

2023 ANNUAL MEETING OF THE GDR SOPHY SOFT PHYSICS FOR HARD MATERIALS

A MEETING @ENS DE LYON ON JUNE 5TH – 7TH 2023

ORGANIZED BY T. DIVOUX & S. DEVILLE

SPONSORED BY CNRS

Location of the meeting: [ENS de Lyon](#), in the *Descartes amphitheater*, [site René Descartes](#)

June 5th

- 12:00pm-1:20pm* **Registration** & Lunch provided on site
- 1:20pm-1:30pm* Welcome & words of introduction
- 1:30pm-2:30pm* **Keynote lecture #1:** *From Soft Matter to hard materials: Applications and Stakes of this transformation for Aeronautical Materials*
Sophie Senani (SAFRAN)
- 2:30pm-2:55pm* *Setting of mineral foams: reaction kinetics vs arrest of foam structure aging*
Marie Le Merrer (ILM, Lyon)
- 2:55pm-3:20pm* *3D microfabrication of silicon-based nanostructures using dual one and two-photon hybrid photoresist for high resolution and grayscale 3D microprinting*
Akos Banyasz (LCENSL, Lyon)
- 3:20pm-3:45pm* *PDLLA design and synthesis: a tool for the improvement of freeze-cast scaffolds properties for biomedical application*
Prescillia Lagarrigue (INP, Toulouse)
- 3:45pm-4:10pm* *On the Spreadability of Stereolithography Pastes for the Design of strong Ceramic Parts - Sylvain Fournier (INSA, Villeurbanne)*
- 4:10pm-4:30pm* *Coffee break provided on site*
- 4:30pm-5:30pm* **Keynote lecture #2:** *Sol-gel synthesis of vitrimers with high glass transition temperatures* - *Damien Montarnal (CP2M, Villeurbanne)*
- 5:30pm-5:55pm* *Mesure d'effets mémoires par spectroscopie diélectrique sur des polymères vitreux sous traction - Caroline Crauste-Thibierge (LPENSL, Lyon)*
- 5:55pm-6:20pm* *Phase separation during geopolymerization*
Jean-Baptiste d'Espinose de Lacaillerie (SIMM ESPCI, Paris)
- 6:20pm-6:45pm* *Role of the precursors and molecular interactions on the self-assembly of organosilanes during the sol-gel elaboration of hybrid mesoporous films*
Jakub Kusz (LCENSL, Lyon)

7:00pm-8:30pm: Cocktail, provided on site

June 6th

- 9:00am-9:20m Breakfast provided on site
- 9:20am-10:20am **Keynote lecture #3: *Design of organic-inorganic networks from nano building units: the "hybrid" effect on dynamic properties of polymers***
Laurence Rozes (LCMCP, Sorbonne-Univ. Paris)
- 10:20am-10:45am *Intracellular biodegradation and recrystallization of gold nanostructures*
Florent Carn (MSC, Paris 7)
- 10:45am-11:05am *Coffee break provided on site*
- 11:05am-11:30am *Synthesis of anisotropic zirconia needles and its alignment using ice-templating technique - Swapneel Thakkar (ILM, Villeurbanne)*
- 11:30am-11:55am *A Pickering emulsion template for 3D printing of porous ceramics based on natural clay - Anne Aimable (IRCER, Limoges)*
- 11:55am-13:30pm **Lunch break provided on site & poster session**
- P1 –Effect of acoustic power on the orthotropic organization of cellulose nanocrystal suspensions subjected to combined frontal ultrafiltration and ultrasound: multiscale characterization by SAXS and SALS – Fanny Bosson (LRP, Grenoble)*
- P2 – Functional materials with hierarchical porosity made using water as a templating agent – Julien Schmitt (ICG, Montpellier)*
- P3 – Hydrogels composites à base d'oxyde de graphène*
Imane Boucenna (MSC, Paris)
- P4 – Mechanical strength enhancement by grain size reduction in a soft colloidal polycrystal – Imane Boucenna (MSC, Paris)*
- P5 – Porous capsules with liquid core prepared by Pickering emulsion: Understanding diffusional phenomena for catalyst implementation – Rémi Duclos (IFP/LCENSL, Lyon)*
- P6 – Reversible Shear-Induced Gelation in Polyacrylamide-Fumed Silica Dispersions*
Jacques Blin (LPENSL, Lyon)
- 13:30pm-14:30pm **Keynote lecture #4: *Fluidification de suspensions non-browniennes: rôle de la formulation et rôle des ultrasons*** - *Annie Colin (ESPCI, Paris)*
- 14:30pm-14:55pm *Spherical balls settling through a quiescent cement paste*
Agathe Robisson (TU Wien)
- 14:55pm-15:20pm *Very early-stage flocculation dynamics of a mineral paste*
Pascal Hebraud (IPCMS, Strasbourg)
- 15:20pm-15:45pm *Heterogenous flows in sheared cement suspensions*
Subhransu Dhar (TU Wien)
- 15:45pm-16:05pm *Coffee break provided on site*
- 16:05pm-16:30pm *Mechanical and structural properties of colloid gels obtained through flow cessations – Thomas Gibaud (LPENSL, Lyon)*

- 16:30pm-16:55pm *Hydrogel Membranes for Selective Filtration*
Sixtine De Chateauneuf (SIMM ESPCI, Paris)
- 16:55pm-17:20pm *Typical three-layer orthotropic organization of articular cartilage achieved through the combined action of frontal ultrafiltration and ultrasound on cellulose nanocrystal suspensions, revealed by in situ SAXS*
Frédéric Pignon (LRP, Grenoble)
- 17:20pm-17:45pm *Cellulose-MOF suspensions: towards self-supported polyfunctional materials designed from ultrafiltration – Lorenzo Metilli (CERMAV, Grenoble)*

7:30pm: Dinner nearby ENS. To be confirmed, information coming soon

June 7th

- 8:50am-9:10am *Breakfast provided on site*
- 9:10am-10:10am **Keynote lecture #5: *Control of the Hierarchical organization processes between complementary building blocks by irreversible Self-Assembly: a few examples of local and macroscopic rules* – Frank Artzner (IPR, Rennes)**
- 10:10am-10:35am *Fast Microfluidic Osmotic Compression with In Operando Meso-structure Characterization by SAXS – Yannick Hallez (LGC, Toulouse)*
- 10:35am-10:55am *Coffee break provided on site*
- 10:55am-11:20pm *Polymer-functionalized mesoporous materials: from the design of building blocks to the control of internal pore structure, external particle surface, and hybrid solid morphology – Corine Gerardin (ICG, Montpellier)*
- 11:20am-11:45am *Fabrication of porous scaffolds for bone substitution: coupling particle design and freeze-casting process – Jérémy Soulié (CIRIMAT, Toulouse)*
- 11:45am-12:10pm *Designing tough and self-healing composite hydrogels for biomedical applications – Alice Gibiino (3SR, Grenoble)*
- 12:10pm-12:25pm **Concluding remarks & perspectives**



Setting of mineral foams: reaction kinetics vs arrest of foam structure aging

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Abstract

Mineral foams like gypsum plasterboard, foamed concrete or artificial bone are porous materials obtained by foaming a hydraulic binder (cement, plaster, etc.), i.e. a reactive suspension. They are sought for their lightness, their porosity or their absorbing or insulating properties. These properties are largely determined by the pore morphology, which results from the balance between aging of the fresh liquid foam due to coarsening, i.e. gas transfer between bubbles, and setting, i.e. solidification following a dissolution-precipitation reaction. To understand this competition, we combine Raman spectroscopy and bubble size measurements in a plaster foam obtained by direct foaming of a suspension. We thus probe at the same time the kinetics of reaction, and the arrest of coarsening due to the stiffening of the liquid foam structure. We first evidence the strong effect of the foaming process on the reaction kinetics. By using a setting retardant, we also show that the reaction timescale controls the final pore size in the solid foam.

*Speaker

Hydrogel Membranes for Selective Filtration

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Abstract

Hydrogels are networks of polymer molecules bound together by covalent bonds. While the diffusive transport of molecules in hydrogels has been well studied in the context of drug delivery, the hydrodynamic transport of water, molecules, and particles in hydrogels in the context of filtration has been barely studied.

Recently our group has synthesized macroporous hydrogels based on the UV cross-linking of polyethylene glycol diacrylate (PEGDA) in water, a mechanically resistant hydrogel. To control the permeability of PEGDA hydrogels we showed that crosslinking PEGDA in the presence of free polyethylene glycol (PEG) chains dramatically increases water permeability by several orders of magnitude. We found that these PEG chains do remain trapped in the matrix and provide nanometric defects that control the permeation of nanoparticles.

In this work, our goal is to use the fact that these free chains remain trapped in the matrix to functionalize the hydrogels. Hence we replace the free PEG chains with electrostatically charged polymers like polyacrylate (PAA). This allows us to obtain selective membranes able of adsorbing or repulsing solutes. As a proof of concept, we chose to filter a positively charged dye (Methylene Blue) and a zwitterionic one (Rhodamine B). This selectivity can be reversed by protonation of the PAA due to an acidification of the pH. Furthermore, we designed a similar membrane capable of making hydrogen bonds with a small acidic molecule to retain it.

This approach will allow the design of new hydrogels for water treatment or the separation of molecules of pharmaceutical interest.

*Speaker

Mechanical and structural properties of colloid gels obtained through flow cessations

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Abstract

Colloidal gels are out-of-equilibrium soft solids composed of attractive Brownian particles that form a space-spanning network at low volume fractions. The elastic properties of these systems result from the network microstructure, which is very sensitive to shear history. Here, we take advantage of such sensitivity to tune the viscoelastic properties of a colloidal gel made of carbon black nanoparticles. Starting from a fluidized state at an applied shear rate $\dot{\gamma}$, we use an abrupt flow cessation to trigger a liquid-to-solid transition. The gel properties are accessed using rheo-saxs experiments and are highly dependent of the amplitude of the shear $\dot{\gamma}$.

Three length scales colloidal gels: the clusters of clusters versus the interpenetrating clusters approach. LV Bouthier, T Gibaud. *Journal of Rheology* 67, 621(2023)

Interpenetration of fractal clusters drives elasticity in colloidal gels formed upon flow cessation. N Dagès, LV Bouthier, L Matthews, S Manneville, T Divoux, A Poulesquen, S. Manneville, A Poulesquen, T Gibaud. *Soft Matter* 18, 6645 (2022)

*Speaker

Mesure d'effets mémoires par spectroscopie diélectrique sur des polymères vitreux sous traction

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Abstract

Je présenterai ici des résultats expérimentaux récents (1,2) concernant les effets mémoires complexes dans les polymères sous traction. Lorsque l'on étire un polymère avec un taux de déformation constant et que l'on arrête cette déformation à un taux de déformation donné L_w pendant une durée t_w , on observe un comportement varié, relié au choix de t_w mais surtout à celui de L_w , selon que L_w se situe dans la zone d'adoucissement du polymère ou dans celle de durcissement. La reprise de la dynamique après l'arrêt, au même taux de déformation qu'à la première phase, dépend elle aussi fortement des conditions expérimentales. Si, après l'arrêt, la contrainte est déchargée, alors le comportement est très différent. L'originalité de notre travail est d'avoir couplé la mesure de contrainte/déformation avec un système de spectroscopie diélectrique mesurant en simultané sur trois décades en fréquence.

L'évolution de la réponse diélectrique est aussi la signature de celle de la distribution des temps de relaxation, ce qui nous donne accès au temps moyen de relaxation mais aussi à la largeur de cette distribution.

Nos résultats imposent donc de fortes contraintes aux modèles de relaxation des polymères sous contrainte et peuvent aussi enrichir notre compréhension des effets mémoire dans les systèmes désordonnés.

(1) J. Hem, C. Crauste-Thibierge, F. Clément, D.R. Long, S. Ciliberto, Simultaneous memory effects in the stress and in the dielectric susceptibility of a stretched polymer glass Phys. Rev. E. 103, 4, L040502, (2021).

(2) J. Hem, C. Crauste-Thibierge, T.C.Merlette, F. Clément, D.R. Long, S. Ciliberto, Microscopic Dynamics in the Strain Hardening Regime of Glassy Polymers. Macromol. 55, 20, 9168, (2022).

*Speaker

Hydrogels composites à base d'oxyde de graphène

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Abstract

Le graphène, un nouveau type de matériau carboné monofeuillet bidimensionnel, a fait l'objet de nombreux travaux en raison de son excellente conductivité électrique, de sa stabilité thermique, de ses propriétés mécaniques et de sa capacité d'adsorption, donnant lieu à de nombreuses applications. Cependant, la dispersion du graphène en phase aqueuse est extrêmement faible. L'oxyde de graphène, précurseur du graphène, possède d'abondants groupes fonctionnels d'oxygène chargés négativement tels que l'hydroxyle, l'époxy, le carboxyle, ce qui assure une bonne dispersion dans l'eau ou dans des solvants organiques. Par ailleurs ces groupes contenant de l'oxygène permettent d'avoir de fortes interactions entre les nanocharges d'oxyde de carbone et des chaînes de polymère pour élaborer des composites dont les propriétés ne sont pas encore complètement connues.

Nous proposons ainsi une étude sur le développement d'hydrogels composites élaborés par introduction d'une dispersion aqueuse de nanocharges d'oxyde de graphène dans des hydrogels de polyvinyl alcool (PVA) obtenus par des cycles thermiques répétés de congélation et de décongélation sans ajout d'agent de réticulation. La fonctionnalisation et l'exfoliation des oxydes de graphène ont été confirmées par spectrométrie de photoélectrons induits par rayons X et par diffraction des rayons X. La morphologie en nanofeuillet a été observée par microscopie électronique à balayage. Nous avons montré que les propriétés viscoélastiques, de gonflement et d'adsorption d'un colorant cationique (bleu de méthylène) pouvaient être modulées en faisant varier les concentrations initiales de PVA et d'oxyde de graphène et du nombre de cycles thermiques. La concentration en oxyde de graphène s'est avérée être le paramètre le plus important pour une augmentation de ces propriétés.

Mots-clés : oxyde de graphène, polyvinyl alcool, composites, viscoélasticité, gonflement, adsorption

*Speaker

On the Spreadability of Stereolithography Pastes for the Design of strong Ceramic Parts

Sylvain Fournier^{*1}, Mario Minale², Claudia Carotenuto², Jérôme Chevalier¹, Saray Perez Robles², Helen Reveron¹, and Guilhem Baeza¹

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Abstract

Stereolithography (SLA) of ceramics is an additive manufacturing technique allowing high accuracy shaping. It is a top-down technique based on the layer by layer selective densification of a paste highly loaded in ceramic powder. Its accuracy relies on the slicing of a CAD part corresponding to a layer thickness of 25-100 μ m ensuring the photopolymerization through laser irradiation. SLA involves challenging steps of fabrication that have a strong influence on parts quality, particularly because ceramics have a brittle behaviour and are therefore very sensitive to defects. Layer spreading is monitored by a scraping blade shearing the paste at a typical shear rate of 100 s⁻¹. Consequently, a shear-thinning behaviour with low viscosity at high shear rates is required to obtain a smooth surface prior to photopolymerization.

Following the paste viscosity as a function of shear rate revealed a bump between 10⁻² s⁻¹ and 10⁻¹ s⁻¹ likely to perturb the SLA processing requiring therefore a deeper investigation of the rheological properties. Focusing on the transient response with the help of step-rate experiments notably emphasized a shear stress build-up combined with unexpected non-monotonic normal forces, confirming the presence of a structural transition that represents a recurrent problem for the paste spreadability.

In the vein of the recent experiments conducted by Pateloup et al. (1), we will demonstrate with Orthogonal Superposition Rheometry that the adjunction of an oscillatory strain on a steady sheared paste can represent a viable solution to the abovementioned issue(2).

(1) V. Pateloup, V. Chartier, C. Chaput. (2017). *Method for manufacturing pieces by the technique of additive manufacturing by pasty process and manufacturing machine for implementing the method* (United States Patent No. 20170355100),

(2) Sylvain Fournier, Jérôme Chevalier, Saray Perez-Robles, Claudia Carotenuto, Mario Minale, Helen Reveron, and Guilhem P. Baeza, Submission in progress

*Speaker

Fast Microfluidic Osmotic Compression with In Operando Meso-structure Characterization by SAXS

Dimitri Radajewski¹, Camille Keita², Pierre Roblin¹, Patrice Bacchin¹, Martine Meireles-Masbernat¹, Jean-Baptiste Salmon², and Yannick Hallez^{*1}

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Abstract

Osmotic compression is used to establish phase diagrams and equations of state (EOS) of colloidal suspensions. It is classically conducted in mL-scale dialysis bags and takes weeks of equilibration. Here we downsized this technique to the nL-scale using new microfluidic chips in which a hydrogel membrane is directly synthesized. The entire meso-structure and EOS of a colloidal dispersion can be measured in a few hours, with precisely controlled pH and chemical potential of ions (1). The EOS can be determined either by optical microscopy or by analysis of SAXS signals recorded in operando, during compression. The latter option provides additional insight into the meso-structure of the dispersion (glass or crystal phases, etc) and does not require access to a synchrotron source provided suitable chip and laboratory beamline modifications that will be presented are performed (2). Experimental results confirmed by theory and simulations will be presented for proteins and latex, silica, and gold nanoparticles.

*Speaker

EFFECT OF ACOUSTIC POWER ON THE ORTHOTROPIC ORGANIZATION OF CELLULOSE NANOCRYSTAL SUSPENSIONS SUBJECTED TO COMBINED FRONTAL ULTRAFILTRATION AND ULTRASOUND: MULTISCALE CHARACTERIZATION BY *in-situ* SAXS AND SALS

Fanny Bosson^{*1}, Nicolas Hengl¹, Vianney Delplace², Samuel Mandin¹, Lorenzo Metilli¹, Thomas Gibaud³, William Chèvremont⁴, and Frédéric Pignon¹

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²Regenerative Medicine and Skeleton – Ecole Nationale Vétérinaire, Agroalimentaire et de l'alimentation Nantes-Atlantique, Institut National de la Santé et de la Recherche Médicale, Nantes Université - UFR Odontologie – France

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⁴European Synchrotron Radiation Facility [Grenoble] – European Synchrotron Radiation Facility (ESRF), Centre National de la Recherche Scientifique - CNRS, Commissariat à l'Énergie Atomique et aux Énergies Alternatives (CEA) - Grenoble – France

Abstract

The degeneration of the articular cartilage is the cause of many diseases such as osteoarthritis and rheumatoid arthritis, mainly because of its poor spontaneous repair capacity. The techniques currently used to treat these diseases do not allow effective long-term repair of the cartilage. Researchers have therefore turned to tissue engineering, a technique that combines cells with biomaterials.

The objective of this work is to develop a biomaterial with the same orthotropic structure (Figure 1a) as articular cartilage (1,2). For this purpose, frontal ultrafiltration and ultrasonic waves (US) were combined and applied to a suspension of cellulose nanocrystals (CNC). A frontal ultrafiltration cell coupled to a vibrating blade generating ultrasound at a frequency of 20 kHz was developed, allowing characterization at nanometric length scales by small-angle X-ray scattering (SAXS) at the TRUSAXS ID02 beamline (ESRF, Grenoble) and at micrometric length scales by small-angle light scattering (SALS) at the LRP. The influence of acoustic power (from 0 to 100%) on the structural organization of CNCs was studied for two CNC concentrations C (6 wt% and 10.6 wt%). From the 2D SAXS and SALS patterns and corresponding azimuthally averaged scattering intensities, time evolution of the

*Speaker

anisotropy and orientation degree of CNCs were revealed as a function of the distance z from the membrane surface to the vibrating US blade (Figure 1b). The results evidenced that the orthotropic structure is preserved from the nanometric (SAXS) to the micrometric (SALS) length scales. It was also shown that the thickness of each of the layers (superficial, intermediate and deep), varies with acoustic power.

- (1) Brody, L. T. Knee Osteoarthritis: Clinical Connections to Articular Cartilage Structure and Function. *Phys. Ther. Sport* **2015**, *16* (4), 301–316. <https://doi.org/10.1016/j.ptsp.2014.12.001>.
- (2) Camarero-Espinosa S. and Cooper-White J. Tailoring biomaterial scaffolds for osteochondral repair. *Int. J.Pharm.* **2017**, *523*(2), 476–489.

Synthesis of anisotropic zirconia needles and its alignment using ice-templating technique

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²Institut Charles Gerhardt Montpellier - Institut de Chimie Moléculaire et des Matériaux de Montpellier – Institut de Chimie du CNRS, Centre National de la Recherche Scientifique, Université de Montpellier, Ecole Nationale Supérieure de Chimie de Montpellier, Centre National de la Recherche Scientifique : UMR5253 – France

Abstract

Technical ceramics such as zirconia are employed in a range of advanced technological applications due to their functional and mechanical properties (1). It is classified as a high performance ceramic due to its remarkable mechanical properties. The toughness of zirconia is strikingly improved when doped with 3 mol% yttrium. This improvement is credited to its phase transformation toughening abilities (tetragonal to monoclinic phase transformation) at the site of mechanical fracture. The increase in volume due to phase transformation induces compressive stress that slow down crack propagation (2). The mechanical properties can also be enhanced by designing textured material with an organised microstructure. Multiple examples exist in nature. Nacre, for example, is an organic-inorganic hybrid material arranged in a "brick-and-mortar" architecture. This microstructure displays a remarkable damage resistance by inducing several processes such as crack bridging and deflection at the origin of fracture (3). Inspired by such designs, this work focuses on the development of zirconia-based ceramics with high strength and toughness by fabricating yttrium doped zirconia anisotropic particles and organising them to have microstructure with highly oriented texture. The chemical composition, shape and uniformity of the particles were investigated to assess their impact on the materials microstructure and properties.

Thus, this project describes the enhancement in functional properties achieved by exploiting the synergy of materials composition and micro-structural arrangement via (i) the synthesis of anisotropic zirconia-based particles using a bottom-up approach technique, and (ii) the alignment of these particles to create novel textured materials. Here, zirconia needles were produced using a sol-gel technique, and the methodology was optimised to produce monodisperse needles with controlled aspect ratio devoid of using surfactants (Fig 1). The needles were then organised by ice templating technique to achieve the desired microstructure. This technique involves in freezing suspensions to induce self-assembly of particles via the growth of ice crystals. The freezing parameters were also studied to facilitate the organisation of the particles and reached the desired microstructure (4). Finally, the properties of the materials were studied and correlated to the needle orientation.

References :

1- Zang X et al (2020). *J Mater Res Technol.* 9(4) :9029–9048

^{*}Speaker

2- Vagkopoulou T et al (2009). Eur J Esthet Dent. 4(2) :130-51

3- N. Abando et al (2021). Journal of the European Ceramic Society. 41:2753–2762

4- R. Henry et al (2022). Journal of the European Ceramic Society. 42:2319–2330

Phase separation during geopolymerization

Jean-Baptiste D'espinoise De Lacaillerie*¹

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Abstract

Geopolymers, the amorphous reaction products of silica-alumina with sodium silicate, are generally considered as Ca-free, low-CO₂ alternative binders. Literature reviews showed that geopolymers could advantageously replace conventional cementitious materials in specific applications such as: encapsulation of nuclear waste, thermal and acoustic isolation, stabilization/solidification of municipal solid waste incineration residue, and cementing of oil wells. This requires a better understanding of the reactivity, structure and porosity of geopolymers in view of controlling their workability and porosity. Contrarily to high temperature glass or ceramic materials, the covalent network of geopolymers harbors a complex porous structure that remains the subject of discussions even for the simplest case of metakaolin-based geopolymers. In particular, it remains to be understood how this porous structure forms during geopolymerization. In other words, how and why does a paste of aluminosilicate (clay or slag) in an aqueous alkali silicate solution transform into a porous solid?

To that effect, we used nuclear magnetic resonance (NMR) to follow the evolution of water and aluminates dynamics as the reaction proceeded. The main conclusion is that, at the beginning of the reaction, the surface area evolves linearly with time suggesting that geopolymerization does not proceed by a nucleation and growth mechanism, as is the case of cement-based materials, but by continuous polycondensation leading to gel percolation. During this step, the presence of silicates in the activating solution is essential as they act as a hydroxide reservoir nurturing the dissolution reaction of the solid phase and favoring the completion of the reaction.(1) Furthermore, it is suggested that the high silicate concentration has a physical effect. It modifies the phase segregation mechanisms in a way favoring porosity.(2)

(1) J. Aupoil, J.-B. Champenois, J.-B. d'Espinoise de Lacaillerie, A. Poulesquen, Interplay between silicate and hydroxide ions during geopolymerization, *Cem. Concr. Res.* 115 (2019) 426–432.

(2) Q.H. Nguyen, M. Hanafi, J. Merkl, J. d'Espinoise de Lacaillerie, Evolution of the microstructure of unconsolidated geopolymers by thermoporometry, *J. Am. Ceram. Soc.* 104 (2021) 1581–1591.

*Speaker

Functional materials with hierarchical porosity made using water as a templating agent

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Abstract

We are using ice-templating combined with PolyIon Complex (PIC) micelles and a silica sol to shape functional macro-mesoporous silica materials. The macroporosity is given by the ice crystals formed during ice-templating while the water contained within the PIC micelles give the mesoporosity. The polymers used in the PIC micelles remains trapped within the silica walls, efficiently functionalising the pores. We are studying the ice-templating mechanisms of pure PIC micelles suspensions and PIC micelles + silica sols using small angle x-ray scattering to unravel the self-assembly mechanisms of the materials and help control the macro and mesopores organisation.

*Speaker

Role of the precursors and molecular interactions on the self-assembly of organosilanes during the sol-gel elaboration of hybrid mesoporous films

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Abstract

Mesoporous hybrid silica materials carrying organic functional groups may show interesting properties, which cannot be simply predicted as a sum of the contributions from single components, especially if more than one organic function is introduced. Understanding the nature of those materials would allow us to control the organic-inorganic interface, which is of great value from an applicational point of view. Organization of mesostructure takes place during the transition between the gel and solid film, but the organic moieties' placement is also determined within this short period. In this study, we show how including organic functions in mesostructured materials can influence the self-assembly process, the porosity, and the formation of the domains in such films. Ordered mesoporous silica thin films were prepared by the co-condensation sol-gel process between hybrid and non-hybrid precursors. Self-assembly of mesophase was achieved by the templating method using an ionic surfactant. Bromoalkylsilanes with different chain lengths were chosen as the model moieties, because of the weak intermolecular interactions and the presence of bromine allowing localization of the moieties with EDX spectroscopy. The influence of several parameters (concentration, relative humidity, sol composition on the film mesostructure) was evaluated providing a systematic analysis. Moreover, we give an insight into the potential influence of hydrogen bonds and π - π stacking when ureido, phenyl, and pyrene moieties are introduced. The microstructural and structural characterization of films was performed by infrared spectroscopy, high-resolution TEM, fluorescence spectroscopy, and ellipsometry.

*Speaker

Designing tough and self-healing composite hydrogels for biomedical applications

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Abstract

The exceptional mechanical performance of living tissues is due to their complex and multi-component molecular structures organized hierarchically in space. Alterations of these microstructures are correlated with age and with diseases, such as rheumatism or cancerous lesions.¹ Over the past few years, there has been growing interest in designing a new class of tough and self-healing biomimetic hydrogel materials to replace damaged soft tissues in human body.² However, controlling their self-assembly to meet these requirements remains an open challenge.

A promising strategy consists in creating a biopolymer network crosslinked via dynamic covalent bonds. The strength of these bonds is similar to classical covalent bonds, but they are capable of breaking and reforming rapidly, which led to the development of self-healing materials with relatively low elastic moduli (E) (below 1 kPa).³ A further breakthrough has been made by Li et al.⁴ who demonstrated the potential of incorporating inorganic nanoparticles (NPs) into the hydrated polymer matrix to form a composite hydrogel. Due to the high surface area of the particles that brings increased cross-links compared to the previously developed hydrogel, this system exhibits a higher toughness.

I will show, for the first time that the addition of NPs into a hydrated polymer matrix with the use of dynamic covalent chemistry is a good design strategy to form a bio-mimetic gel at physiological pH.

Our system is composed of hyaluronic acid (HA) crosslinked through boronic ester bonds with inorganic silica nanoparticles (SiNPs) that also act as reinforcing agents. This HA composite hydrogel is engineered by functionalizing the two components with boronic acid/diol groups. I will present the NPs functionalization route and rheological measurements of the viscoelastic properties of the composite hydrogel as well as a coarse-grained molecular dynamics simulations of a model system to probe the physical microscopic mechanisms at play.

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*Speaker

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Intracellular biodegradation and recrystallization of gold nanostructures.

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Abstract

Biohybrid nanostructures involving inorganic elements essential to life have been observed in a variety of organisms. Often these nanostructures are composed of elementary bricks that are self-assembled in order to fulfil a function. For instance, magnetic assemblies, composed of iron oxides, are produced by organisms ranging from bacteria through higher vertebrates for magnetoreception. The biosynthesis of useless nanostructures involving non-essential elements is more scarce. This is what we are interested in.

Recently, we have studied the long-term intracellular fate of gold nanoparticles which are increasingly encountered in biomedicine and in some manufactured products. Prior to our study, it was generally admitted that the inertness of gold particles prevents their degradation. Nevertheless, we studied *in vitro* their fate in primary fibroblasts during 6 months by using electron microscopy. In this way, we revealed an unexpected 2-step process of biotransformation.⁽¹⁾

First, we revealed the intracellular degradation of the particles with a degradation dynamic that depends on the reactivity of the particles and therefore on their size.

Second, we showed that the released ionic gold undergoes a biomineralization process and ends up in well-defined structures consisting of 2.5 nm crystalline particles self-assembled into nanoleaves.

Thus, a cell that does not have *a priori* a metabolism specifically dedicated to gold ions is able to transform them into well-defined and biopersistent nanostructures with no particular function. Reviewing of the literature dedicated to therapeutic gold salts used for the treatment of rheumatoid arthritis evidences that similar structures, called aurosomes, have previously been described *in vivo* in human and different animal species. It suggests that ionic and crystallized gold have a common intracellular fate. I will propose a general mechanism for this intracellular degradation/recrystallization process based on transcriptomic analysis and various *ex situ* experiments.

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*Speaker

Mechanical strength enhancement by grain size reduction in a soft colloidal polycrystal

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Abstract

It has long been known that the mechanical strength of finely grained solid state polycrystals could be enhanced when the grain size is reduced. Indeed, the equation linking the yield stress and the inverse square root of grain size was introduced in the 1950s by Hall and Petch. Since then this relationship has been widely used to engineer structural metals and alloys. To date, no similar behavior has been reported in materials other than atomic systems where the grain size usually lies in the nanometric range. The purpose of our work was to study the influence of grain size on the mechanical strength enhancement of a soft colloidal ‘alloy’ made of micellar polycrystalline grains and nanoparticles.

The samples are formed of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer micellar solutions with embedded spherical silica nanoparticles. The concentrated micellar solutions exhibit a phase transition from fluid to crystal induced by temperature. Addition of nanoparticles is found to trigger the formation of polycrystallized micellar micrograins, above the transition temperature, instead of a cubic monocrystal. This transition is associated with the segregation of the nanoparticles, which play the role of impurities, in the interstices between the grains. This system bears resemblance to solid state polycrystals; however the achieved grain length scale is situated in the micrometric domain.

Our main result is that the yield stress rigorously obeys the Hall–Petch law and follows a linear variation as a function of the inverse square root of the grain diameter. We also show that the grain size evolves non-monotonically with the nanoparticle concentration without affecting the Hall-Petch relation. We believe that our experimental approach offers new possibilities to study poorly understood mechanical aspects of polycrystalline and nanocrystalline structures, such as their plasticity, with non-destructive techniques.

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*Speaker

Typical three-layer orthotropic organization of articular cartilage achieved through the combined action of frontal ultrafiltration and ultrasound on cellulose nanocrystal suspensions, revealed by in situ SAXS.

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Abstract

A typical multilayer orthotropic structure that mimics the articular cartilage organization was achieved in one step using aqueous suspensions of rodlike cellulose nanocrystals (CNCs) thanks to a novel processing method combining frontal ultrafiltration (FU) and ultrasound (US). The dynamic of the structural orientations and the local concentrations of CNCs induced by combining FU and US were investigated by time-resolved, in situ synchrotron small-angle X-ray scattering (SAXS) in a cell where the CNC suspension was confined between an ultrafiltration membrane and a vibrating blade oscillating at 20 kHz.

Recently, we were able to evidence the ability of the ultrafiltration processes to develop well-defined layered structures of CNCs (1-3). Furthermore, we discovered by using ultrasound waves, it was possible to align the CNCs along the wave propagation direction (4).

In this work, thanks to FU/US set-up and in situ SAXS, typical multilayer orthotropic structuring that mimic the articular cartilage organization (5), was achieved in one single FU/US processing on CNC suspensions (Fig. 1). The complex hierarchical structure of articular cartilage tissue, composed of three layers (superficial, middle, and deep), continuously structured in vivo from the articulating surface to the subchondral bone, was mimicked by the model system of CNCs, using one single FU-US processing, starting from an initial homogeneous CNC suspension at a concentration of 10 wt % and reaching equilibrium over a few tens of minutes.

The first layer (1000 μm -thick) pertaining to the superficial zone was composed of tightly

*Speaker

packed CNCs having their directors aligned parallel to the membrane surface and a concentration gradient established perpendicular to the membrane surface, reaching up to 50.5 wt % at the membrane surface. The second intermediate layer (400 μm -thick), analogous to the isotropic middle transitional zone of the articular cartilage, was located in a region where the vertical acoustic radiation force balanced the transmembrane pressure forces, inducing an isotropic orientation of the CNCs with a uniform concentration of 15.1 wt %. The third layer (3600 μm -thick), similar to the deep region, with objects arranged perpendicular to the subchondral bone, was located near the vibrating blade, where the ultrasound waves induced an alignment of the CNCs with their director perpendicular to the membrane surface, along the ultrasonic wave direction of propagation with a uniform concentration of 15.1 wt %. In addition to this three-layer architecture, a boundary layer (600 μm -thick) was observed in the close vicinity of the vibrating blade, with a global orientation of the CNCs along ultrasonic wave direction of propagation, yet with some fluctuations of the orientation at short time scales, below 1 s.

From the 2D SAXS patterns, the anisotropy PCA were calculated in the (0.071-0.368) nm-1 q -range. It allowed to follow the time dependent evolutions of the anisotropy levels of CNCs orientations inside the different zones as a function of time and distance Z from the membrane surface (Fig. 2).

This three-layer orthotropic organization of CNC paves the way to: (i) a new method to assemble complex structure in one shot, (ii) the possibility to mimic cartilage structure with CNC, (iii) opens the way for developing novel orthotropic biomaterials with tunable structured cellulosic organizations for tissue engineering applications.

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A Pickering emulsion template for 3D printing of porous ceramics based on natural clay

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Abstract

This work is part of the IDEMAP project ("Impression 3D D'Emulsions céramiques. Application à l'élaboration de MATériaux Poreux architectures"), which aims at shaping ceramic materials with a multi-scale porosity. The originality of the project is to develop hybrid formulations of Pickering emulsion/suspension that are suitable for the 3D printing process named microextrusion, in order to benefit from a versatile and efficient shaping for new applications in the field of porous ceramics. Here, the dispersed phase serves as a template for the porosity and is removed after the heat treatment (1). A specificity of the project lies in the use of phyllosilicates, like kaolinite and halloysite, which present amphiphilic properties but also anisotropic morphology (2,3). One ambition of the project is also to favor the use of additives and materials that are environmentally friendly.

Our approach consists in studying the impact of the formulation and of the operating parameters (order of introduction of the constituents, mode of mixing, stirring speed, etc...), to obtain the best control on the emulsions properties, in particular their stability, the size and size distribution of the droplets, and their rheological properties. Indeed, the interactions existing between the two liquid phases (oil and water), the additives, and the solid phase are complex, and will be studied through electrokinetic and rheological measurements. Having in mind these emulsions must be compatible with a specific shaping process which impose high solid fractions, and adapted rheological behaviors to ensure both stability and flow when extruded, and sufficient cohesion in its liquid state when deposited, a good understanding of these systems is a real challenge. Finally in the final steps the emulsion will be converted into a porous ceramic material thanks to a good control of the thermal treatment (drying and sintering) applied to the material, to conserve the porosity templated by the emulsion.

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*Speaker

Fabrication of porous scaffolds for bone substitution: coupling particle design and freeze-casting process

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Abstract

Numerous scaffolds have been developed to replace bone defects in non-bearing sites. Ideally, such scaffolds should: i) stimulate new bone formation (cell adhesion, differentiation, proliferation) ii) exhibit adequate macropore size and volume (cell colonization, angiogenesis), iii) maintain mechanical properties during handling. Several inorganic materials, such as calcium phosphate bioceramics or bioactive glasses, partially meet some of these criteria. Nevertheless, the mechanical cohesion of such scaffolds is usually the result of powder consolidation processes often obtained after high temperature treatment that prevents the shaping of metastable materials or their association with active molecules. These drawbacks can be avoided using low temperature processes such as electrospinning or robocasting with polymeric-based composites materials.

The present work is focused on the freeze-casting technique that is based on the control of solvent crystal nucleation/growth and its subsequent sublimation. Through several examples, the aim of this contribution is to highlight the interest of coupling this process with the controlled synthesis of inorganic fillers in order to produce composite scaffolds for bone reconstruction.

Different particles (substituted core-shell apatite, bioglass-metal composite, hybrid amorphous calcium carbonate) were synthesized, thoroughly characterized (XRD, NMR, DLS, granulometry, TEM, SEM) and associated with synthetic (polyesters) or biosourced (alginate) polymers and freeze-cast. Resulting scaffolds were studied *via* SEM, porometry, X-Ray microtomography, SAXS and mechanical compression tests.

We showed that both formulation and process parameters have a significant impact on i) particle dispersion and their final spatial distribution, ii) pore size, orientation and wall thickness, iii) mechanical properties, and iv) *in vitro* biological properties. These results demonstrate that adequate filler/polymer combinations associated to the freeze-casting technique lead to well-controlled scaffolds with tunable properties allowing adaptation to bone pathologies.

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*Speaker

PDLLA design and synthesis: a tool for the improvement of freeze-cast scaffolds properties for biomedical application

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Abstract

In the recent years several solutions adopting bioactive glass nanoparticles-based composites were proposed in the field of bone repair, especially concerning the maxillofacial area. Bone substitutes require properties such as adequate mechanical properties, biodegradability, osteoconductivity, osteoinductivity, that are mostly satisfied by the development of organic/inorganic macroporous composites.

Polyesters have been often described as organic matrices for such materials. In particular, it could be carried out with the freeze-casting process that allows to generate macroporosity. Despite promising results, these polymers are: i) commercial ones with high dispersity and poorly characterized, ii) associated with micronic bioactive glass particles by simple mixing leading to sedimentation and heterogenous spatial distribution of inorganic fillers in the final material.

To overcome these drawbacks, we carried out synthesis and functionalization of well-controlled poly(d,l-lactic acid) (PDLLA) with the aim to improve the final scaffolds properties. In this work, we will highlight the impact of two parameters. In a first example, PDLLA with three different molecular weight ($M_{n,P1} = 7000$, $M_{n,P2} = 60000$ and $M_{n,P3} = 160000$ g·mol⁻¹) have been synthesized through different routes and fully characterized (NMR, SEC MALDI-TOF). In a further step, we studied how the molecular weight and the concentration of such polyesters can affect the viscosity of pre-freezing solutions and the porosity (volume, size, orientation gradient) and mechanical properties of the resulting freeze-cast scaffolds.

The second example is related to the grafting of amino-modified bioactive glass nanoparticles with functionalized PDLLA chains. We demonstrated that this covalent bonding improves the spatial distribution of these fillers in the organic matrix et then impact the recovery rate of final materials. These results demonstrated that the design PDLLA is a promising tool to tune the properties of freeze-cast scaffolds for biomedical applications.

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^{*}Speaker

Cellulose-MOF suspensions: towards self-supported polyfunctional materials designed from ultrafiltration

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Abstract

Metal-organic frameworks (MOFs) are promising materials to address critical issues such as petrochemical and gas separation, filtration, catalysis, sensing and energy storage (1). Large-scale deployment of MOFs is however hampered by their crystalline powder state, which results in poor processability. Recently, the hybridization of MOFs with biopolymers has emerged as a greener, biocompatible strategy with improved processability into membranes, films, and porous materials (2). Nevertheless, the physiochemical properties of the biopolymer-MOF mixtures, and their relationship to the composite structure and functionality, need to be investigated to promote their use in real applications. The present work focuses on the preparation of thin nanocomposites from commercial ZIF-8 (a synthetic zeolite) and cellulose nanocrystals (CNCs) aqueous suspensions using membrane ultrafiltration. Results showed that small amounts of CNCs (1:20 CNC:ZIF-8 volume ratio) are sufficient to disperse the ZIF-8 particles, preventing further aggregation and phase separation, and enabling the formation of a compact deposit under filtration. The stabilization derived from the electrostatic interaction between the CNCs and ZIF-8, leading to the formation of a layer of adsorbed CNCs on the surface of ZIF-8 particles, as observed by TEM. The rheology of ZIF-8 suspensions shifted from shear-thinning to a Newtonian behaviour in presence of CNCs. The filtration process was investigated *in situ* with Small-Angle X-Ray Scattering, showing that the deposition of ZIF-8 particles occurred concurrently to the formation of a layered structure of CNCs, perpendicular to the transmembrane pressure. Finally, the porosity of ZIF-8 to water was tested with a custom-made porosimeter (3), showing that the adsorbed CNCs did not affect the intrusion/extrusion pressure, or the available pore volume in the hybrid material.

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*Speaker

Heterogenous flows in sheared cement suspensions

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Abstract

Fresh cement pastes are complex suspensions, with a yield stress that depends upon the material recipe (cement-to-water ratio and additives) and increases with time at rest. High yield stress concretes typically need to be vibrated to flow and be placed, while low yield stress concretes flow easily under their own weight. The measurement of the yield stress is therefore crucial both for practice and to estimate the early cohesion between hydrating cement particles.

The yield stress of cement and other rheological properties are often investigated using geometries like parallel plate and co-axial cylinders, although the correctness of the results is questionable, and requires detailed analysis. 1,2

In this study, we measure the yield stress of various cement pastes using a stress-controlled rheometer with different geometries, namely serrated parallel plates, vane, concentric cylinders, and helix. Depending on the cement recipe, the yield stress obtained from parallel plate geometry is lower than that of the vane/helix geometry by a factor of 5 to 18. To explain this inconsistency, we image the flow in the parallel plate geometry at the edge, i.e the cement air interface, using a high rate camera, and treat the data using various image analysis techniques, including PIV. Results show shear banding, with a stationary band near the static plate and a moving band near the upper rotating plate and the width of the moving band depends on the angular velocity (Ω) of the top plate. Using the width of the stationary band, the shear stress is recalculated from the applied torque, but the moderate value increase cannot explain the above discrepancy. We hypothesize that material heterogeneities develop during flow, and a band of less concentrated cement paste is formed.

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^{*}Speaker

Reversible Shear-Induced Gelation in Polyacrylamide-Fumed Silica Dispersions.

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Abstract

Dispersions of fumed silica nanoparticles in a high molecular weight polyacrylamide water/glycerol solution display a shear thickening transition above a critical shear rate at low particle volume fractions. Here we show that these dispersions display, under external shear, a dual behavior relative to that critical shear rate. Below the critical shear rate, the dispersions experience a shear-induced gelation. The gel viscoelastic properties increase with the strain accumulated, hinting at a structural rearrangement under shear allowing polymer extension and the formation of interparticle links through polymer-bridging. Conversely, the sample is fluidized above the critical shear rate, resulting from the breaking of polymer-bridging bonds yielding a liquid-like sample of isolated flocs stabilized by adsorbing polymer. Finally, we show the shear-induced sol-gel transition is reversible, and that the viscoelastic spectra measured for increasing strains can be rescaled onto a single master curve, which hints at a universal strain-connectivity superposition principle for colloid-polymer mixtures.

*Speaker

Polymer-functionalized mesoporous materials : from the design of building blocks to the control of internal pore structure, external particle surface and hybrid solid morphology

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Abstract

Ordered mesoporous inorganic materials resulting from the synergy between supramolecular self-assembly of amphiphilic macromolecular compounds and sol-gel processes present unique porous textural and surface properties, which make them attractive as drug delivery systems, sensors, adsorbents, catalysts, ion conductors and more generally for various applications in the fields of health, environment and energy. The control of their structure at the nanoscale is mainly governed by the interactions between the amphiphilic entities and the silica precursors under the specific physicochemical conditions of the material synthesis. Different types of interactions (hydrogen bonding, van der Waals, electrostatic complexation) occur simultaneously and their cooperativity or competitiveness determine the structural parameters of the obtained materials : system curvature at the nanoscale, pore size, nature of the mesophase and wall thickness of the pore structure.

The functionalization of their mesopores is also a key step in the material preparation for applications. Functionalization by organic, organometallic or bioactive groups can be achieved by well-controlled routes. But the introduction of polymers in the mesopores remains a major challenge. Yet, this could confer new properties to the materials. Conventional routes for polymer post-functionalization of mesopores do not allow to obtain dense and homogeneous distributions of polymers at the nanoscale. The use of polyion complex micelles (PICs) as structuring agents can overcome the main problems encountered. PIC micelles are dynamic assemblies obtained by electrostatic complexation between a double-hydrophilic block copolymer and an oppositely charged polyelectrolyte acting as an auxiliary of micellization. When the two polymers are designed as weak polyelectrolytes of well-chosen pKa, the formation of PIC micelles is reversible in water as a function of pH and ionic strength. The use of PIC micelles in place of conventional amphiphilic structuring agents is of major interest since they allow (1) the simple control of hybrid silica-based mesostructures (2D hexagonal, lamellar, 3D spherical cubic) and pore sizes, (2) the recovery and recycling of pore-forming polymers, and (3) the direct preparation of pore structures functionalized by homogeneously distributed polymers. Another great advantage of the use of PIC micelles is the easy preparation of mesoporous nanoparticles of controlled size. This is rendered possible by using

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tripartite PIC micelles with two types of DHBCs, one controlling the silica-pore interface, while the other one controls the particle-solvent interface. The study of the mechanisms of formation of the hybrid mesoporous structures showed that the nature of the polymer blocks and their preferential interactions with silica, with the micellization auxiliary or the solvent are key parameters to control the internal pore surface of the material, but also its external surface. Finally, this new route, called the MesoPIC approach, based on the use of PIC micelles as templating agents is now being extended to the preparation of films and monoliths.

Spherical balls settling through a quiescent cement paste

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Abstract

Fresh cement pastes are complex suspensions of micron-size cement particles (ground clinker) and nano-size C-S-H particles that result from a dissolution-precipitation process. They exhibit a colloidal behavior due to interactions between charged particles through an interstitial solution of high ionic strength, giving rise to a macroscopic yield stress, that increases with time at rest. Upon flow, this multiscale network is broken down (fluidized). In this study, we investigate the evolving rheology properties of a cement paste in quiescent conditions by measuring the velocity of metallic balls settling in the paste using high speed X-ray CT imaging (TESCAN UniTOM XL).

We look at the influence of time before first ball drop, ball size, ball weight and time interval between two successive ball drops. In parallel, an extensive rheological characterization of the mortar, capturing the rheological properties "at rest" and under flow, focusing on the effect of time and shear history, is performed. Compiled results are then compared with literature of non-aging (1,2) and aging (3,4,5) yield stress fluids.

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3D microfabrication of silicon-based nanostructures using dual one and two-photon hybrid photoresist for high resolution and grayscale 3D microprinting

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Abstract

Sol-gel technology is based on a versatile chemical process that allows the preparation of hybrid and inorganic materials under mild conditions. One major characteristic of the sol-gel process is the use of low temperatures to carry out the involved chemical reactions so that evaporation losses and phase transformations are minimized.

Materials with very different morphology at the molecular level can be synthesized in acid- or base-catalyzed hydrolysis-condensation reactions from one or multiple alkoxide precursors. Moreover, organic or bioactive moieties can be integrated or trapped within the pores of silicon or metal oxide networks (e.g. SiO₂, ZrO₂, Al₂O₃, TiO₂) to synthesize specifically tailored materials. Sol-gel-derived ORganically MODified CERamic (ORMOCER®) materials have been extensively studied and chemically engineered over the last twenty years. ORMOCER®s can be processed either thermally or in light-initiated reactions using photoactivable components (e.g. photoinitiators and/or photosensitizers). They behave as negative tone photoresists; hence, they solidify as soon as the sol-gel transition is completed upon irradiation at a specific wavelength. Thus, ORMOCERs can be processed by UV lithography techniques to obtain functional optical devices in 2D and 2.5D, such as waveguides or microlenses.

Nowadays, hybrid materials combined with 3D printing processes are also responding to the increasing demand of the industry for novel functional materials.

For instance, Digital Light Processing (DLP) offers possibilities for light-initiated cross-linking of sol-gel resins used in layer-by-layer 3D printing process. In this way, transparent 3D silica structures have been obtained from 3D printed objects fabricated by this technique. Many functional micrometer-size systems have been fabricated from organosilane-, metal-based organic-inorganic sol-gel materials or ceramics using the two-photon absorption induced direct-laser writing (2P-DLW). Despite the high-resolution attained by 2P-DLW,

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preparation of large 3D printed surfaces remains an issue of the process and a critical challenge for scientists.

The use of a specifically designed resin allows a dual chemical approach using both one-photon absorption process for large surface fabrication and two-photon absorption process for locally high-resolution microfabrication. Thus, an organosilane-based hybrid material compatible with both UV maskless projection lithography and two-photon direct laser writing techniques is proposed by combining a radical photoinitiator and a recently reported photobase generator. We demonstrate the potential of the strategy using a single resin to prepare large 2D photopatterned surfaces with high-resolution 3D microstructures. Moreover, by modification of the photoactive components and the precursor, the reported hybrid material can be easily adapted to different 3D printing setups enabling miniaturization of macro-scale functional systems and properties of the final system can be tuned. This process has been for instance used to build microfluidic systems with high resolution.

Very early stage flocculation dynamics of a mineral paste

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Abstract

We study the very early age flocculation of a mineral suspension consisting of an alkali-activated slag (AAS) paste, that may be used as a substitute. Immediately upon mixing with water, the suspension flocculates. We are interested in the relaxation modes of the formed aggregates, as measured by Diffusing Wave Spectroscopy, a light scattering technique suitable for very turbid media. We show that the dynamics of the suspension is characterized by two distinct relaxation modes, whose decay time and amplitude vary with time. The fast relaxation mode slows down with the elapsed time and diverges at a "hard gel" time. We characterize the critical exponents of the fast relaxation mode when at the "hard gel" transition. These results are compared to linear rheology measurements.

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Porous capsules with liquid core prepared by Pickering emulsion: Understanding of diffusional phenomena for catalyst implementation.

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Abstract

The ideal catalyst is likely to merge the advantages of both homogeneous and heterogeneous catalysis. For example, it may exhibit the performance of a homogeneous catalyst in terms of activity and selectivity combined with the ease of use of a heterogeneous catalyst. In that context, the possibility to entrap a homogeneous phase catalytic system within a solid capsule would lead to a system that allow the catalytic performances to be maintained under certain conditions (1), with a material that is easy to handle. Therefore, the conditions for maintaining its performances lie partly in the efficiency of diffusional transfers:

- The transfer of reagents from the external medium (phase immiscible with the internal phase of the capsule) to the interior of the capsule. This transfer takes place via a solid medium which constitutes the capsule shell.
- The transfer of the reaction products from the liquid phase inside the capsule (phase immiscible with the phase outside the capsule) to the outside of the capsule.
- The transfer of the catalytic system from a liquid phase inside the capsule to an immiscible phase on the outside via the shell. This phenomenon must be absolutely limited to maintain the catalytic activity.

Such type of material can be obtained from a Pickering emulsion (2, 3) (emulsion stabilized with solid nanoparticles), where the dispersed phase is a homogeneous phase catalyst. Then, in order to prepare liquid filled microcapsules, shell consolidation can be achieved by sol-gel process to create a metal oxide (such as SiO₂) porous wall allowing reagents and products to diffuse easily (2, 4).

Here, we describe the design of such material obtained by a Pickering emulsion using hydrophobized silica nanoparticles with ionic liquids ((BMIM)(NTf₂) and (BMIM)(BF₄)), water and a catalyst (HNTF₂) as the dispersed phase and heptane as the continuous phase. The

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final capsules are formed from the emulsion droplets by hydrolysis of trimethoxysilane and condensation of the products. Those capsules have been studied using optical microscopy, scanning electron microscopy (SEM), nitrogen physisorption and mercury porosimetry.

At first glance, it seems that washing and thermal pre-treatment of capsules prior to nitrogen physisorption and mercury porosimetry have an important role in the measurement of textural properties. In fact, even after several washes (until no more ionic liquids are extracted), some ionic liquids remain in the capsules and clog the pores. Their decomposition by heat treatment would therefore release the pores.

The first syntheses showed that capsules' porosity was in the meso-macro area and that some parameters have an influence on the porosity. Thus, several parameters will be studied, in particular those allowing to modify the kinetics of the hydrolysis and condensation reactions of the sol-gel process (temperature, stirring time, pH, trimethoxysilane concentration) but also other parameters such as the stirring speed during emulsification or the quantity of water in the dispersed phase, which makes it possible to vary the thickness of the capsules.

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