Research paper

Modeling self-healing behavior of vitrimers using molecular dynamics with dynamic cross-linking capability

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HIGHLIGHTS

• Vitrimers epoxies can enable advanced self-healable/recyclable aerospace composites.
• This work addresses molecular modeling of vitrimers during thermomechanical loading.
• CAN is modeled by temperature-based probability for thermomechanical response in MD.
• Simulated healing of CNT pull-out damage defect shows full elastic modulus recovery.

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ABSTRACT

Vitrimers are a special class of polymers that undergo dynamic cross-linking under thermal stimuli. Their ability to exchange covalent bonds can be harnessed to mitigate damage in a composite or to achieve recyclable aerospace composites. This work addresses the primary challenge of modeling dynamic cross-linking reactions in vitrimers during thermomechanical loading. Dynamic bond exchange reaction probability change during heating and its effect on dilatometric and mechanical response are simulated for the first time in large scale molecular dynamics simulations. Healing of damage under thermal cycling is computed with mechanical properties predicted before and after self–healing.

1. Introduction

Thermoset polymers find applications in fields ranging from robotics, aerospace, automobile, electronics, and batteries either as is or as a part of fibrous composites [1]. There are some challenges in their usage that need to be addressed, for instance, the inability to recycle and re-process due to the irreversibility of the cross–linking bonds and damage evolution in structurally loaded components. Vitrimers are a promising alternative material system that has been recently designed to address these issues[2–6]. Vitrimers contain dynamic cross-links that enable them to behave like thermosets at low temperatures and behave like thermoplastics at higher temperatures [7]. This enables self–healable aerospace composites where damage can be reversed through heating, or recyclable matrix materials where the matrix can be reclaimed after use [8,9,1]. Numerous covalent bond exchange mechanisms have been discovered in the recent past such as amines [10,11], transesterification reactions [12], Diels–Alder reaction [13], radical formation [6], etc. Vitrimers have been recently incorporated in carbon fiber composites [14,3] and nanocomposites [15] which expands their scope of applications.

Molecular dynamics (MD) models of conventional thermosets have now found use in the aircraft industry. In recent years, these models have demonstrated reliable prediction of the glass transition temperature [16], gelation point [17], thermal expansion coefficient [18], thermal conductivity [19,20], elastic properties [21], and even complete yield surface [22] without any experimental inputs allowing for computational materials design. The primary challenge for vitrimers is the presence of temperature-dependent reversible cross–link reactions that dynamically alter their mechanical response. Exchange reactions have been modelled in the past via methods such as embedding Monte Carlo (MC) moves into molecular dynamics (MD) or fully MC simulations to simulate bond swaps [23–27]. These simulations have typically employed coarse-grained models (bead–spring) that provide high computational efficiency while approximating the mechanical response. For more quantitative modelling, all–atom MD methods are attractive [28,29], however, these methods become computationally demanding when simulating slow chemical and mechanical dynamics. Yang et al. [30]
modelled bond exchange reactions in all-atom MD by implementing a distance-based reaction cutoff, which greatly accelerates the chemical dynamics. Bonds were created based on the proximity of reacting atoms and the topology was accepted based on the energy of the new bond. However, the simulation had to be started with a low distance cutoff for stability considerations (to avoid large changes in energies due to initial reactions) and the cutoff was subsequently increased. In this paper, we avoid this issue using an algorithm for chemical reactions based on a pre and post–reaction templates with fixed proximity cutoff [31,32]. Our approach employs an explicit temperature dependence of reaction probabilities drawn from experimental insights. The approach allows, for the first time, modeling of mechanical property changes in vitrimers during thermal cycling above and below topology freezing point (Tv) while demonstrating healing of damage and subsequent recovery of mechanical properties.

In this work, we considered epoxy monomer diglycidyl ether of bisphenol A (DGEBA) cross-linked with 4-aminophenyl disulfide (AFD) vitrimer (structures shown in Fig. 1(a)). This particular system was chosen due to its ability to achieve dynamic cross-links in the absence of catalysts [33]. This isomer of AFD also demonstrates mechanochromatic behavior within the visible spectrum (due to the position of the amine group at ortho position [34]) which is useful for damage detection. Further, this is one of the few vitrimeric systems that has been integrated into a fiber composite [35]. Through reconfigurable sulfur–sulfur (S–S) linkage (Fig. 1(c)), the network can change its topology, preserving the number of bonds but at the same time relaxing its stresses. When the temperature decreases (cooling), the exchange reactions slow down and the network topology appears to be fixed on experimental time scales. Hence, it behaves like an elastic thermoset without the self-healing behavior, which is assigned to all the atoms with pair, bond, angle, dihedral and improper coefficients modeled [37]. The non-bonded interactions are modeled using Lennard-Jones (LJ) and Coulombic pairwise interaction with a cutoff. The mixture is compressed to a liquid density of 1.0 g cm−3 at 300 K and 1 atm NPT. Then the mixture is cured via curing reaction modeling in LAMMPS [32]. This is not a force-field based reaction modeling, but a bonding procedure for two atoms which mimics a chemical reaction [31] and the sites are identified by the pre– and post–reaction templates as well as on the mapping between the two templates [31] (a schematic shown in Figure S1 of supplemental information (SI)). The primary and secondary amine reactions are modeled with their respective reaction templates as well as their reaction maps (refer Figure S2 of SI). The cut off distance between C and N atoms is set to be 3.5 Å and 5.0 Å for the primary and secondary amine reactions, respectively. In addition to bonding cutoff distance, a reaction probability of one was assigned for the curing reaction. The system is able to achieve up to 95% cross-linking density (Figure S3, S4 of SI).

The dynamic S–S bond exchange process is modeled as a two step reaction. A pre and post-reaction templates are constructed for both the reactions along with a reaction map (refer Figure S6 of SI for reaction templates). When two pairs of disulfide sites come together, they can exchange the chains attached to them as shown in Fig. 1(c). The bond exchange reaction can happen when the distance between any sulfur atoms from different chains come within a cutoff distance of 4.12 Å (double of the S–S bond length [38], 2.06 Å) and when such sites are identified, the probability of the reaction is modeled as a function of temperature. For vitrimers, the temperature at which the acceleration of the reaction rate occurs is referred as topology freezing temperature (Tv) and this value can be different or close to the glass transition temperature (Tg) of the vitrimer [4,39]. In this paper, we assumed that both the transitions occur at the same temperature (Tv = Tg = 403 K). However, in case of different transition temperatures, the vitrimer’s behavior can be modeled by considering Tv as the reference for dynamic bond exchange reaction probability. It is observed in experiments that the dynamic bond exchange reactions are very slow at room temperature but can accelerate near or above the topology transition temperature of this vitrimer system [33,34]. The modulus is seen to soften and the mobility of the chains accelerate around the transition temperature in a sigmoidal manner [40]. Based on this insight, we model the topology transition by accelerating the dynamic bond exchange reactions in a sigmoidal manner around the vitrimer transition temperature. Note that the actual experimental time scales of the exchange reactions are slower [41], and accelerated rates serve to...
realistically capture the thermomechanical behavior within the time scale of molecular dynamics simulations [28,29]. To model the onset of dynamic exchange reaction phenomena in the current model, we assign the probability of S–S bond exchange reaction as a function of the temperature as shown in Fig. 2.

The probability of the dynamic bond reaction as a function of temperature is given by Eq. 1.

$$p(T) = \frac{1}{\left[ \exp\left(-\frac{a(T - T_c)}{T - T_c}\right) - \ln\left(\frac{p_0}{1 - p_0}\right) + 1\right]}$$

where, $a = \frac{\beta_0 w}{(w - p_0)}$ is determined by $w$ which is the measure of the width of the transition from glassy to rubbery phase, for example, using the modulus vs temperature response (we consider, $w = 20 K$), and $p_0 = 0.9$ is the probability of the dynamic bond exchange reaction at $T_c$ ($T_c$ line in Fig. 2), we assume that at $T_c$, most of the transition starts occurring but it is not complete hence $p_0 = 0.9$. And, we assume that at the beginning of the transition window, $T_i - w$, the probability is $p(T_i - w) = 1.0 - p_0 = 0.1$. This is considered in order to obtain a smooth increase in the reaction rate near $T_c$.

3. Results and discussion

We first analyze the molecular dynamics model without dynamic S–S bond (indicated in plots as ‘static’ model) and then the vitrimer is investigated with dynamic S–S bond exchange modeled. The annealed structure is equilibrated for 150 ps [42] at each temperature starting from 200 K to 550 K at an increment of 5 K. The change in volume is computed and normalized with respect to the initial volume at 200 K ($V_0$). The algorithm keeps a cumulative count of bond exchange reactions that occurred in the system [31]. In this system, the number of bonds remain conserved, and hence, bond breaking is accompanied with new S–S bond formation (as sketched in Fig. 1(c)). The number of S–S bond–exchange reactions occurring at each temperature is depicted as a red line in Fig. 2 alongside the chosen reaction probability (in blue). This plot indicates that the number of reactions begin to increase as we get close to $T_c$ and stabilizes around $T_c$. At temperatures well beyond $T_c$ (when the probability of the reaction is 1.0), the number of reactions increase further with increase in temperature. This is attributed to an increase in the frequency of collision events of bonding atoms at higher temperatures. These features are achieved by developing a reaction probability centered around the topology freezing transition point based upon experimental insights [33,34]. If the vitrimer transition temperature were lower than the glass transition temperature, then the reaction rates will be lower owing to higher stiffness of the polymer which will significantly decrease the collision frequency. As an example, we find that the number of exchange reactions over 150 ps was 53% lower for $T_c$ set at 200 K vs 403 K for this polymer. By changing the $T_c$ value, we expect the model to capture the topology transition behavior for other such vitrimers as well.
behaves like a viscous fluid beyond the topology transition temperature ($T_i$) \cite{3,14,15}, molecular dynamics results show sustained stresses beyond $T_i$ due to the high loading rates (as is also seen in MD literature \cite{28,29}).

We now exploit the dynamic S–S bond exchange reaction capability to demonstrate healing of vitrimers in MD simulations. The damage corresponds to a carbon nanotube (CNT) pullout from the matrix \cite{48–50}. We first insert a (12,12) single walled CNT of 91 Å length along z-axis, and displace the atoms radially in xy plane. The rest of the curing protocol, described in the methods section, remains same as the neat vitrimer model with a final density of $\rho = 1.19$ g cm$^{-3}$ at 1 K (refer Figure S5 of SI). To generate the damage, the CNT was removed out of the equilibrated simulation box. Then the simulation box is heated up to a temperature $T_v + 100 K = 503$ K for 250 ps. The hole heals under the influence of dynamic S–S bond exchange reactions. The healed system is then relaxed back to analyze its elastic response at room temperature. Fig. 5 shows the elastic response of the damaged and healed vitrimers (average of three different direction stretches with the bounds shown by light colors) at 300 K. We observe that the stress–strain response of the healed vitrimer is consistently higher than that of the initial damaged sample along all the three loading directions demonstrating healing. In order to plot the elastic properties over a range of temperatures, we computed the stiffness by linear regression in $\varepsilon = 4$% range and the elastic modulus was averaged in all the three directions. Fig. 6 demonstrates that the healed structure is able to recover the pristine vitrimer elastic modulus over the range of the temperatures below topology freezing point. Snapshots of damage healing showing the hole left by CNT pullout being filled via a dynamic bond exchange mechanism post $T_i$ are shown as insets (refer animation in SI).

4. Conclusions

In conclusion, a vitrimer’s ability to dynamically reform covalent bonds during thermal cycling allows one to achieve superior behavior over traditional thermostets such as damage healing. To model this behavior, we have developed a novel temperature dependent reaction probability which is integrated with molecular dynamics modeling of vitrimers. The reaction probability is empirically based on the observed reaction kinetics of dynamic bond exchange near or above topology freezing transition temperature ($T_v$). It is shown that the model captures the onset as well as the increase in the number of reactions above this transition point owing to higher mobility of chains, without the need to alter reaction distance cutoffs. The vitrimer is seen to achieve softer behavior around and beyond topology freezing transition temperatures while maintaining the glassy behavior at pre-transition temperatures upon thermal cycling. In the simulation of the healing of a cylindrical pore created due to CNT pullout, the model is able to show both the healing of the vitrimer and complete recovery of elastic modulus upon cooling. Such modeling capability can be further used to achieve insights into the interplay of mechanics and chemistry in a variety of other dynamic bond exchange materials.

CRediT authorship contribution statement

Gurmeet Singh: Conceptualization, Investigation, Methodology, Supervision, Formal analysis, Validation, Visualization, Writing - original draft, Writing - review & editing. Veera Sundararaghavan: Conceptualization, Formal analysis, Investigation, Methodology, Supervision, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cplett.2020.137966.

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