



least 10 times higher than that of transparent polymeric materials. Furthermore, the team found that cracks caused less structural damage to the new composites than to harder glasses. Bending tests and high-resolution imaging revealed that the fracture resistance of the composites increased with crack growth, yielding fracture toughness 2.5–3 times greater than that of common glass.

In the visible range, the researchers measured a total diffuse transmittance of 45–55% for 1-mm-thick samples. This is significantly less than typical optical glasses, but the researchers expected that

optimizing the infiltration process could partially reduce the difference. Optical characterizations also revealed a significant hazing effect, likely due to air pockets in the material. This makes it best suited for applications close to a light source, such as protective display covers, say the researchers. They hope this research will spur efforts to quantify the structure–property relationships of the material, which could lead to enhanced mechanical and optical properties and a wider range of applications.

The ETH approach offers a simple and scalable route to bulk materials with

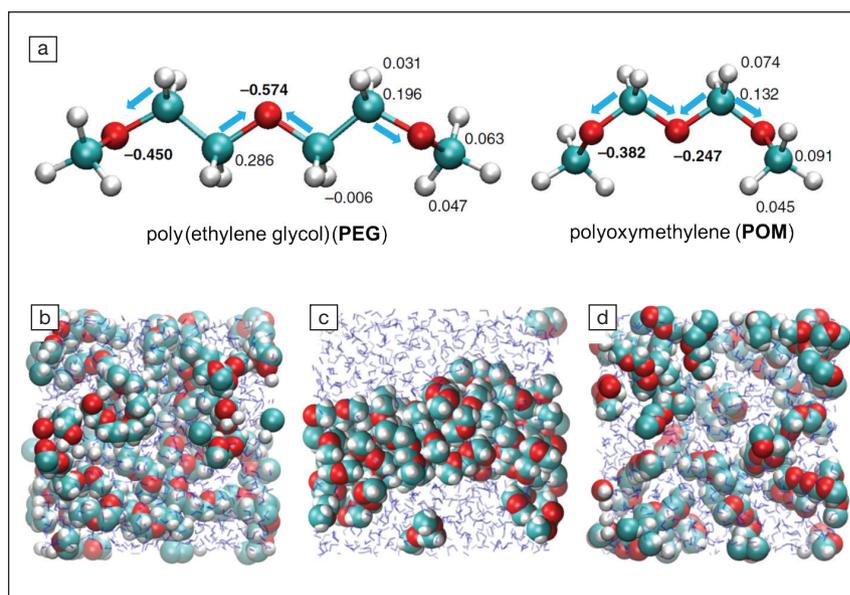
a remarkable combination of transparency, strength, and toughness, according to Flavia Libonati, an expert in the toughening mechanisms of biological structural materials at the Politecnico di Milano. “This work demonstrates the possibilities of implementing microstructural nacre-like toughening mechanisms into glass-based materials, overcoming the intrinsic limitations of such materials, for example, brittle fracture, and offering a valid alternative to silica-based glasses for numerous applications,” she says.

Kendra Redmond

The puzzle of water solubilities of polyethers solved

The anomalous water solubilities of polyethers have long puzzled researchers. Typically, increasing the oxygen-to-carbon ratio of an organic compound enhances its water solubility. This principle, however, is invalid in the case of polyethers. Polyoxymethylene (POM), a polyether with one carbon atom and one oxygen atom in its repeating unit ($[-CH_2-O-]_n$), is entirely insoluble in water. In contrast, poly(ethylene glycol) (PEG), a polyether having two carbon atoms and one oxygen atom in its repeating unit ($[-CH_2-CH_2-O-]_n$), is infinitely water soluble. The origins of the polyethers' counterintuitive water solubilities have remained a mystery for decades.

Recently, a research team at the University of Amsterdam in The Netherlands led by Bernd Ensing and Sander Woutersen, together with Johannes Hunger and Mischa Bonn of the Max Planck Institute for Polymer Research in Germany, has shed light on this solubility puzzle for polyethers. Combining spectroscopic and computational techniques, the researchers concluded that the difference in the oxygen charge density dictated the water solubilities of polyethers. This was published in the journal *Nature Communications* (doi:10.1038/541467-019-10783-z).



(a) Atomic charges (the numbers) of poly(ethylene glycol) (PEG) (left) and polyoxymethylene (POM) (right). The blue arrows are directions of electron-withdrawing forces. (b–d) Snapshots of the atom positions of (b) PEG molecules, (c) POM molecules, and (d) POM molecules with oxygen charge equal to that of PEG oxygen. Red, blue, and white spheres represent oxygen, carbon, and hydrogen atoms, respectively. The blue V-shaped sticks are water molecules. Credit: *Nature Communications*.

Computational simulations indicated that the oxygen atoms in PEG were more negatively charged than those in POM. Due to different electronegativities, oxygen atoms pull valence electrons from neighboring carbon atoms. In POM, only one carbon atom segregates two adjacent oxygen atoms. This central carbon atom thus experiences electron-withdrawing force simultaneously exerted by the two side oxygen atoms. The opposite directions weaken the two attractive forces. Whereas

in PEG, two carbon atoms divide adjacent oxygen atoms. Each oxygen atom thus attracts electrons from its immediate neighboring carbon atom, with little competition from its oxygen neighbors. Thus, the oxygen atoms in PEG are more negatively charged than those in POM.

This discrepancy in the oxygen charge density influences the extent of water solvation, and consequently, the water solubility. Due to the more negatively charged oxygen atoms, PEG forms stronger hydrogen

bonds with water than POM, resulting in excellent water solubility. This conclusion was verified experimentally using infrared and dielectric spectroscopies, as well as theoretically using force-field molecular dynamics. In the theoretical study, PEG molecules uniformly mixed with water molecules after 1 ns, while POM chains still aggregated locally within the same time frame. When the oxygen charge density of POM was increased to the value of

PEG, POM started to disperse among the water molecules uniformly, meaning its solubility enhanced considerably.

Qigang Wang of Tongji University, China, highlights the significance of this work: “It is tricky to predict the water solubilities of macromolecules, as they do not always obey the ‘like dissolves like’ principle and empirical rules valid for small molecules. The advanced spectroscopy techniques and the

comprehensive molecular simulations demonstrated in this work constitute a novel toolbox to tackle this challenge.”

The conclusion reported in this work is also applicable to explain the water solubilities of other polyethers, for example, dioxane versus trioxane. More generally, this work provides a new theory to predict the water solubilities of oxygen-containing polymers.

Tianyu Liu

Proteins designed to bind to a specific surface

Proteins are organic biopolymers consisting of a sequence of smaller amino-acid units. However, unlike synthetic polymers, which are made from a single monomer repeated over and over, these amino acids come from a library of 20 different varieties, enabling proteins to fold into complex three-dimensional (3D) shapes that directly control their function. The research led by James J. De Yoreo and David Baker from the Pacific Northwest National Laboratory and the University of Washington, and published in a recent issue of *Nature* (doi:10.1038/s41586-019-1361-6) focus on the self-assembly of proteins in the presence of crystals. Indeed, from ice-binding proteins to bone formation, there are indications showing that proteins and minerals can show strong binding affinity and play a role in the mineralization process.

To study the binding of proteins to mineral surfaces, the team designed proteins that specifically bind to mica and self-assemble into ordered patterns on this surface. This binding is driven not only by electrostatics, but also via the specific 3D shapes that proteins adopt in liquid, to allow the carboxyl groups on the protein to match the crystal lattice. Therefore, to design the protein, they used a preexisting helical repeat protein (DHR) whose repeat unit is close to the spacing of the target mica lattice, namely 1.04 nm. The main hypothesis that the researchers validated is that for a protein to adsorb in a predictable orientation

onto the surface, the carboxylate groups of the protein should be spaced with the same distances as the atoms of the surface.

First, the researchers used simulation tools to predict which protein sequence with the DHR repeat unit is required to achieve this specific binding. This sequence was then used to modify the DNA of a bacteria that was cultured to produce the artificially designed protein *in vivo*. After separation and purification of the protein, they used atomic force microscopy (AFM) to visualize the

self-assembled protein structures onto mica. In a typical experiment, the protein solution was deposited onto the mica surface in the presence of K^+ ions. These ions play an important role in defining the interactions between the protein and the surface, which in turn impacts their assembly into designed structures. Scanning the surface with AFM, they observed the formation of liquid-crystal-like assemblies that depended on the ion concentration and the protein sequence. By incorporating protein–protein interactions, they could design, model, and

