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# Vitrimers: combining the best of both polymeric worlds

**Vitrimers are a promising new type of polymer glasses that combine the recyclability of thermoplastics with the high mechanical performance of thermosets. At the heart of their exceptional material properties lies highly unusual glass-forming behaviour.**

Polymers are conventionally classified as either thermosetting or thermoplastic, depending on whether the polymer chains are covalently cross-linked or not. Each class has its own advantages: thermoplastics are generally easily malleable and recyclable, whereas cross-linked thermosets are insoluble and mechanically robust. With the recent advent of vitrimers—a polymer glass invented by Ludwik Leibler and co-workers [1]—it is now possible to combine the best of both polymeric worlds. Vitrimers are covalently cross-linked polymer networks, but the cross-linking bonds can swap reversibly by thermally activated reactions. This enables vitrimers to behave as viscoelastic liquids at high temperatures and as rigid thermosets at low temperatures, culminating in a recyclable yet high-performance plastic with vast application potential.

## Fragility

The exceptional processability and recyclability of vitrimers is manifested in the so-called fragility—an empirical property that quantifies how rapidly a glass-forming material changes from liquid to amorphous solid upon cooling. Materials in the ‘fragile’ category solidify rather abruptly, whereas ‘strong’ glass formers vitrify in a more gradual manner. Curiously, while many glassy polymers are fragile, vitrimers turn out to be ‘superstrong’, solidifying even more gradually than the prototypical strong glass-former silica. This behaviour not only constitutes a striking departure from conventional glassy phenomenology, but it also explains in part why vitrimers are so easy to process: a superstrong fragility implies a very broad glass-transition-temperature range, creating a large temperature window in which the material can be molded and (re)shaped.



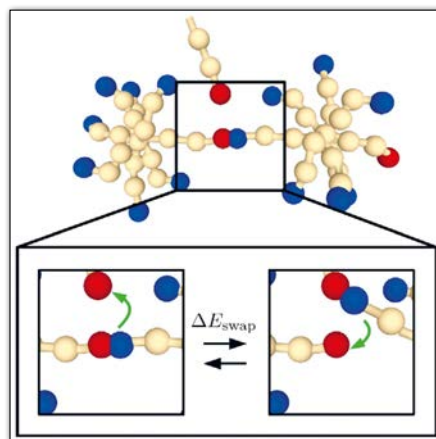
▲ Vitrimer samples. © CNRS Photothèque / ESPCI / Cyril FRÉSILLON

## In-silico vitrimers

How can we better understand the remarkable glass-forming properties of vitrimers from a molecular perspective? A recent study addresses this question using computer simulations and theory [2]. First, to mimic vitrimers *in silico*, a coarse-grained simulation model was developed that represents vitrimers as cross-linked star-polymer networks; the vitrimeric bond-swapping functionality was implemented through a three-body potential that preserves the total number of bonds. Interestingly, the simulations could reproduce the anomalous superstrong fragility of experimental vitrimeric materials, thus capturing the main phenomenology of vitrimers in a minimal computational model. But the simulations also predicted another effect: by increasing the bulk density by a factor of 2-3, the simulated vitrimers were found to solidify as a strong or even fragile glass former upon cooling. This suggests that the bulk density may provide a suitable control parameter to tune the vitrimer fragility and even induce a superstrong-to-fragile crossover—a prediction that will hopefully also be tested in experiment.

## Linking structure to glassy dynamics

Next, to elucidate the microstructural origins of the vitrimeric fragility, the simulation results were subjected to a theoretical analysis. To this end, an approximate but purely first-principles-based theory of the glass transition was employed—so-called Mode-Coupling Theory (MCT). Briefly, this theory seeks to predict the glassy relaxation dynamics of a material (as a function of time, temperature, density, and wavevector  $k$ ) using only simple microstructural information—such as the static structure factor  $S(k)$ —as input. Hence, MCT provides a fit-parameter-free framework to rationally relate structural properties to dynamical ones. By taking the simulated static structure factors of the vitrimers as input, MCT could predict the same fragilities as observed in simulation: fragile vitrimer behaviour at high densities, strong behaviour at intermediate densities, and superstrong behaviour at low densities. This result is *a priori* surprising, as MCT is conventionally assumed to



▲ Vitrimer simulation model [2].

only account for fragile behaviour. Furthermore, the striking agreement between theory and simulation made it possible to establish a direct link between the vitrimer microstructure and the fragility—a link that still remains elusive for most glass-forming materials.

## Suppressed cage effect

A detailed analysis of the MCT results revealed the physical origin of the anomalous fragility of vitrimers, as well as of the superstrong-to-fragile crossover induced by increasing the bulk density. The key underlying structural property was found to be the main peak of the static structure factor,  $S(k_0)$ , where  $k_0$  corresponds to the average (inverse) nearest-neighbour distance. Briefly, within conventional MCT, a growing  $S(k_0)$  peak gives rise to the so-called cage effect: particles become trapped in local cages formed by their nearest-neighbours, causing a non-linear dynamical slowdown and eventual kinetic arrest across all length scales. It was found that a significant growth of  $S(k_0)$  upon cooling indeed led to a rapid

slowdown of the vitrimer dynamics, most notably in the high-density (fragile) regime. Interestingly, however, at *low* vitrimer densities, the temperature-dependent growth of  $S(k_0)$  became anomalously weak—almost logarithmic with inverse temperature—, thus causing a *suppression* of the cage effect. This in turn resulted in a far more gradual dynamical slowdown and an extremely low fragility. The same MCT analysis also provided an explanation for the observed fragile-to-superstrong crossover in simulation: as the bulk density decreased, nearest-neighbour correlations encoded in  $S(k_0)$  became less sensitive to temperature variations, leading to a weakening of the cage effect and a manifestly lower fragility.

The results of this study [2] reveal some unusual aspects of glass formation in a model system of vitrimers. It is hoped that future experiments will test some of these predictions, in particular the role of the density as a tunable fragility parameter, and the anomalously weak growth behaviour of the static structure factor in superstrong materials. Such a combined experimental and theoretical approach holds exciting potential for the ultimate rational design of the next generation of recyclable high-performance polymer materials. ■

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▼ Conventional fragility classification (left) and vitrimer fragilities obtained from simulation (right) [2].

