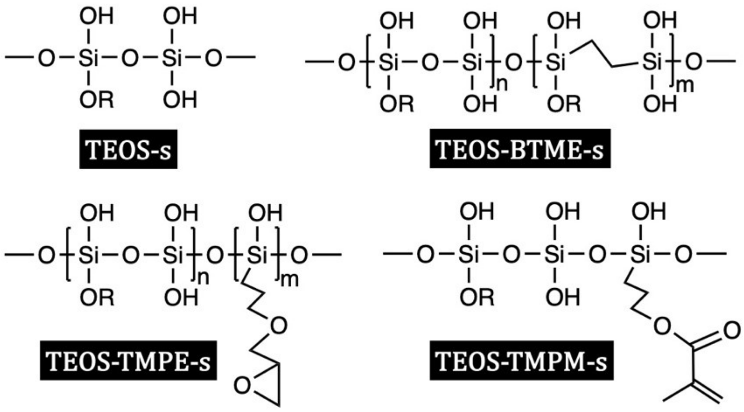
How high-tech measurement methods can help to find new ways for the conservation of ancient fossils

Fossils are physical evidence of a prehistoric plant or animal, and play a crucial role in understanding ancient life. Unfortunately, once exposed to the environment, fossils will deteriorate due to many factors like wind, rain, soluble mineral salts, microorganism and dramatic environmental changes. Water poses the most serious threat as it not only can destroy fossils itself, but also can further trigger problems caused by soluble salts or microorganism which accelerate the deterioration of fossils. To preserve these historic relicts, researchers have developed organosiloxane-based hybrid materials that can be applied to the fossil´s surface. On the one hand, the Si–O bonds inside siloxane molecules can restore the mechanical integrity by combining with the fossils; On the other hand, the addition of organic groups can reduce the weight loss and shrinkage of the siloxane backbone, weaken cracks, and also increase the hydrophobicity of the fossils. Recently, Peng et al. have reported the first systematic research using siloxane-based materials for the protection of precious fossils.

In this work, the authors fabricated four organosiloxane hybrid materials (**Picture 1**) from organosiloxane monomers to study their abilities in fossil protection: Tetraethyl orthosilicate sol (TEOS-s), TEOS/Bis(trimethoxysilyl)ethane sol (TEOS-BTME-s, 1:1), TEOS/γ-

(2,3-epoxypropoxy) propytrimethoxysilane sol (TEOS-TMPE-s, 1:1), and TEOS/3-(Trimethoxysilyl) propyl methacrylate sol (TEOS-TMPM-s, 1:1).



Picture 1: *Molecular structures of four hybrid organosiloxanes (R = methyl/ethyl): TEOS-s, TEOS-BTME-s, TEOS-TMPE-s, TEOS-TMPM-s*

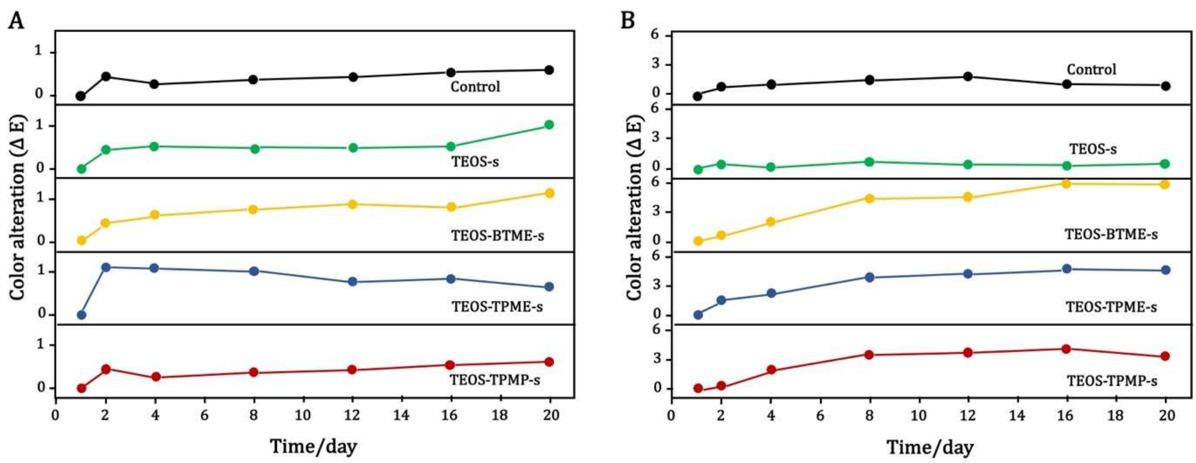
As a first test they coated these materials onto glass slides and visualized the formed films by microscopy. They observed obvious cracks in films made from TEOS-s and TEOS-BTME-s sols but smooth films made from TEOS-TMPE-s and TEOS-TMPM-s. Generally cracks form due to the inner stess produced during sol-gel process. The bigger organic groups in TEOS-TMPE-s and TEOS-TMPM-s made the inner stress lower by reducing the weight loss and shrinkage of the gels, thus weakening the cracks.

In the next step some delicate fossils were coated with the organosiloxanes. While untreated samples fell apart immediately upon contact with water, treated samples (TEOS-s, TEOS-BTME, TEOS-TMPE-s and TEOS-TMPM-s) were stable. The authors found higher water content in the disintegrated samples leading them to the conclusion that water resistance plays an important role in the protection of fossils. Hence, they evaluated the water resistance behaviors of different samples through water contact angle measurements with an optical contour analysis system OCA from DataPhysics Instruments. **Table 1** shows that the contact angles of treated samples were much higher than that of the control group (0°). The samples could still be wetted but were much more hydrophobic after treatment, and exhibited better water resistance behaviors than control group.

Table 1: Water resistance of untreated and treated groups

	Contact angle (°)	Water absorption (%)	Water resistance
Control	0	11.63 ± 0.17	Poor
TEOS-s	27.3 ± 7.5	7.11 ± 0.23	Good
TEOS-BTME-s	86.6 ± 5.3	5.15 ± 0.21	Good
TEOS-TMPE-s	104.2 ± 4.4	6.64 ± 0.19	Good
TEOS-TMPM-s	124.2 ± 3.2	6.15 ± 0.14	Good

Given that strong sunlight and heat are also key factors for material aging, the authors furthermore did an aging resistance evaluation (including light aging and heat aging) of five different samples (**Picture 2**). **Picture 2A** shows that all samples have a pretty good resistance to light (only slight color changes in the early stage and then almost no changes later, ΔE <1.2). In this case, the color changes in all samples probably derived from the water loss. **Picture 2B** shows the heat aging test revealing that the control and TEOS-s groups experience a small color changes (ΔE <1.4), while the other three groups experienced larger color changes (ΔE >4). In this case, the color changes derived from the higher amounts of organic moieties inside the hybrid materials that reduce the heat resistance of materials. An additional benefit of the organosiloxane coatings is an increase of the fossil´s stability to compression and abrasion because more organic groups provide additional binding/crosslinking sites to strengthen fossils.



Picture 2: *Color changes of untreated and treated groups during aging processes. (A) Light aging under an UV lamp; (B) Heat aging at 60 °C*

Overall, the authors synthesized four siloxane-based materials *via* traditional sol–gel processes for protecting precious fossils. The results show that TEOS-s had the best aging stability against light and heat but a lower water resistance. On the contrary, the organic side groups in the other three hybrid materials (TEOS-BTME, TEOS-TMPE-s and TEOS-TMPM-s) strengthened the fossils and improved the water-resistance. These protection materials are expected to have a great potential for fossils protection in the future.

The optical contour analysis system OCA 15EC (DataPhysics Instruments GmbH, Germany) was used in this research.

For more information, please refer to the following article:

Sol–Gel derived hybrid materials for conservation of fossils; Xiaohong Peng, Yue Wang, Xi-Fei Ma, Haifeng Bao, Xiao Huang, Hongjiao Zhou, Hongjie Luo, Xiaolin Wang; *Journal of Sol-Gel Science and Technology,* ***2020****, 94, 347-355*; DOI: 10.1007/s10971-020-05242-x