Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Bioinspired Microstructures of Chitosan Hydrogel Provide Enhanced Wear Protection

Jimmy Faivre, Guillaume Sudre, Alexandra Montembault, Stéphane Benayoun, Xavier Banquy, Thierry Delair, Laurent David**

J. Faivre, G. Sudre, A. Montembault, Prof. T. Delair, Prof. L. David

Université de Lyon, Université Claude Bernard Lyon 1, CNRS, IMP, UMR 5223, 15 Boulevard Latarjet, F-69622, Villeurbanne, France

*E-mail: laurent.david@univ-lyon1.fr

J. Faivre , Prof. X. Banquy

Canadian Research Chair in Bioinspired Materials, Faculty of Pharmacy, Université de Montréal, Montréal, Qc, Canada

*E-mail: xavier.banquy@umontreal.ca

Prof. S. Benayoun

Laboratoire de Tribologie et Dynamique des Systèmes, UMR 5513 CNRS, Ecole Centrale de Lyon, 36 Avenue Guy de Collongue, 69134 Ecully Cedex, France

1. Experimental Section

1.1 Rheological characterization

Chitosan hydrogel disks were characterized for their rheological properties using an AR2000 rheometer (TA Instruments, USA). A parallel plate geometry was mounted with a water trap to limit water evaporation during measurement. Viscoelastic properties were performed at 1% gel deformation in frequency sweep mode in the linear domain (n = 5).

1.2 Stress-strain curves

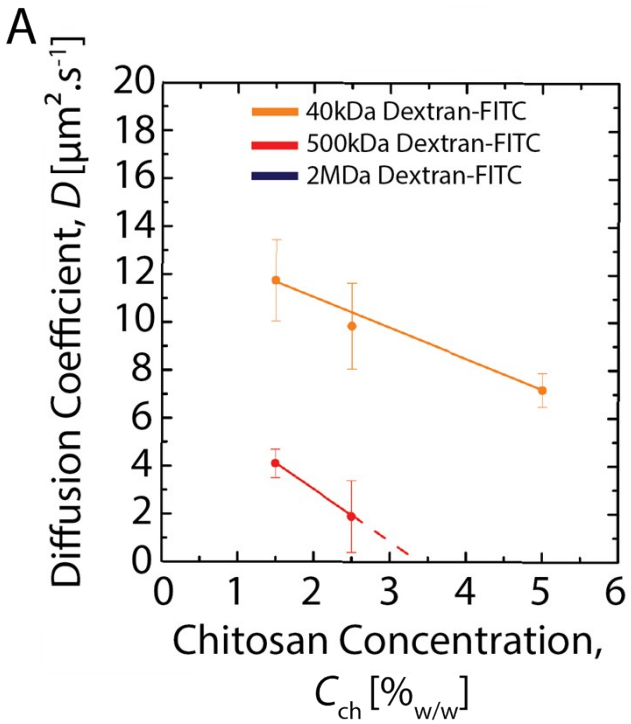
Stress-strain curves were recorded for each gel using a Shimadzu AG-X+ 10 kN tensile tester. Load/Unload cycles were applied on top of a gel with increasing strain (10, 20, 30, 50, 70, and 80% of initial gel thickness) and the resulting stress is recorded. The compression plates were lubricated with mineral oil to avoid barreling effects. A compression study was performed following the same procedure as for the stress-strain curve except that a linear strain at a rate of 0.6 mm/min was applied on top of the gels. Water exudation was directly observed by the means of a camera.

1.3 Osmotic pressure assessments

Chitosan gel osmotic pressure was evaluated to determine the gel permeability using Eq. 5. The gel osmotic pressure determinations were carried out after de-swelling the gels by the dialysis bag method described elsewhere[1, 2]. The gel disks were positioned at the contact of semi permeable regenerated cellulose membranes (MWCO 2 kDa, spectrum lab) and the sealed bags were immersed in an aqueous polyvinylpyrrolidone solution ($8.7\ 10^{-2}$ mg/mL, Mw = 29 kDa, Sigma-Aldrich) with a known osmotic pressure equal to 30.5 kPa and buffered with HEPES at 0.1 M and pH 7.4 at constant room temperature. After equilibrium is reached (4 days), gels are removed, weighed and viscoselastic measurements are performed using an AR2000ex rheometer to assess the shear moduli.

2. Results

2.1 Structure of chitosan hydrogels



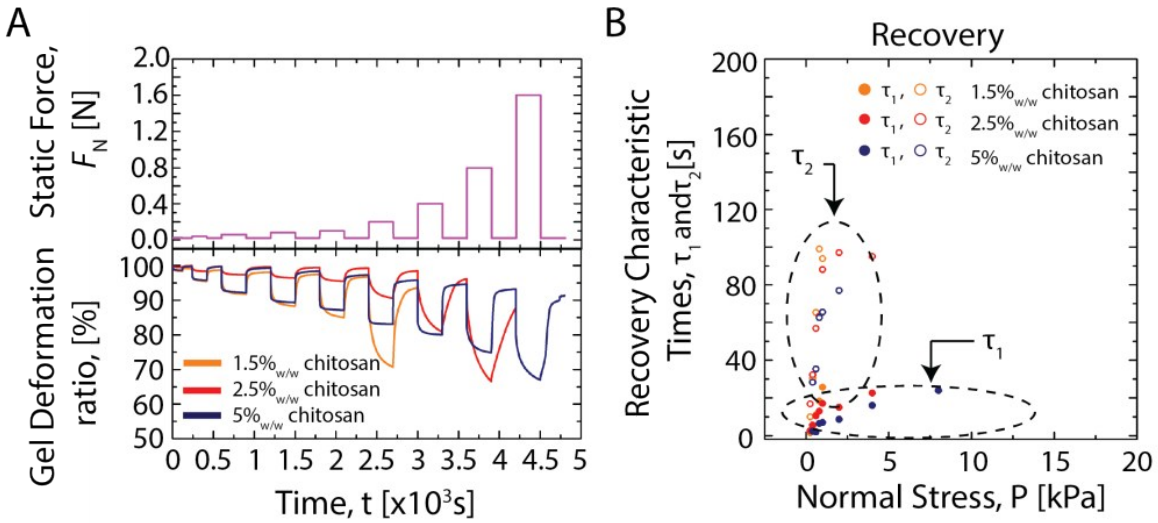
S1. Diffusion properties of chitosan hydrogels using different dextran-FITC probe sizes. 2 MDa Dextran-FITC diffusion was not detected by the FRAP technique.

Table S1. Fluorescent probe characteristics (molecular weight (Mw), dispersity (PdI) and radius of gyration (Rg)) in HEPES buffer pH 7.4 NaCl 50mM.

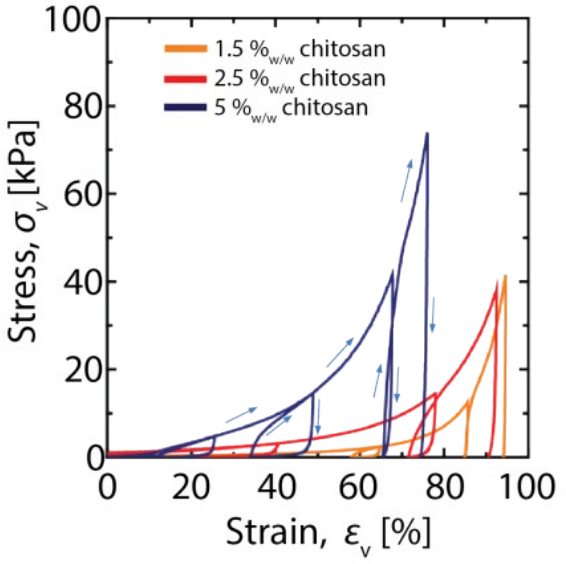
Fluorescent probe	Mw (g/mol)[a]	PdI[a]	Rg (nm)[a]	Rg ($Rg=0.025*Mw^{0.5}$)[b]
40kDa DexFITC	3.85×10^4	1.31	8	5
500kDa DexFITC	4.68×10^5	1.81	22.5	17.7
2MDa DexFITC	1.81×10^6	1.50	41.2	35.4

[a] measured by GPC; [b] from literature[3]

2.2 Poroelastic properties of structured chitosan hydrogels

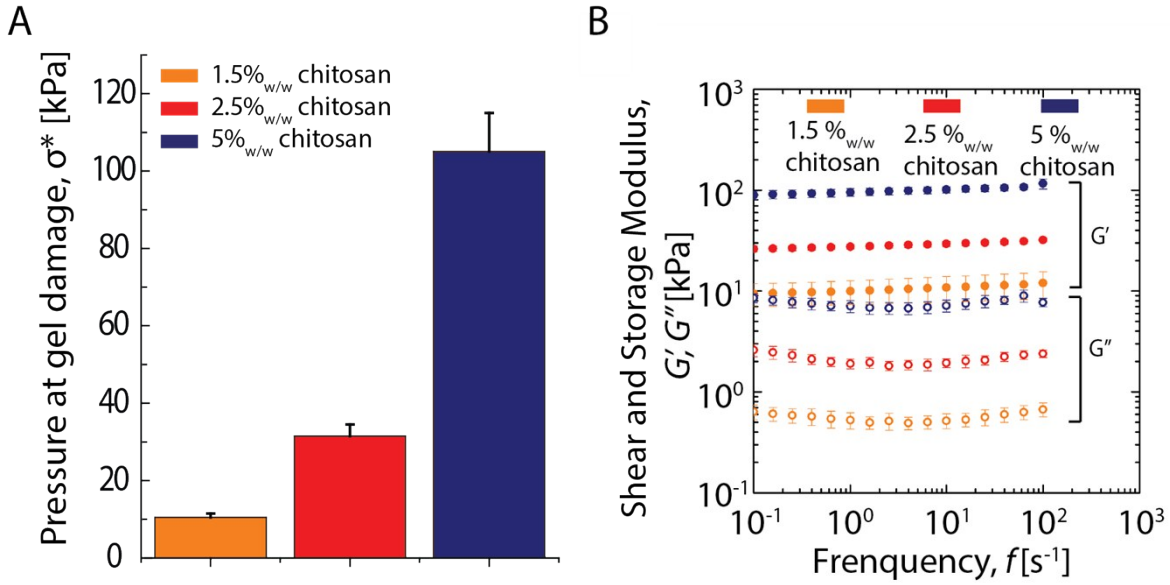


S2. (A) Creep/recovery cycles with increasing load of chitosan hydrogels assessed by DMA and (B) characteristic times of chitosan hydrogels during recovery

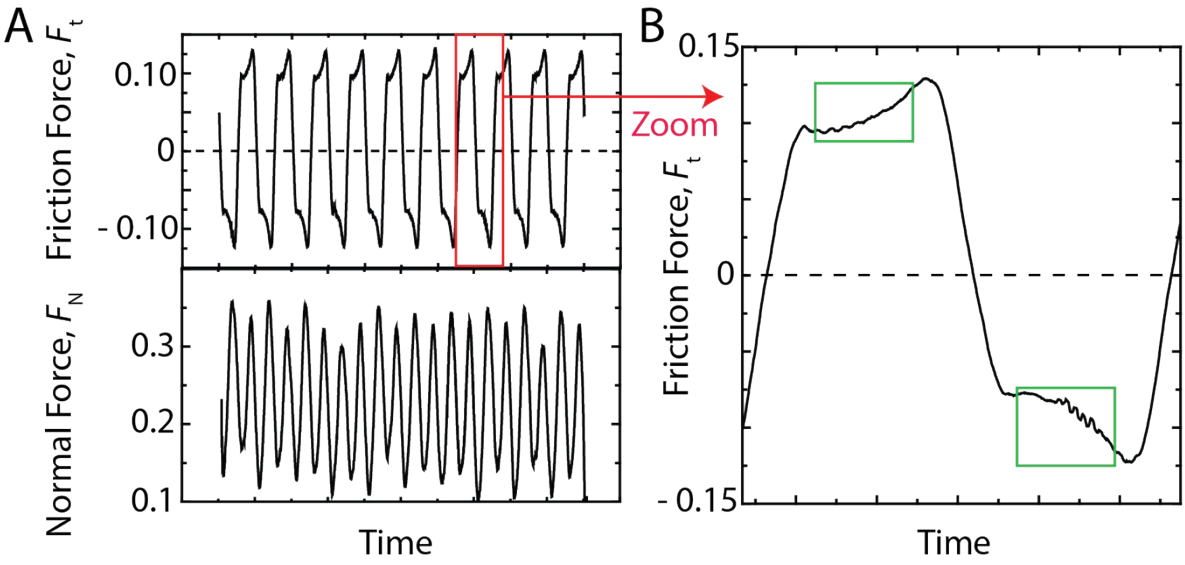


S3. stress versus strain curves of chitosan hydrogels

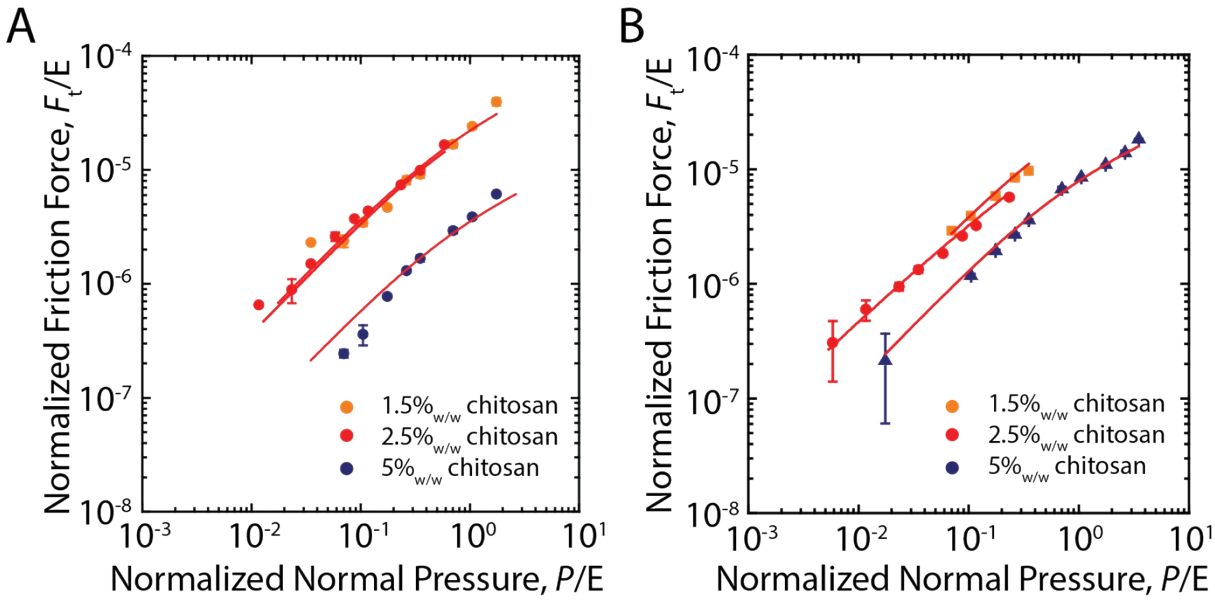
2.3. Tribological properties of chitosan hydrogels



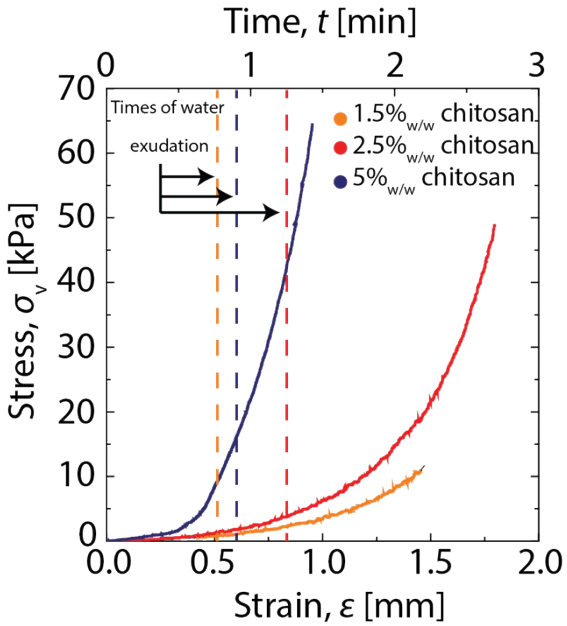
S4. (A) Pressure at gel damage measured for the chitosan hydrogels on the DZ/DZ configuration and (B) shear and storage moduli of chitosan hydrogels.



S5. (A) Typical friction and normal forces profiles for 2.5 $\%_{w/w}$ chitosan gels on the DZ/DZ configuration at a speed of v = 5 mm/s and (B) zoom in the friction profile showing no stiction in the friction signal. These data correspond to that of Figure 3B for the chitosan gel at 2.5 $\%_{w/w}$ at P = 3 kPa. Green rectangles represent the areas where the friction/normal forces were measured.



S6. Friction forces as a function of normal pressure for (A) SZ/SZ configuration and (B) DZ/DZ configuration. Red lines are fitting obtained from Eq. 1.



S7. Compression study of chitosan hydrogels showing the critical strains for exudation of water for different chitosan hydrogels.

References

1. E. Geissler, F. Horkay and A. M. Hecht, *Macromolecules*, 1991, **24**, 6006-6011.
2. F. Horkay and P. J. Basser, *Journal of polymer science. Part B, Polymer physics*, 2008, **46**, 2803-2810.
3. K. Andrieux, P. Lesieur, S. Lesieur, M. Ollivon and C. Grabielle-Madelmont, *Analytical Chemistry*, 2002, **74**, 5217-5226.