 2 h.^[4] In contrast to the previous results, the sample from the cold sintering method reveals a slightly higher percentage of SiQ⁴ (60%) and lower amounts of SiQ² (0%) and SiQ³ (40%) (Figure 6c), suggesting a different mechanism governing the CSP process. This pattern shows good match with



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Figure 6. ²⁹Si MAS NMR spectroscopy conducted on a) silica microbeads as received and b) microbead HyPS sample processed under 450 MPa in water for 5 min after one week in air-drying. c) CSP sample processed under 450 MPa, at 200 °C, in water for 2 h. SiQn denotes the single silica species.

silica densified by hydrothermal sintering, suggesting similar mechanisms between these two techniques.^[25]

2.2. HyPS of Amorphous Nanosilica

Amorphous silica nanoparticle samples were processed by HyPS, giving relative densities of 99.99%, 99.95%, and 99.95% at 600 MPa in water, 450 MPa in water, and 450 MPa in NaOH (0.5 M), respectively, all of them for a total duration of 5 min. Processing times compared to the microbeads were shortened because of the high specific surface area of the nanopowder. This material was previously densified at room temperature under a hydrostatic pressure of 4.5 GPa.^[40,41] The significance of the HyPS process is that it allows production of dense silica samples at room temperature (22–25 °C), with pressures ten times lower than previously reported. The values of the relative densities are higher than HyPS silica microbead samples, irrespective of the adopted HyPS parameters.

The SiO₂ sample processed at 450 MPa in water also revealed translucency (see Figure S3 in the Supporting Information), due to the extremely high relative density of the sample approaching 100% as also observed in the sintering of transparent α -alumina reported by Petit et al.^[42]

Vickers microindentation tests carried out on nanosilica HyPS samples (450 MPa in water, 5 min) gave an average HV 0.2 hardness value (from ten indentations) equal to 155 (1.52 GPa), four times lower than a silica-based sintered material,^[43] and only half the value reported for nanoindentation on biosintering products,^[44] or a silica product made through hydrothermal sintering.^[25] Surprisingly, the indentation fracture toughness (IFT) calculated by measuring median cracks on indentations gave 0.7 MPa m^{1/2}, in line with the IFT of silica sintered ceramics.^[43] Nanosilica samples processed by the CSP method (450 MPa, 200 °C, water, 2 h)^[4] resulted in low density, gave an HV 0.2 hardness equal to 32 (0.31 GPa), and showed no evidence of cracks. In the case of silica, unlike HyPS,

CSP was ineffective in producing dense materials (a detailed study of the mechanical properties is reported in Figure S3 in the Supporting Information).

These results are even more surprising if one considers that the HyPS process is an accelerated method of densification inspired by the more intelligent biosilicification process. The effectiveness of the HyPS process in distilled water at ambient temperature makes this method totally eco-friendly and suitable for practical applications (optical properties, bioceramics, electrical conductors, etc.). Future work, taking inspiration from nature, should look at the development of intelligent organic–inorganic hybrid structures using HyPS.

3. Conclusion

In this study, an innovative method of powder densification, inspired by the biosilicification in diatoms and named hydropressure sintering, was carried out for the first time by pressing a suspension of amorphous silica microbeads/nanoparticles in water and caustic solution, though the technique itself is extendable to many types of materials. Image analysis showed a relative density always higher than 99%. This HyPS process was thought to follow four stages: 1) clustering, 2) compaction and dissolution, 3) second-phase preferential precipitation, and 4) polycondensation. The first three stages are governed by the minimization of the surface energy (Ostwald ripening). The last stage induces a hardening of the material over time and water evaporation proved by the TGA analysis. TEM revealed a variability of the chemical composition of the second phase, as observed in EDX of spicules. FTIR spectra showed that after drying the HyPS sample experienced a shift of the characteristic bands toward lower wavenumbers, suggesting a rearrangement of the product of dissolution. An absorption band relative to the -OH bonds vibration was observed in HyPS samples but not in silica as received, suggesting a partial hydration of the second phase. These peaks are typical for biosintered materials

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(spicules). ²⁹Si NMR confirmed this rearrangement showing a change in intensities of the characteristic chemical shifts, with a high presence of less structured species in the HyPS sample. This demonstrated a polycondensation reaction occurring in the second phase. ²⁹Si NMR on cold-sintered samples showed a cross-linked silicon network, suggesting different involved mechanisms. The HyPS process was also applied to nanosilica, showing translucency and mechanical properties comparable to sintered silica ceramics and biosintered products.

4. Experimental Section

Materials: Three types of silica particles were used: microbeads (1 µm) (Cospheric LLC, Santa Barbara, USA) with a narrow particle size distribution to define/understand the HyPS densification model, microbeads with a widespread particle size distribution (9–13 μ m) to understand the Ostwald ripening mechanism, and nanosized silica to allow full densification of translucent samples, all of them purchased from Sigma-Aldrich. Distilled water and NaOH (0.5 M) were used to investigate the influence of the media. NaOH pellets were purchased from Sigma-Aldrich (ACS reagent, 97%, pellets) and 20 g was dissolved in 1 L of distilled water, by way of achieving the desired 0.5 M concentration. Amorphous microbeads were also instrumental in understanding the dynamics involved in the process. Silica nanometric amorphous powder (20-50 nm) from Sigma-Aldrich was also employed. The powder was densified in distilled water and NaOH solutions. The liquid to solid ratio (I/s) was appropriately selected to ensure the fluidity of the slurry, as it is dependent on the particle size, and pH of the aqueous solution. In the microbead-water system, a ratio between 0.3 and 0.4 was sufficient to yield compaction, whereas, for the nanosilica-water system, a higher ratio of 0.6-0.8 was required, due to the larger specific surface of the powder.

Experimental Setup for HyPS: Sintering of the slurry was performed with an evacuable die normally used for FTIR samples and installed within a screw-driven testing machine Zwick Z250. The evacuable pellet die used in all the experimental cases was purchased from Specac Company, including one die body and base, one plunger, and one stainless steel cylinder, with a nominal hole size of 13 mm (die to cylinder clearance = 0.02 mm). Once the mixture of powder and solution was put in the die chamber, the system was then sealed to leakproof, loaded into the compression testing machine, and kept under uniaxial load (P = 60 kN) for a time frame of 5–30 min. The leakproofness was tested using pure water. One of the differences between HyPS and CSP was the use of a leakproof setup. For the duration of a single experiment, the temperature was kept constant at room temperature (22–25 °C). To compare HyPS and CSP, powders were also sintered using a similar setup without leakproof sealing.^[4]

TEM and Focused Ion Beam (FIB) Analysis: Point-to-point resolution 0.3 nm transmission electron microscope (Philips CM12 STEM) was used for high-magnification observations. The microscope was equipped with a large tilting goniometer (\pm 45° main tilt and \pm 20° transversal tilt) working in both TEM and scanning TEM (STEM) regimes and equipped with ultrathin window EDAX X-ray analyzer for chemical evaluations. The lamellae cutting was done with a scanning electron microscope (Tescan LYRA 3XMU FEG/SEMxFIB).

SEM Observation and Relative Density Evaluation: The observation of the microstructure was conducted on polished samples (1 μ m diamond paste) mounted in epoxy resin, through high-definition SEM microscopy, using a Tescan LYRA 3 XMH FIG/SEM microscope equipped with an X-Max 80 EDS detector for X-ray microanalysis. Once the micrographs were captured, the quantification of the porosity was performed on samples through image analysis, with the relative density calculated by measuring the percentage of the total area of the image not covered by porosity. The connection between surface fraction and volumetric fraction of pores (relative density) was guaranteed by the Delesse-Rosiwal law under IUR restrictions^[45]:

$$\Phi = \frac{V_{\text{pores}}}{V} = \frac{A_{\text{pores}}}{A}$$

(1)

ImageJ software was utilized for image processing.^[46] The assessment of the relative density was averaged across a set of at least ten different images from the same sample. The influence of process variables (pressure, soaking time, and nature of the solvent) was qualitatively assessed by measuring the relative density, still with the same method, on eight different samples, resulting from processing silica microbeads under 450 and 600 MPa, in distilled water and NaOH solution (0.5 M) for 5 and 30 min, respectively.

FTIR and NMR Spectroscopy: FTIR spectra of silica samples were obtained using a Bruker Tensor 27 spectrometer in a wavelength range of 4000–400 cm⁻¹, with a standard KBr beam splitter, in transmittance mode, available for solid and liquid state analysis.

 $^{29}{\rm Si}$ NMR spectra were collected using a Bruker Avance-500 spectrometer (Germany). The rotation frequency of 10 kHz and a recycled delay of 20 s were used. The spectra were deconvoluted in the single chemical shifts, using the DMfit software. The admitted error was calculated to be about ± 1 ppm.

Thermal Analysis: For thermal analysis, the simultaneous thermal analyzer Netzech STA449C was used under flowing argon (50 mL min⁻¹), with the sample placed in an alumina crucible and heated to 900 $^{\circ}$ C.

Microindentation: Preliminary mechanical performance of the hydro-pressure samples was qualitatively evaluated from Vickers microhardness results. Microindentations were carried out on the polished surface of the specimens mounted in epoxy resin with a screw-driven testing machine Zwick Z2.5 equipped with microhardness head ZHU0.2 with optics. The Vickers hardness (HV 0.2) was then calculated according to the following equation^[47]:

$$HV = 1.8544 \frac{P}{d^2}$$
(2)

where *P* is the applied load (N) and *d* is the diagonal length of the Vickers indentation mark (mm). The microindentation test also enabled us to calculate the IFT by measuring the characteristic crack (median crack) lengths and using the following formula provided by the theory of Anstis^[48]:

$$K_{\rm IC} = 0.016 \left(\frac{E}{H}\right)^{1/2} \frac{P}{c^{3/2}}$$
(3)

where *E* is the Young's modulus, *H* is the Vickers hardness value, *P* is the maximum load of the indentation test, and *c* is the crack length of the indentation. The Young's modulus was calculated from the reduced one (*E*_t), deduced from geometrical considerations of the unloading side of the indentation curve.^[49,50] The median nature of the cracks was ensured by multiple polishing of the surface sample.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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