Supplementary Materials for Effect of Dynamic Bond Concentration on the Mechanical Properties of Vitrimers

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Simulation details

The three-dimensional polymeric network, based on the Kremer-Grest bead-spring framework, is used in this study [1]. The bonded interactions between were set based on the finite extensible nonlinear elastic bond model [1], and pairwise interactions between the beads were based on repulsive LJ interactions with a cutoff radius of $r_c = 2.5$. All the units reported in this study are in the form of reduced LJ parameters, *i.e.*, σ is the diameter of a bead, ϵ represents the well-depth of the LJ potential, with beads of mass m respectively. The model network consists of 1944 linear polymer chains, connected strings of 10 beads each, and tetra-functional crosslinkers in a 2:1 stoichiometric ratio to ensure that none of the reactive beads are unbonded. All other simulation protocols closely follow our previous methodologies, and all simulations were performed using the LAMMPS package [2, 3].

Bond characteristics during triaxial stretching experiment

As mentioned in the main text, we determine the bond characteristics of the hybrid networks during the triaxial stretching experiment. In Fig. S1.A, we present the total accumulated bond swaps in the hybrid networks. The increasing number of bond exchanges as a function of ξ, presented here as a function of strain, ε, showcases the ability of hybrid networks to undergo stress-induced bond exchanges. These exchanges allow for topological rearrangements that enhance the hybrid networks' mechanical response like delayed craze development and higher elongation at fracture. To supplement the σ_{xx} response at higher strain ($4 \leq \varepsilon \leq 6$), we determine the total number of bonds broken in the hybrid networks, presented in Fig. S1.B, and C. Here, the strand bonds refer to the bonds connecting the constituent polymer beads, while the crosslinker bonds include bonds between the crosslinker and the polymeric beads. As mentioned earlier, the hybrid networks allow for bond exchanges and thus at higher ξ ($\xi \geq 0.8$), we observe significantly lower bonds broken in the hybrid networks.

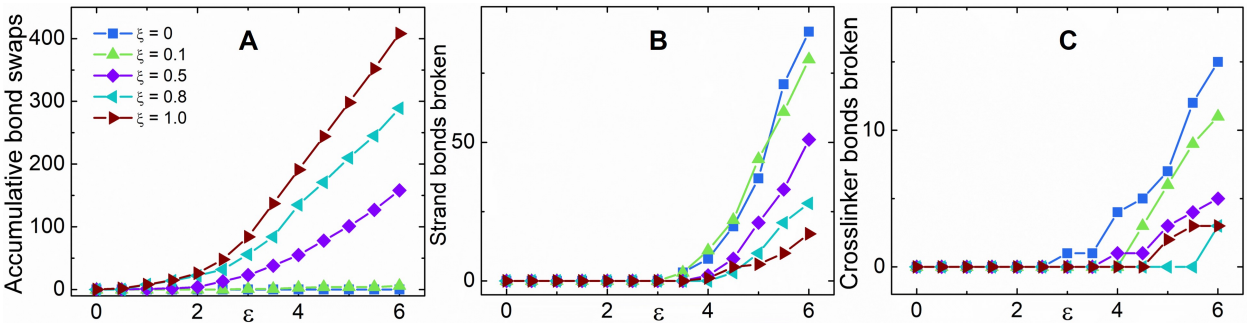

Fig. S1. (A) Accumulative bond exchanges in hybrid vitrimer networks as a function of the strain during the triaxial stretching experiment. (B) Number of network strands (connecting polymer beads) broken during the triaxial stretching test, and (C) Number of crosslinks broken during the triaxial stretching test, both as a function of the strain ε.

Shear creep experiment

We perform a shear creep experiment on the hybrid networks, presented in Fig. S2. Fig. S2.A represents the shear compliance for the creep experiment performed at $\sigma_{xy} = 0.1$ whereas Fig. S2.B represents the shear compliance for a test with $\sigma_{xy} = 1.0$. Under low stress, the deformation experienced by all hybrid networks is low, but at high stress the phenomenon of stress-induced bond exchange is observed. Interestingly, increasing the ξ up to 0.5 induced a significant amount of bond exchanges in the network, yet the creep compliance achieves only a limiting value.

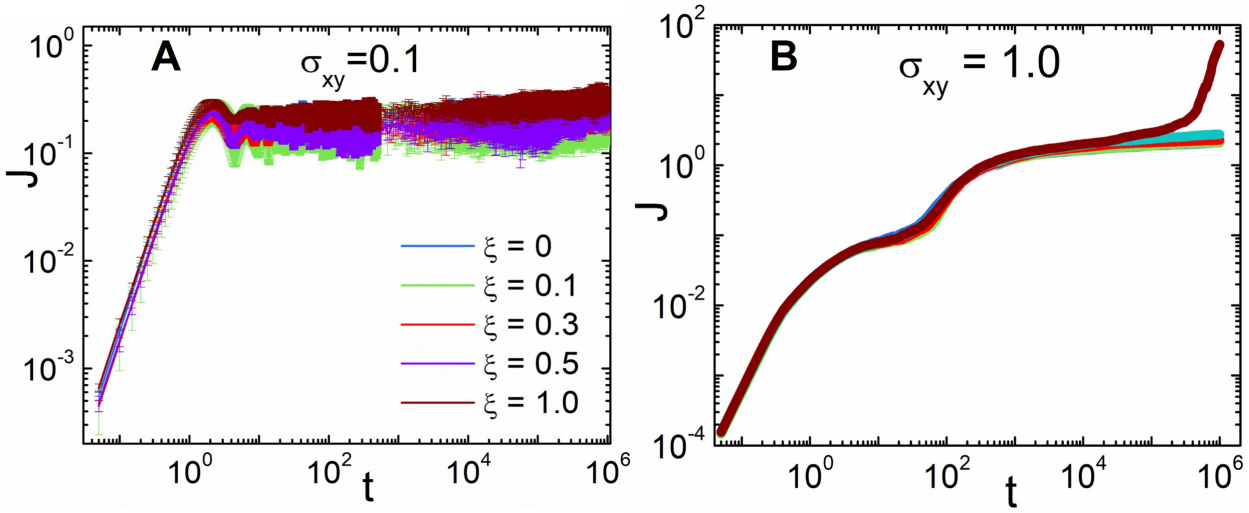

Fig. S2. Shear compliance as a function of time for hybrid networks under applied stress of (A) $\sigma_{xy} = 0.1$ and (B) $\sigma_{xy} = 1.0$.

Bond characteristics during shear creep experiment

We also determine the accumulated bond swaps in the hybrid networks, presented in Fig. S3. A comparison between Fig. S3.A and Fig. S3.B showed a marked increase in the bond exchanges in the hybrid networks at higher applied ($\sigma_{xy} = 1.0$) which supplements the shear compliance presented in the Fig. S2.B. The increase in ξ increases the network's ability to undergo creep.

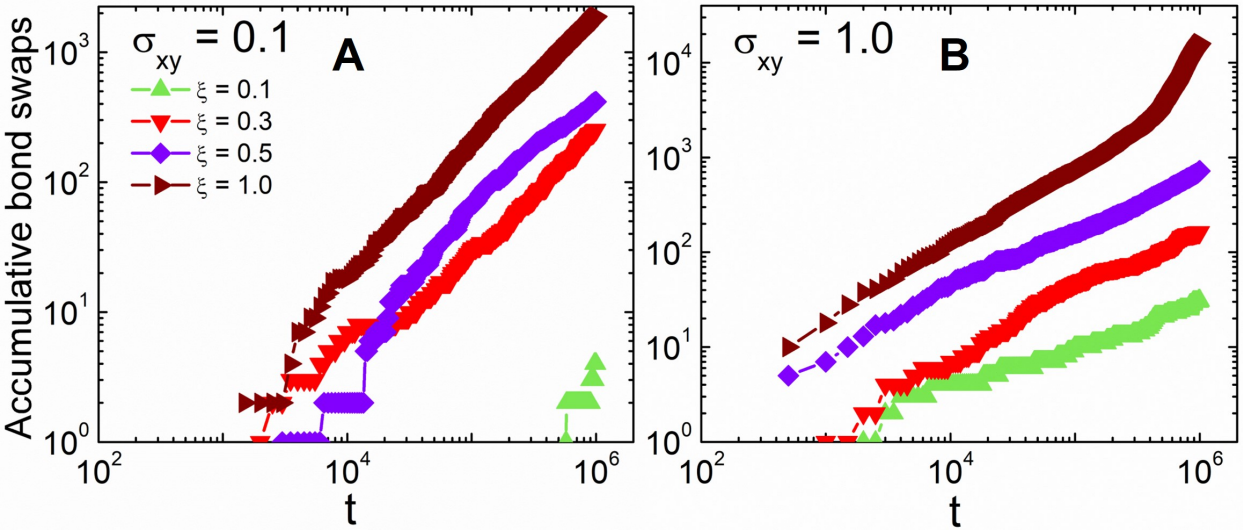

Fig. S3. Accumulative bond exchanges in hybrid vitrimer networks as a function of time during the shear creep experiment under applied shear stress of (A) $\sigma_{xy} = 0.1$, and (B) $\sigma_{xy} = 1.0$.

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