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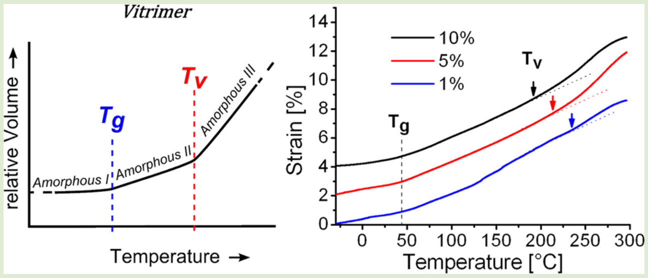
# Catalytic Control of the Vitrimer Glass Transition

Mathieu Capelot, Miriam M. Unterlass, François Tournilhac, and Ludwik Leibler*

Matière Molle et Chimie, UMR 7167 ESPCI-CNRS, Ecole Supérieure de Physique et Chimie Industrielles de la Ville de Paris ESPCI ParisTech, 10 rue Vauquelin 75005 Paris, France

S Supporting Information

**ABSTRACT:** Vitrimers, strong organic glass formers, are covalent networks that are able to change their topology through thermoactivated bond exchange reactions. At high temperatures, vitrimers can flow and behave like viscoelastic liquids. At low temperatures, exchange reactions are very long and vitrimers behave like classical thermosets. The transition from the liquid to the solid is reversible and is, in fact, a glass transition. By changing the content and nature of the catalyst, we can tune the transesterification reaction rate and show that the vitrimer glass transition temperature and the broadness of the transition can be controlled at will in epoxy-based vitrimers. This opens new possibilities in practical applications of thermosets such as healing or convenient processability in a wide temperature range.



When an amorphous polymer melt is cooled down, it undergoes the glass transition. In the vicinity of the glass transition temperature, $T_g$, the polymer hardens abruptly as its viscosity increases by several orders of magnitude following a non-Arrhenius, Williams−Landel−Ferry (WLF) law (Figure 1A).[1−4] Fragility describes how abrupt the temperature variation of viscosity near the glass transition is.[5] Polymers like all other organic compounds are fragile glass-formers.

In striking contrast, silica, the archetype of glass, and few other inorganic compounds undergo a very gradual Arrhenius-like viscosity change near $T_g$.[6−9] They are called strong glass-formers, the term strong being coined to underline their unique behavior. Indeed, glass blowing or easy shaping by local heating without need of precise temperature control or a mold is possible because silica is a strong glass-former.

Recently, Leibler and co-workers introduced and demonstrated the concept of vitrimers, organic strong glass-formers.[10,11] Vitrimers are made of atoms that are covalently bonded to form a network and the design principle is based on reversible network topology freezing. When the network is able to change its topology through bond exchange reactions, the material relaxes stresses and flows,[12−17] even though the total number of bonds stays constant in time and does not fluctuate. The material behaves like a viscoelastic melt. In a vitrimer, the exchange reactions are thermally activated. As a result, upon cooling, the relaxation time and viscosity controlled by exchange reactions rate decrease slowly and it follows an Arrhenius law (Figure 1B). At some temperature $T_v$, the mechanical relaxation time controlled by the exchange reaction rate becomes longer than the experimental time scale and on this time scale, the network topology is frozen. The material appears to be an elastic solid with the elastic modulus between 1 MPa and 100 MPa, depending on the cross-link density. Like for a classical glass transition,[18] the value of the topology freezing transition temperature $T_v$ depends on the cooling rate. Thermal expansion measurements on vitrimers confirmed the glass-like nature and rate dependence of the transition at $T_v$.[10]

We would like to stress that the freezing topology transition is not a viscous-to-elastic gel transition. When approaching the gelation transition, the number of bonds and the connectivity of the molecules increase.[19−21] At the gel point, the system is composed of a broad distribution of linked clusters[22] with one of them being “infinite” and percolating through the sample: the system becomes elastic. In vitrimers, the connectivity does not change and the network is always “infinite”, that is, beyond the percolation threshold (gel point). Remarkably, although the network flows above $T_v$, the material is insoluble at all temperatures, since the number of bonds remains constant.[23]

Upon further cooling, below $T_v$, vitrimers undergo another much more abrupt transition from an elastic to a hard solid, a glass with modulus of about 1 GPa. This transition from an elastic solid to a hard glass is analogous to $T_g$ observed in classical thermosets and elastomers.

Relying on thermal activation considerably limits the practical importance of vitrimer systems. Catalysis offers an efficient way of controlling exchange reaction rate and, as a consequence, the broadness of the topology freezing transition. Here, we demonstate this concept for the simple and practical system of epoxy/acid networks and transesterification exchange reactions. Transesterifications are equilibrium reactions, where an ester and an alcohol are transformed into another ester and another alcohol, via alkoxy interchange. Various catalysts, such as organic bases or inorganic salts, have been used in the literature to control transesterification reactions.[24] All epoxy/

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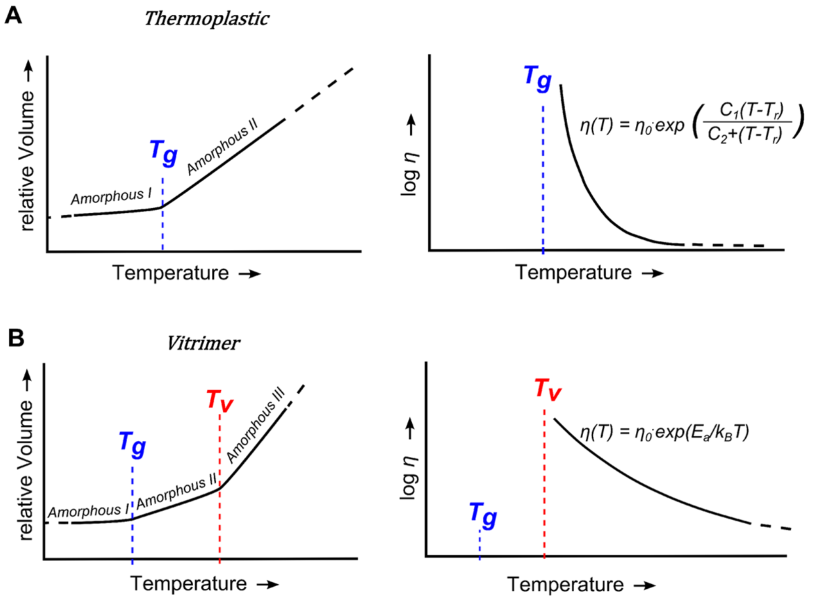

**Figure 1.** (A) Left: V−T characteristics of a thermoplastic polymer. At $T < T_g$ (*Amorphous I*), the physical state is conventionally referred to as glass, at $T > T_g$ (*Amorphous II*) as liquid. Right: Above $T_g$, the viscosity of a thermoplastic polymer follows a WLF power law with the temperature. (B) Left: V−T characteristics of a vitrimer, thus, depicting two glass transitions: the classical $T_g$ and $T_v$, a glass transition that reflects topology freezing upon cooling. Right: The viscosity follows an Arrhenius law in the vicinity of $T_v$.

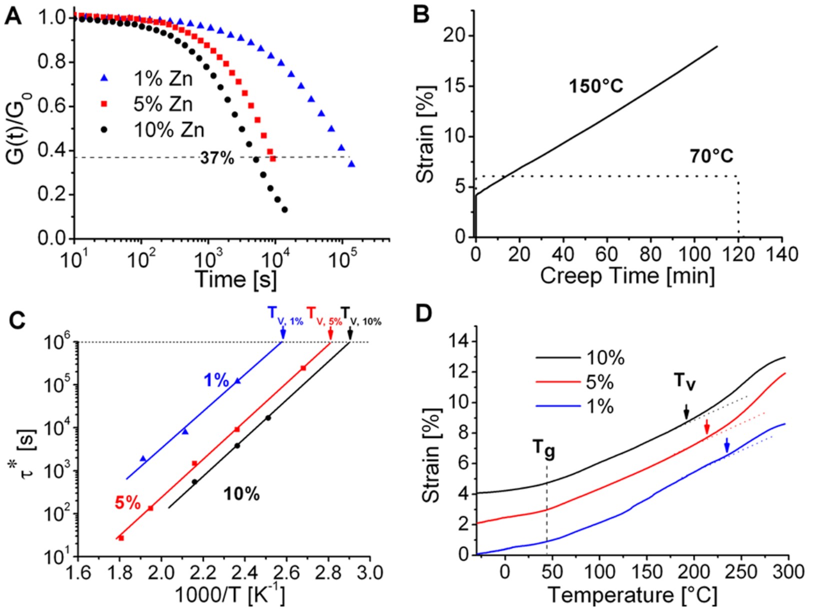

**Figure 2.** (A) Shear stress relaxation experiments: normalized relaxation modulus as a function of time for three different concentrations of $Zn(OAc)_2$ at 150 °C. Relaxation times are measured for a 63% relaxation. (B) Elongational creep experiments at 150 °C for a sample catalyzed at 10 mol % of $Zn(OAc)_2$ at 70 and 150 °C with a nominal stress $\sigma = 0.1$ MPa. Please note that because of thermal expansion, the strain at initial time is slightly different for two temperatures. (C) Arrhenius plot of the measured relaxation times for 1, 5, and 10 mol % of $Zn(OAc)_2$. (D) Dilatometry experiments for 1, 5, and 10 mol % $Zn(OAc)_2$ with a heating rate of 5 K/min.

acid networks investigated here seem to behave like insoluble strong glass formers. We show that by changing the content and nature of the catalyst, the value of $T_v$ and the broadness of the transition can be changed in a controlled way.

Vitrimers were synthesized from diglycidyl ether of bisphenol A (DGEBA) and a mixture of tricarboxylic and dicarboxylic fatty acids. The epoxy-acid reaction is rather complicated, because of several backside reactions occurring during the curing, such as homopolymerization of the epoxy groups.[25] Thus, catalysts are conventionally used to facilitate the epoxy ring-opening.[26] The stoichiometry was adjusted to one carboxylic acid per epoxy function, which leads to the formation of $\beta$-hydroxyl-esters, prone to transesterifications.[25] All transesterification catalysts used in this study are also efficient catalysts regarding epoxy-acid polymerizations.[27] The resulting networks are elastomeric, since $T_g$ is below room temperature (15 °C from DSC studies).

The effect of the catalyst concentration on the network dynamics was investigated. Previous studies on model molecules indicated that exchange reaction rate varies with

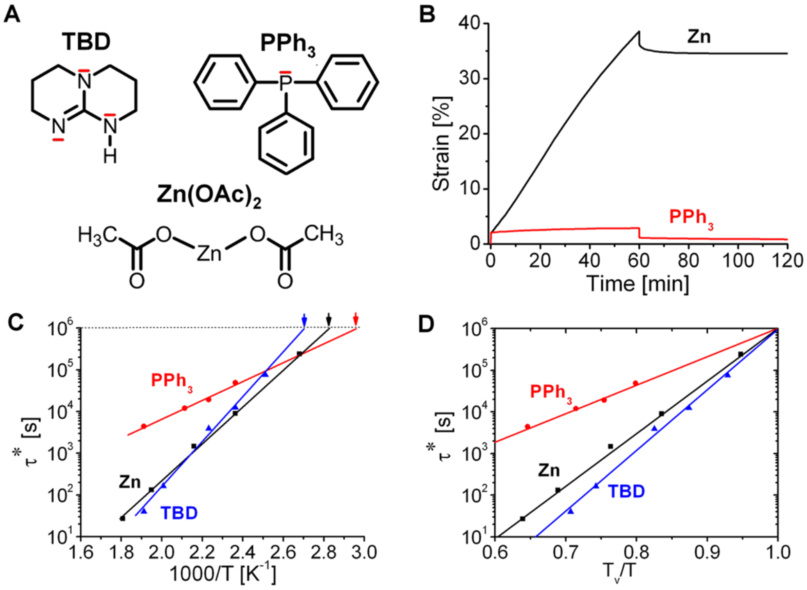

**Figure 3.** (A) Catalysts used in the study. The acetate ligands are replaced by the fatty acids in our systems. (B) Creep and recovery experiments at 200 °C for samples catalyzed at 5 mol % by $Zn(OAc)_2$ and $PPh_3$ with an applied stress $\sigma$ = 0.1 MPa. The stress was released after 60 min. (C) Arrhenius plot of the relaxation times for $Zn(oAc)_2$, $PPh_3$, and TBD at 5 mol %, measured from shear stress relaxation experiments. (D) Angell fragility plot, normalized at $T_v$ for $Zn(oAc)_2$, $PPh_3$, and TBD at 5 mol %.

the catalyst content.[11] Networks were synthesized with different concentrations of zinc acetate: 1 mol %, 5 mol %, and 10 mol %. The exchange reactions and resulting topology rearrangements allow the networks to relax stresses. Shear stress relaxation experiments were conducted in the linear regime on the samples at different concentrations of catalyst at temperatures varying between 100 and 280 °C. Figure 2A shows shear stress relaxation curves obtained at the same temperature (150 °C) for the 3 different concentrations for an applied strain $\gamma$ = 5%. As expected, the higher the catalyst concentration, the faster the stress relaxation. By convention, we chose to determine relaxation times $\tau^*$ from the curves as the time necessary to relax 63% of the initial stress.

Creep experiments confirm that materials flow. Figure 2B shows the results from elongational creep experiments for the networks catalyzed with 10 mol % of zinc acetate ($Zn(OAc)_2$) at 150 °C. After the elastic response, the deformation varies linearly with time, as expected for a viscoelastic liquid.

Relaxation times $\tau^*$ follow an Arrhenius law with the temperature $\tau(T) = \tau_0 \exp(E_a/RT)$ (Figure 2C). Conventionally, the liquid-to-solid transition temperature (i.e., $T_v$ for vitrimers) is considered as the point at which the viscosity becomes higher than $10^{12}$ Pa·s.[2,3,6] The liquid-to-solid transition temperature, $T_v$, may therefore be determined from the Arrhenius curves for relaxation times of $10^6$ s.[28] For 10 mol % of $Zn(OAc)_2$, this transition temperature is about 75 °C. Below this temperature, the material behaves like a conventional thermosetting network, as confirmed by a creep experiment at 70 °C (Figure 2B). With smaller amounts of catalyst, this transition temperature increases. Interestingly, for all three catalyst concentrations, the same activation energy for the topology freezing is observed ($E_a$ ~ 90 kJ/mol). Dilatometry experiments (Figure 2D) nicely confirm the existence of the glass transition at $T_v$ in networks capable of topology rearrangements. Indeed, a network with its degrees of freedom constrained by cross-links is expected to show a lower thermal expansion coefficient than a corresponding system without cross-links. In the absence of the Zn catalyst, the transesterification reactions are very slow and the linear expansion coefficient remains constant from 100 to 300 °C. This observation is consistent with the notion of a permanent network. When a catalyst is added, exchange reactions are faster and an increase in the expansion coefficient is clearly observed at $T_v$. An increase in the catalyst concentration clearly shifts this transition to lower temperatures. Dilatometry also shows the other glass transition at a lower temperature, $T_g$, which is identical for all samples. This reversible transition corresponds to freezing-in local bond orientational motions and is usually referred to as the "rubber-glass transition" for rubbers and tightly cross-linked networks. In our systems, the proper term should be glass-to-glass transition. Indeed, a permanent covalent network is nonergodic and can be viewed as a glass.[29,30] Therefore, the catalyst concentration controls the transition temperature $T_v$, in a very similar way a plasticizer affects the classical glass transition $T_g$.

Numerous catalysts can be employed to control the transesterification rate. Triphenylphosphine[31] ($PPh_3$) and triazobicyclodecene[32] (TBD) were studied and compared with zinc acetate (see chemical structures in Figure 3A). Indeed, the mechanisms of catalysis with organic compounds are very different to those of metal salts and strong effects on activation energies can thus be anticipated. Creep experiments allow for the determination of the efficiency of the catalysts at a particular temperature. Indeed, the more efficient the catalyst is for the transesterification reactions, the faster the exchange reactions and the lower the viscosity. Figure 3B depicts the elongational creep experiments obtained for $Zn(OAc)_2$ and $PPh_3$, under identical conditions (200 °C, applied stress of 0.1 MPa for 1 h, amount of catalyst: 5 mol %). Interestingly, the two catalysts lead to a very different viscoelastic behavior. For example, after the stress release, the sample loaded with $Zn(OAc)_2$ exhibits a residual deformation of 35%; whereas, the sample with $PPh_3$ recovers its original length almost entirely. We measured for different temperatures the relaxation times $\tau^*$

via stress relaxation for the three catalysts at the same concentration. The variations with the temperature follow Arrhenius law. As expected, the more efficient transesterification catalysts, $Zn(OAc)_2$ and TBD, yield lower relaxation times at high temperatures (Figure 3C).

The three catalysts display different freezing topology temperatures $T_v$, whereas the glass-to-glass transition $T_g$ does not change (from DSC studies). The activation energies are remarkably different for different catalysts, as emphasized by the "Angell fragility plot" in Figure 3D. This flexibility brought by the catalyst could prove to be useful to tune vitrimer flow properties for different applications and service temperatures.

Vitrimers constitute a new class of materials: they behave like strong organic liquids and display two glass transitions, $T_g$ and $T_v$. The topology freezing transition, occurring at $T_v$, is solely due to exchange reactions and can therefore be controlled via both catalyst type and concentration. The glass transition temperature $T_g$ can be controlled by the used composition.[33] Both transition temperatures, $T_g$ and $T_v$, vary when the cross-linking density is changed. Technologically, vitrimers can thus be designed at will to obtain healing properties or malleability in a chosen temperature range. Fundamentally, a $T_v$ much lower than that of inorganic strong glasses may help to carry out physical studies to obtain a better understanding of the physics of the glass transition. This concept could be readily used for other exchange chemistries.[34]

## ASSOCIATED CONTENT

### Supporting Information

Experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: ludwik.leibler@espci.fr.

### Notes

The authors declare no competing financial interest.

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