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Supplementary Materials

Review

What was old is new again: the pennate diatom *Haslea ostrearia* (Gaillon) Simonsen at the multi-omic age

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1. Supplementary Material and Methods S1: Experimental details on Frustules exploitation

The two required oligomers with a triethoxysilane group at a chain end and a hydroxyl group at the other (Mn 1900 g/mol, Đ 2.2) and the di-acrylate oligoisoprenes (Mn 4100 g/mol, Đ 2.1) were synthesized from solid natural rubber following a procedure described in Tran *et al.* 2021. Model mesoporous silica particles were synthesized dissolving 12 g of hexadecyl trimethyl ammonium bromide (1 eq.) and 16,1 g of tetraethylorthosilicate (1,3 eq.) in 250 mL of ethanol and adding a solution of 65 mL of NH_4OH in 200 mL H_2O. The solution was stirred for 1h at RT, then the whitish suspension was filtered and the silica particles were washed with 150 mL of ethanol, dried at 80°C overnight and calcined in an oven at 500 °C during 24h. TEM images showed that the particles had a perfect spherical morphology, with 150 nm average diameter and pores oriented perpendicularly to the surface, with 21 Å pore diameter (Figure 12 main text). The elimination of the organic matter from *Haslea ostrearia* was carried out by treating the dry biomass (2 g) at RT overnight with a mixture of concentrated nitric and sulfuric acid (30 mL of each), then washing with distilled water until pH 7. The frustules were dried at 80°C and TEM micrographs showed debris with a dispersion of sizes and morphology, with complete elimination of the organic content even from inside the squares of the regular network. BET measures showed that the silica of the frustules is mesoporous too, with 0.35 cm^3/g pore volume and 41 Å pore diameter. The grafting conditions were optimized using the mesoporous silica particles (0.5 g) and incubating them in dry toluene (10 mL), at reflux overnight, under argon, in suspension in a 0.09 M solution of silane-oligomers (1.5 g in 10 mL toluene). After filtration, the functionalized particles were extensively washed with dichloromethane and dried in an oven at 80°C. The same procedure was used with the frustules debris. BET measurements showed that the specific surface for the mesoporous particles diminished from 1269 m^2/g to 425 m^2/g after grafting, while for the frustules decreased from 336 m^2/g to 6.4 m^2/g. TEM images confirmed that both synthetic and biosilica were surrounded by a layer of polymer coating (Figure 12 main text). Thick films were obtained by mixing 200 mg of di-acrylate oligomers and 1 or 5% weight of silica particles, in presence of 5% weight of Darocure photinitiator, and irradiating the formulation deposited in teflon molds (1 cm diameter, 0.5 cm depth) for 10 minutes under a UV-lamp (intensity ~29,4 mW/cm^2). Visual observation showed that both bare synthetic and biosilica particles formed aggregates in the film volume, while functionalized particles were more easily dispersed, confirming the initial hypothesis that the rubber thin layer would improve dispersion in the rubber matrix. Of course, the silica frustules will not replace carbon black or silica as charges in elastomers applications such as joints or tyres but this study showed that the biosilica can give the same chemistry as the synthetic one, opening the way for other interesting applications.

2. Supplementary Information S1: Sequence of *H. ostrearia* DNMT homologues

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