Recyclability of Vitrimer Materials: Impact of Catalyst and Processing Conditions

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ABSTRACT: With sustainability at the forefront of material research, recyclable polymers, such as vitrimers, have garnered increasing attention since their introduction in 2011. In addition to a traditional glass-transition temperature \((T_g)\), vitrimers have a second topology freezing temperature \((T_v)\) above which dynamic covalent bonds allow for rapid stress relaxation, self-healing, and shape reprogramming. Herein, we demonstrate the self-healing, shape memory, and shape reconfigurability properties as a function of experimental conditions, aiming toward recyclability and increased useful lifetime of the material. Of interest, we report the influence of processing conditions, which makes the material vulnerable to degradation. We report a decreased crosslink density with increased thermal cycling and compressive stress. Furthermore, we demonstrate that shape reconfigurability and self-healing are enhanced with increasing compressive stress and catalyst concentration, while their performance as a shape memory material remains unchanged. Though increasing the catalyst concentration, temperature, and compressive stress clearly enhances the recovery performance of vitrimers, we must emphasize its trade-off when considering the material degradation reported here. While vitrimers hold great promise as structural materials, it is vital to understand how experimental parameters impact their properties, stability, and reprocessability before vitrimers reach their true potential.

INTRODUCTION

Vitrimers and other dynamic polymer materials hold great promise in various applications ranging from structural materials to coatings and actuators.\(^1\)−\(^5\) Coupling the strength and stiffness of a thermoset with the processability of a thermoplastic makes vitrimers particularly exciting for the increased push toward polymer sustainability.\(^5\)−\(^9\) For example, recyclable and self-healing polymers can increase the lifetime of materials, allowing one to move away from single-use components.

However, before vitrimers and other covalently adaptable networks (CANs) can be utilized in real-world applications, it is vital to understand how their composition and processing conditions impact their cycle lifetime. Previous research has clearly demonstrated that environmental conditions (e.g., temperature and stress)\(^10\)−\(^12\) and compositional conditions (e.g., catalyst type and catalyst concentration)\(^11,13,14\) impact vitrimer and vitrimer composite performance.\(^1,13\)−\(^17\) Primarily, vitrimer characteristic performance can be quantified by measuring the topology freezing temperature \((T_v)\), where these dynamic covalent bond exchange reactions freely occur.\(^10,11,18\)−\(^21\) To name a few, Capelot et al.\(^14\) initially reported that varying the catalyst composition and increasing its concentration can decrease the \(T_v\). In addition, Kaiser et al.\(^10\) and our previous research\(^11\) confirm that increasing stress on the sample and decreasing the sample heating rate both quantitatively decrease the \(T_v\). Overwhelmingly, it is clear that catalyst composition and concentration are the two primary factors determining vitrimer performance.

While these fundamental impacts are well documented, the effect on overall applicability is far less understood. Herein, we discuss how compositional and environmental factors impact the self-healing, shape memory, shape reconfigurability, and overall network resistance of vitrimer materials. For example, to the authors’ knowledge, quantified changes in shape reconfigurability as a function of catalyst concentration and stress on the same are yet to be explored. We should, at this time, note the difference between self-healing, reprogramming, and reprocessing. While the mechanism behind these methods is the same (dynamic covalent bond exchange reaction), they are phenomenologically different. Self-healing corrects damage...
inflicted upon the sample in the form of scratches, cuts, or internal damage accumulated in service.\textsuperscript{12,22–24} Reprogramming/reconfigurability transforms the material to a new permanent shape with the material not being broken down (e.g., palletization, melting, etc.), which will be discussed in a later section.\textsuperscript{16,18,25,26} Finally, reprocessing breaks down the polymer materials for regeneration of a new sample, which is outside the scope of this work.\textsuperscript{1,2,23,27–31} It is worth noting that shape memory is similar to reprogramming, where instead of a new permanent shape, the polymer material is programmed into a temporary shape.

While shape memory capability does not appear to be significantly impacted by catalyst concentration or applied stress on the sample, the same cannot be said for either self-healing or shape reconfigurability. This correlation is reasonable given the fact that shape memory behavior takes advantage of the matrix’s glass transition temperature ($T_g$) or melt temperature ($T_m$), while self-healing and shape reconfigurability take advantage of the $T_v$. We demonstrate, for the first time, that increasing the catalyst concentration can make the vitrimer network susceptible to a decreased crosslink density and $T_v$ as a result of cyclic processing with compressive stress; this finding is in direct opposition to the commonly held notion that vitrimers maintain a constant crosslink density with processing. Although vitrimers demonstrate cyclic healing behavior, understanding and quantifying their susceptibility to network structure and physical property changes throughout these cycles are essential to using vitrimers in their diverse range of potential applications.

\section*{RESULTS AND DISCUSSION}

Herein, we demonstrate the effect of processing (i.e., repeated thermal cycling and the application of compressive stress) on material performance in the presence of a catalyst of various concentrations. It should be noted that we only explore one vitrimer chemistry to fully understand the impact of each experimental parameter and additional vitrimer chemistries will be explored in future work. Throughout this work, the dynamic covalent bond exchange reaction is a transesterification reaction, as detailed in the Materials and Methods section where the components of this vitrimer material are seen in Figure 1.\textsuperscript{4,6,8,9,11,32} Overall, we report that increasing the catalyst concentration decreases the $T_v$ and increases the vitrimer’s processability (cf. Figure 1).

\textbf{Mechanical Characterization and Self-Healing.} First, it is important to characterize the properties (i.e., mechanical and thermomechanical) of the neat vitrimer material. As previously reported, the $T_g$ changes minimally with variations in catalyst concentration with a value of around 35 °C for a sample with a 5 mol % concentration.\textsuperscript{11} Meanwhile, the $T_v$ decreases with increasing catalyst concentration with a value of around 250 and 200 °C for samples with a 1 and 5 mol % catalyst concentration, respectively (cf. Figure S1). In the absence of a catalyst, the $T_g$ is noticeably higher, around 53 °C, and there is no reported $T_v$. This trend of decreasing $T_g$ with increasing catalyst concentration makes sense as the crosslink density is shown to be indirectly related to the catalyst concentration (cf. Figure S2). These transition temperatures ($T_g$ and $T_v$) are the key parameters dictating the shape memory and shape reconfigurability behavior of the material, respectively. Shape memory can be achieved by cycling above and below the $T_g$, only, while shape reconfigurability involves cycling above and below the $T_v$.

In addition, we also demonstrate a decrease in mechanical properties with increasing catalyst concentration (Young’s modulus of 1.7 and 1.1 GPa for samples with 0 mol % or 5 mol % catalyst concentration, respectively), where all tested materials exhibit ductile behavior and necking, as seen in Figure S1.\textsuperscript{33} Modulus values agree well with previous literature (e.g., Young’s modulus values of 0.56–1.6 GPa),\textsuperscript{2,16,28} and the inverse relationship between catalyst concentration and mechanical properties is consistent with dynamic mechanical analysis (DMA) data presented in our previous work,\textsuperscript{11} along with the resulting values for molecular weight between crosslinks (cf. Figure S2).

A key application space for vitrimer materials is self-healing, which takes advantage of the dynamic covalent bond exchange
reaction at elevated temperatures. In Figure S3, we show that self-healing (cf. Figure S4) fails in the absence of a catalyst and succeeds in its presence. To quantify this healing behavior, we perform tensile tests on both pristine samples and samples that have been cut and healed (cf. Figure 2). It is reasonable to assume that the relevant experimental parameters in determining the degree of self-healing are time, temperature, pressure, and surface area contact between the healing surfaces.

For clarity, we only vary pressure and time in this study and attempt to measure the change in mechanical response as a function of healing for a sample with a 5 mol % catalyst concentration. Comparing the tensile test results of pristine and healed samples shows reasonable recovery. As expected, increasing the applied pressure during hot pressing (HP) increases the degree of self-healing and recovery of mechanical properties (cf. Figure 2a). Previous research has demonstrated that the transesterification reaction is stress-favored, so that increases in stress should increase the rate of transesterification reactions; additionally, it is reasonable to assume that increasing the compressive stress will increase the surface area contact between the two healing surfaces.12,23,29,34 For clarity, we only vary pressure and time in this study and attempt to measure the change in mechanical response as a function of healing for a sample with a 5 mol % catalyst concentration. Comparing the tensile test results of pristine and healed samples shows reasonable recovery.

Interestingly, increasing the hot press time does not appear to significantly impact the degree of self-healing and recovery of mechanical properties for these pressure and temperature conditions (cf. Figure 2b). This makes sense as both times exceed the stress relaxation constant for these materials, as previously reported.11 It is important to note that we do not see a complete recovery of the mechanical properties (i.e., comparable modulus and yield stress between pristine and healed samples), which is expected given the minor surface scaring as seen in Figure S3b. We postulate that increasing the temperature or pressure would result in full recovery; however, increasing these conditions makes the material vulnerable to network changes, as will be discussed in the next section. We should note that the healing Figure 2. Representative mechanical testing data are shown comparing pristine vitrimer materials with those that have been damaged and self-healed. All samples contained a 5 mol % catalyst concentration, and a minimum of five samples were tested to achieve normal statistical distribution. (a) Samples are healed in a hot press at 200 °C for 1 h, with varying pressures; unsurprisingly, increasing the pressure increases the degree of healing and recovery of mechanical properties. (b) Samples are healed in a hot press at 200 °C under 0.67 MPa of pressure, with varying times. The length of time appears to have a negligible impact on the degree of self-healing; this trend is reasonable as both times exceed the stress relaxation constant for these materials, as previously reported.11

Figure 3. (a) Changes in the \( T_g \) are determined via DSC for a variety of catalyst concentrations after a series of HP. (d) Similar results are reported for samples after a series of temperature sweep experiments cycled with HP. The sample size is four to ensure statistical significance; bars denoted with * indicate statistical significance (\( p < 0.05 \)). The temperature sweep results are reported for samples with no catalyst (b–c) and for samples with a 5 mol % catalyst concentration (e–f) as the storage modulus (b,e) and tan(\( \delta \)) curves (c,f).
times utilized here are significantly shorter than those in previously reported work.\textsuperscript{22,24,35}

**Impact of Processing Conditions.** As demonstrated, a finite amount of pressure must be applied to the sample to achieve self-healing. For example, if vitrimers were simply placed next to each other with time and temperature, no self-healing would be observed in our system (cf. Figure S5). Some softer CANs have previously reported\textsuperscript{22,35} not requiring pressure for self-healing due to their tacky/sticky nature, which ensures proper contact between the two respective surfaces. However, for stiffer materials like ours, they will not naturally stick together and therefore require pressure to ensure proper contact. In addition, the applied pressure facilitates self-healing by increasing the effective contact area between the broken surfaces, therefore increasing the opportunities for the polymer chains to cross-diffuse.

It is worth noting that vitrimers are claimed to have constant crosslink density as a function of temperature and processing conditions, which should enable the materials to tolerate the self-healing conditions as has been noted previously in the literature.\textsuperscript{9,18,36} However, we report here for the first time that by processing these materials with compressive stress, we see a noticeable change in material properties (e.g., \(T_g\) and storage modulus), which is not present in the absence of pressure.

Figure 3a shows how the \(T_g\) changes for samples with varying catalyst concentrations when they are repeatedly hot pressed at 200 °C for 1 h under 0.5 MPa. Differential scanning calorimetry (DSC) was performed between each cycle where a minimum of four samples were tested (achieving normal statistical distribution) to determine the \(\Delta T_g\) with processing. All relevant DSC data are shown in Figure S6 with statistical significance being verified. In the absence of a catalyst, the \(T_g\) increases slightly with repeated processing; with the addition of a catalyst, the \(T_g\) decreases with repeated processing where this trend magnifies with increasing catalyst concentration. We postulate that the increase in \(T_g\) without a catalyst present can be due to many factors, such as the removal of water and residual curing, which will be discussed in greater detail later. In contrast, the surprising decrease in \(T_g\) with repeated HP and in the presence of a catalyst is more complicated and is indicative of some degradation of material properties. While the same processes described for samples without a catalyst are occurring in the presence of a catalyst (i.e., water removal and residual curing), there is clearly some other dominant, competing mechanism driving a reduction of the \(T_g\).

To test this, we performed a cycle of experiments on samples with either no catalyst or a 5 mol % catalyst concentration. The samples were cycled between temperature sweeps in DMA and either HP with applied pressure or thermal annealing (A) without applied pressure. The HP and A steps were performed at 200 °C for 1 h; DSC was done between each processing step to track changes in the \(T_g\). As seen in Figure 3d, the \(T_g\) again increases or decreases with processing for samples without and with a catalyst, respectively, when cycled between DMA and HP.

Of greater interest, the temperature sweep results between each HP are seen for samples without (cf. Figure 3b,c) and with (cf. Figure 3e,f) a catalyst. For samples without a catalyst, the storage modulus and \(\tan(\delta)\) curves are almost identical regardless of processing, which agrees well with the previous literature.\textsuperscript{2,15,27,28,31,37,38} In contrast, in the presence of a catalyst, the storage modulus decreases with processing and the \(\tan(\delta)\) broadens as indicated by the arrows in Figure 3. While some of the previous literature have alluded to this change,\textsuperscript{2,9,34,39,46} it signifies an increase in the heterogeneity of the polymer network and suggests that there is some shortening of the primary chain or reduction in crosslink density. We postulate that this change is due to undesired network structure modification (e.g., an increase in free volume). The application of heat and compressive stress...
appears to enhance the interaction between the catalyst and the network, allowing for greater network rearrangement. This is further supported by previous research, which has demonstrated that the transesterification reaction is stress-favored. It should also be noted that the \( \Delta T_g \) reported via DSC is mirrored in the DMA results, and these trends continue to persist with repeated numbers of cycles. To confirm that there is no significant chemical change taking place with the presence of compressive stress, we report FTIR on a pristine and processed sample, showing negligible changes (cf. Figure S7).

To confirm the importance of compressive stress, we repeated this set of experiments where the samples are cycled between temperature sweeps and annealing steps. As seen in Figure 4a, in the absence of pressure, the sample without a catalyst again exhibits a slight increase in \( T_g \); however, this time, the sample with a 5 mol % catalyst concentration also exhibits a slight increase in \( T_g \). We postulate that without the compressive stress on the sample, there are minimal changes in free volume and the polymer network is not significantly changed. This claim is supported by the storage modulus and \( \tan(\delta) \) of the annealed samples (cf. Figure 4b,c,e,f). In this case, there is some initial increase in \( T_g \) and storage modulus with one annealing step coupled with a sharpening of the \( \tan(\delta) \) curve; this sharpening of the \( \tan(\delta) \) curve points toward an increase in the homogeneity of the network structure, which we postulate is a result of water removal and some residual curing. However, any change in the material property becomes negligible with repeated cycling. Such a change in \( T_g \) has previously been reported for thermoplastics, where it was attributed to nonequilibrium voids trapped in the sample.\(^{41}\) While our study clearly confirms the importance of

**Figure 5.** Shape memory demonstrations are performed for samples with either no catalyst (a) or a 5 mol % catalyst concentration (b). The scale bars are 5 mm. (c) A series of five shape memory cycles are performed where the temperature and force are controlled, and the strain is recorded; even numbered cycles are shaded gray for clarity. (d) Shape memory results are shown for a variety of catalyst concentrations with two applied forces (0.5 and 1.0 N force). In all cases, the change in strain increases with increasing force on the sample. (e) Shape memory results are compiled demonstrating that the change in strain increases with increasing catalyst concentration. (f) These results are quantified and validated by the decrease in the storage modulus of the rubbery regime with increasing catalyst concentration.
Table 1. \( R_c \) and \( R_f \) Reported for All Catalyst Concentrations as Gathered from the Set of Five Shape Memory Cycles (Columns 2–3, Figure 5e)\(^a\)

| Catalyst Concentration | \( R_c \) | \( R_f \) | \( R_c \) | \( R_f \) | \( \varepsilon_{SR} \) | \( \varepsilon_{fSM} \) | \( R_c \) | \( R_f \) |
|------------------------|---------|---------|---------|---------|----------------|----------------|---------|---------|
| none                   | 100.5% | 94.5%  | 97.4%  | 54.7%  | 94.1%          | 98.5%          | 88.7%   |         |
| 1 mol %                | 99.7%  | 93.0%  | 93.1%  | 62.9%  | 93.7%          | 98.4%          | 91.3%   |         |
| 3 mol %                | 99.9%  | 87.1%  | 93.2%  | 93.1%  | 97.9%          | 93.7%          | 98.2%   | 96.7%   |
| 5 mol %                | 99.9%  | 84.3%  | 97.9%  | 93.2%  | 182.2%         | 97.9%          | 98.2%   |         |

\(R_c\) and \(R_f\) are also reported for the final shape reconfigurability and shape memory cycle as taken from the shape reconfigurability experiments (Figure 6d).

Compressive stress on changes in the network structure, additional research must be done to fully quantify its impact.

In addition to \(T_g\) we also quantify the change in the molecular weight between crosslinks (\(M_c\)) reported with cyclic processing as calculated from the storage modulus (cf. Figure 4d).\(^{42,43}\) The subsequent increase or decrease in \(M_c\) mirrors the trends found for \(T_g\) in DSC, verifying the importance of processing conditions on the network structure. When compressive stress is applied to a sample with a 5 mol % catalyst concentration, the \(M_c\) increases; while the volume variations should be small, they clearly lead to large changes in local dynamics, prompting the noticeable changes in the \(T_g\).

To confirm that the degradation of mechanical properties and \(T_g\) is not a result of material degradation due to temperature, we performed a series of thermal degradation studies via thermogravimetric analysis (TGA), as seen in Figure S8. The material exhibits negligible degradation (<5 wt %) at temperatures \(T \leq T_g\) for all catalyst concentrations up to 4 h. In addition, there is a negligible difference between nitrogen and ambient environments (cf. Figures S9 and S10); this distinction is critical as thermomechanical tests are conducted under nitrogen environments while annealing and HP are performed under atmospheric conditions. We also report the thermal degradation values for 1 h, which is the time required for a single processing step. Finally, we should note that there is an initial drop in weight retention for these TGA curves indicative of water removal, as evidenced by cyclic thermal profiles seen in Figure S11.

**Shape Memory.** In addition to self-healing, it is important to understand how the experimental and compositional parameters impact shape memory behavior. Qualitatively, shape memory behavior is exhibited for samples without a catalyst, as seen in Figure S5a,b, respectively. The shape memory behavior relies on cycling above and below the \(T_g\); therefore, the presence of a catalyst (and the transesterification reaction) does not appear to play a role.

To quantify the shape memory capabilities, we performed a series of five shape memory cycles in DMA where the temperature and the applied force are controlled, and the resulting sample strain is monitored (cf. Figure 5c).\(^{16,44}\) The temperature is cycled 25 °C above and below the \(T_g\) and temporary strain is embedded into the material with applied forces of either 0.5 N (solid lines) or 1.0 N (dotted lines). Shape memory cycles are performed for all catalyst concentrations, as seen in Figure S12, while a single cycle is plotted in Figure S13 for clarity. Figure 5d shows that increasing the applied force on the sample increases the resulting strain per cycle, while Figure 5e shows that increasing the catalyst concentration increases the resulting strain per cycle.

These trends can be explained by the increased deformation with a higher applied load and the average storage modulus in the rubbery regime (\(E_{rubber}\) as measured via DMA), which decreases with increasing catalyst concentration (cf. Figure 5f). As previously mentioned, the crosslink density, and therefore the \(T_g\) is indirectly related to the catalyst concentration (cf. Figure S2)\(^{11,45–47}\) as the crosslink density and the \(E_{rubber}\) are directly related, we postulate that the relationship between catalyst loading and strain input during shape memory is fundamentally a result of crosslink density. To account for the noted difference in \(T_g\) with catalyst concentration, Figure S14 shows how the shape memory behavior changes as the set point maximum temperature varies above the \(T_g\). Strain input increases slightly as the maximum temperature increases, but the catalyst concentration is the clear dominant factor determining strain input. It should also be noted that this shape memory behavior can be cycled many times; a total of 25 shape memory cycles are reported for samples without and with a catalyst as seen in Figure S15a and S15b, respectively, showing no degradation in properties.

Additionally, we quantify shape memory behavior by reporting the shape recovery (\(R_c\)) and shape fixity (\(R_f\)) ratios. \(R_c\) measures a material’s ability to retain its permanent shape, while \(R_f\) measures a material’s ability to temporarily fix any newly introduced mechanical deformation.\(^{26,44,46}\) These values are calculated as eqs 1 and 2,

\[
R_c(N) = \frac{\varepsilon_m(N) - \varepsilon_p(N)}{\varepsilon_m(N) - \varepsilon_p(N - 1)} \times 100 \\
R_f(N) = \frac{\varepsilon_f(N)}{\varepsilon_m(N)} \times 100
\]

where \(N\) represents the cycle number, \(\varepsilon_m\) is the maximum strain at \(T_{max}\), \(\varepsilon_p\) is the strain of the sample in the stress-free state before stress application at \(T_{max}\), and \(\varepsilon_f\) is the strain on the sample in the stress-free state after the \(N^{th}\) programming step at \(T_{min}\). Note in this case that \(T_{min} < T_g < T_{max}\). We demonstrate all \(R_c\) values are >99%, regardless of catalyst concentration, as seen in Table 1. Essentially, this indicates that while the amount of strain embedded is dependent upon catalyst concentration (due to the lower \(T_g\) and modulus), the ability to embed and release this strain is catalyst-independent. However, we should note that the \(R_f\) values are all >84%, with an inverse relationship between the catalyst concentration and \(R_f\). We postulate this lower \(R_f\) value is due to some finite amount of thermal contraction coupled with issues in
temperature uniformity magnified by the large sample thickness.

**Shape Reconfigurability.** Finally, we explore the shape reconfigurability of these materials as a function of catalyst concentration and processing conditions, which, to the authors’ knowledge, has not been previously reported. Reconfigurability, similarly to self-healing, is found to be catalyst-dependent as the mechanism is based on the dynamic covalent bond exchange reaction, unlike shape memory, which is a function of polymer chain rearrangement in the rubbery regime. In other words, shape memory involves cycling above and below the $T_g$ to embed temporary strain, while shape reconfigurability involves cycling above and below the $T_v$ to modify the permanent shape. Qualitatively, we see in Figure 6a,b that shape reconfigurability fails for samples in the absence of a catalyst, whereas it succeeds for a sample with a 5 mol % catalyst concentration, respectively. We should note that there is no true $T_v$ for samples without a catalyst, as previously reported; in this case, the $T_v$ for samples with a 5 mol % catalyst concentration (200 °C) is utilized for all samples for demonstrative purposes.

To quantify the shape reconfigurability of these materials, we performed studies on all catalyst concentrations where we control the temperature and applied force and monitor the strain (cf. Figure 6c and S16). A shape memory cycle (white background) is performed between each shape

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**Figure 6.** Shape reconfigurability demonstrations are performed for samples with either no catalyst (a) or a 5 mol % catalyst concentration (b) where the demonstrations are unsuccessful in the absence of a catalyst. The scale bars are 5 mm. (c) A series of alternating shape memory and shape reconfigurability cycles are performed where the temperature and force are controlled, and the strain is recorded; all shape memory cycles are shaded light blue for clarity. (d) Results are shown for a variety of catalyst concentrations where the applied force during shape reconfigurability cycles is either incrementally increasing or held constant. (e) In all cases, the permanently embedded strain increases with increasing force on the sample and catalyst concentration. When the force is kept constant, there is a slight increase in embedded strain. The first three bars for each sample type are recorded from the upper graph of Figure 6d, while the last three bars for each sample type are recorded from the lower graph of Figure 6d. (f) Shape reconfigurability tests are repeated where samples with either a 1 mol % or a 3 mol % catalyst concentration are heated near their $T_v$ of 256 and 219 °C, respectively. 

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reconfigurability cycle (light blue background) to verify that the strain embedded is indeed permanent (cf. Figure S17). The applied force during each shape reconfigurability cycle either incrementally increases by 0.1 N from 0.1 to 0.3 N with each cycle (solid lines) or it is kept constant at 0.2 N for each cycle (dashed lines), as seen in Figure 6d. The applied force for each shape memory cycle is 0.5 N. The amount of permanently embedded strain clearly increases with increasing catalyst concentration and applied force (cf. Figure 6e); when the force is kept constant for each shape reconfigurability cycle, there is a slight increase in the embedded strain due to a shrinking cross-sectional area, resulting in a slightly increasing stress on the sample.

To confirm the importance of catalyst concentration, a shape reconfigurability cycle was performed for samples with 1 mol % and 3 mol % catalyst concentrations at temperatures of 250 and 225 °C, respectively. This was done so that the experiments were performed near the T_g of each respective catalyst concentration (13) (cf. Figure S1a); regardless of this change, we see that increasing the catalyst concentration increases the amount of the final embedded strain (cf. Figure 6f) without varying the stress on the sample. Again, we postulate this is due to the fact that the number of transesterification reactions increases per unit volume and time with increasing catalyst concentration.

Quantitatively, we can calculate the R_s and R_f for the final shape reconfigurability and shape memory cycles plotted as cycles 6 and 7, respectively, in the upper portion of Figure 6d. These values, reported in Table 1, clearly show a decreasing R_s with increasing catalyst concentration for the shape reconfigurability cycles; the opposing trend is seen for R_f. These trends make perfect sense as a new, permanent shape is being fixed into the material for higher catalyst concentrations. One would expect R_s to decrease since an entirely new “permanent” shape is being programmed; contrastingly, one would expect R_f to increase as it can “fix” this new, permanent mechanical deformation.

To take this one step further, we have also calculated the ratio between ε_f as taken from subsequent shape reconfigurability and shape memory cycles. In this case, if no new shape was being fixed, one would expect this ratio to be ~100%, which holds true for samples with low catalyst concentrations. However, as the catalyst concentration increases, this ratio increases closer to 200%, indicating that a significant amount of new strain is being permanently embedded.

Finally, we also report in Table 1 R_s and R_f values close to 100% for the final shape memory cycle. These high values indicate that the ability to undergo shape memory is not impacted by the addition of permanent strain.

**CONCLUSIONS**

Herein, we demonstrated the impact of compositional and environmental conditions on the reprocessability of vitrimer materials. While increasing the catalyst concentration increases the ability of vitrimer materials to undergo shape reconfigurability and self-healing, neither process is possible in the absence of a catalyst, as the transesterification reaction is the underlying mechanism. In contrast, a vitrimer’s shape memory capabilities are catalyst-independent (R_s > 99%), while the amount of temporary strain embedded increases with increasing catalyst concentration (R_f decreases with increasing catalyst concentration).

However, while increasing the catalyst concentration increases the applicability of these materials, it also increases their susceptibility to processing conditions, notably compressive stress. This is evidenced by the decrease in crosslink density and T_g as a function of thermomechanical cycling for samples with a 5 mol % catalyst concentration. This degradation in properties is not seen for samples without a catalyst. In addition, we confirm that the compressive stress on the sample is responsible for this degradation by performing thermal stability studies and cycling between temperature sweeps and annealing steps. It is crucial to understand how these processing conditions impact the overall network structure and thermomechanical properties of vitrimers before their far-reaching application space can be truly explored.

**MATERIALS AND METHODS**

**Vitrimer Synthesis.** The components for our vitrimer materials were bisphenol A diglycidyl ether (DGEBA), as purchased from Sigma, along with sebacic acid (SA, 99%) and 1,5,7-triazabicyclo[4.4.0]de-5-ene (TBD), as purchased from Aldrich. All vitrimers in this study were synthesized in-house and prepared according to our previously reported methodology.11 Silicone molds were used to generate either bars or dog bone shapes; bars were made with dimensions 1 × W × H: 60 mm × 6 mm × 1 mm, while dog bone shapes were made according to ASTM D638-14 (Type V). All samples were polished to remove any imperfections prior to testing.

**Vitrimer Characterization.** Non-isothermal creep and temperature sweep experiments were performed using a TA Instruments Discovery hybrid rheometer (DHR-III) in tension mode under a nitrogen environment. The sample gap distance was 15 mm in all cases. For non-isothermal creep experiments, the applied axial force was 0.5 N, while the sample was heated from 25 to 300 °C at a temperature ramp rate of 5 °C min⁻¹. For temperature sweep experiments, an axial strain of 0.01% was applied at a frequency of 1 Hz, while the sample was heated from 25 to 150 °C at a temperature ramp rate of 5 °C min⁻¹.

Tensile tests were performed using an MTS Insight electromechanical testing machine; all tests were performed at room temperature with a strain rate of 2 mm min⁻¹. The modulus value was recorded as the slope of the stress–strain curve over the initial 0.2% strain.

DSC was performed using a TA Instruments Discovery Series DSC 2500. All runs were performed under a nitrogen environment with temperatures cycling between 10 and 200 °C, with a temperature ramp rate of 5 °C min⁻¹. The T_g was recorded as the inflection point of the second heating curve.

Thermal stability experiments were performed using a TA Instruments TGA Q500 series under either a nitrogen or an air environment. Samples were heated at a temperature ramp rate of 10 °C min⁻¹ to their respective set point temperature, where a 4 h isotherm was applied.

Shape memory and shape reconfigurability experiments were performed using a TA Instruments Discovery DMA 850 in tension mode under a nitrogen environment. The samples were tested between 10 °C and either 60 °C or 200 °C, depending on the experiment, at a temperature ramp rate of 10 °C min⁻¹. The axial force applied on the sample varied from 0.1 to 1.0 N, with a force ramp rate of 1.0 N min⁻¹, and is specified for each test.

Fourier transform infrared spectroscopy (FTIR) was performed using a Nicolet 380 FTIR to show no significant
chemical change in the material with processing, regardless of catalyst concentration.

Processing Conditions. Processed samples were either hot pressed in a 30 ton Wabash hydraulic press or were annealed in a standard oven. For HP (cf. Figure S4), samples were placed back into their silicone mold (for alignment purposes) and placed between Kapton sheeting and metal plates. This entire sample was then placed between the two platens of the Wabash press, heated to 200 °C for the specified values of time and normal pressure. For annealing, the samples were placed back into their silicone mold and simply heated in an oven at 200 °C for 1 h.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02677.

Detailed description of the characterization methods used, representative non-isothermal creep results, mechanical testing results, calculated molecular weight between crosslinks, samples showing self-healing demonstrations, schematics of the apparatus used for HP damaged samples, samples showing healing process attempted with no applied pressure, representative DSC curves, P-values reported for the $T_g$ values, and FTIR results (PDF)

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Author Contributions
A.M.H., Y.R., and D.N. were involved in project conceptualization and developing testing methodologies. A.M.H. and Y.R. were involved in the research investigation. A.M.H. wrote the initial draft of the article. All authors were involved in the review and editing process. A.S., D.K., C.P., A.R., V.V., and D.N. supervised the project.

Notes
The authors declare no competing financial interest.

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