INVESTIGATING THE VITRIMERIZATION OF A COMMERCIAL THERMOSET RESIN SYSTEM

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ABSTRACT

Dealing with fibre-reinforced composite products at their end-of-life has been a perennial problem due to the inability to reprocess the thermoset matrix after cure. Very recently, there has been an effort to look at utilizing vitrimer polymers, which combine the desirable properties of thermosets with the reprocessability of thermoplastics due to the incorporation of dynamic reversible covalent bonds. Despite their potential promise, the adoption of vitrimers by the composite industry has been limited with few commercial products available due to their relatively recent invention and complex synthesis procedures. In this work, a facile method to prepare vitrimer polymers from commercial thermoset products is investigated, which involves only minor modification of the commercial product's stoichiometry and addition of catalyst to facilitate dynamic bond exchange. Thermomechanical properties of the resulting vitrimer produced were subsequently characterized and compared to those of the conventional commercial thermoset where reprocessability was investigated through stress relaxation tests. Results showed that the vitrimer polymers produced were able to be reprocessed through the dynamic bond exchange, while also maintaining comparable properties to that of the conventional commercial thermoset. Ultimately, this work demonstrates a simple, practical approach to fabricate vitrimer polymers which can consequently be used in the manufacture of fibre-reinforced composite products.

1 INTRODUCTION

As society transitions to a more sustainable future, there has been a greater focus on composite recyclability at end-of-life (EoL). Typically comprised of a thermoset-based polymer matrix and fibre reinforcement, these composites are formed through the irreversible curing of the thermoset, which forms a three-dimensional network of irreversible covalent bonds that are unable to be reprocessed after initial fabrication [1]. As a result, any efforts to recycle these materials has largely focused on recyclability through permanent bond destruction, typically achieved through mechanical (e.g. size reduction), thermal (e.g. pyrolysis), or chemical (e.g. solvolysis) methods which produce a myriad of mixed products [1].

To address these shortcomings, there has been significant advancement in the manufacture of thermoplastic composites, in which the polymer matrix is replaced by a thermoplastic which offers the prospect of reprocessability. As structural cohesion is achieved through a combination of chain entanglement and reversible secondary bonds (e.g. hydrogen bonding, van der Waals) [2], reprocessability can be facilitated through thermal or

chemical routes [3,4]. Despite offering clear advantages in recyclability, their competitiveness falls short due to inferior chemical resistance and high processing temperatures and pressures that are required [2,4,5].

At the frontier of composite sustainability, vitrimer composites have been gaining traction as they are deemed to combine the desirable properties of thermosets with the reprocessability of thermoplastics. For these composite materials, the matrix is replaced by a vitrimer, a new class of polymer in which the three-dimensional network incorporates dynamic reversible covalent bonds. In response to a thermal stimulus (i.e. heat), these dynamic bonds can exchange with nearby dynamic sites, resulting in the macroscopic flow (and therefore reprocessability) of the material [5,6]. Upon cooling, the material then returns to a rigid thermoset structure. Furthermore, there is the prospect of leveraging these dynamic bonds to facilitate the physical separation of the fibre and matrix materials, mediated via a chemical solvent that also possesses dynamic bond sites [7]. The reclaimed constituents can then be used in subsequent manufacturing processes, ultimately enabling closed-loop recycling.

Though vitrimer composites may show potential promise, adoption by industry has been limited due to their recent innovation. Few commercially available products currently exist on the market, and most other synthesis procedures described in academia prove intrinsically complex, barring their adoption by industry [8,9]. However, there has also been development in more practical approaches to vitrimer synthesis, in which vitrimers may be relatively easily synthesized from pre-existing commercially available products [10,11]. In this work, a facile method to prepare a vitrimer polymer from a commercially available thermoset product was investigated, where it was shown that "vitrimerization" can be achieved through minor modification of stoichiometry and addition of a vitrimer catalyst. Thermomechanical properties of the resulting vitrimer produced were subsequently characterized and compared to those of the conventional commercial thermoset, where reprocessability was investigated through stress relaxation tests. The data obtained from these tests was furthermore used to construct thermal reprocessability maps, which can assist in subsequent reprocessing of the vitrimer product.

2 Materials & Methods

2.1 Materials

The commercially available thermoset product used in this work was a 3-part epoxy-anhydride with amine accelerator known as Araldite LY556/Aradur 917-1CH/Accelerator 960-1, kindly provided by Huntsman. For vitrimerization of the conventional thermoset, zinc acetylacetonate xhydrate was additionally used as a vitrimer catalyst, purchased from Ambeed Bio. All reagents were used as received.

2.2 Processing

For all subsequent characterization, a 229 mm x 229 mm x ~2 mm neat resin plate was synthesized for both the commercial thermoset and vitrimer polymer. Prior to synthesis, all liquid reagents were preheated to 50 °C. The conventional thermoset material was synthesized according to the technical data sheet guidelines [12], in which epoxy, hardener, and accelerator were mixed 100:90:3 (by weight). Epoxy and hardener were first mixed before then adding the accelerator. Once homogeneous, the mixture was then degassed under vacuum for 15 mins at 50 °C before being poured into an aluminum mould preheated to 80 °C. The mould was then subjected to a 4-hour cure at 80 °C followed directly by a 4-hour post-cure at 140 °C. Once the cure cycle was complete, the oven was then switched off and the mould was allowed to cool to room temperature before the neat resin plate was demoulded.

For vitrimer synthesis, zinc acetylacetonate xhydrate was first dissolved in anhydride hardener before adding epoxy resin and amine accelerator. The overall mix ratio of resin:hardener:accelerator:vitrimer catalyst was 100:45:3:14.2 (by weight), this quantity of catalyst resulting in a final part which contained approximately 10 mol% Zn relative to the epoxy. After thorough mixing, further processing (i.e. degas and cure) was identical to that of the thermoset.

2.3 Thermal Characterization

Cured thermoset and vitrimer samples were prepared for thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to characterize thermal stability and glass transition temperature respectively. TGA was performed on a TA Instruments Q500, in which samples of ~20 mg were first equilibrated at 30 °C before performing a 10 °C/min temperature ramp from 30 - 800 °C under either inert (Nitrogen) or reactive (Air) atmospheres to determine the 1 wt% and 5 wt% degradation onset temperatures. For DSC, ~10 mg samples were run on a TA Instruments Q100, subjected to a heat/cool/heat cycle as outlined in ASTM standard D3418-15, ranging from 25 °C to 260 °C at a 20 °C/min heating rate and 40 °C/min cooling rate in inert (Nitrogen) atmosphere.

2.4 Thermomechanical Characterization

To characterize stress relaxation of the thermoset and vitrimer samples, torsional rheometry was performed on an Anton-Paar MCR302 rheometer at a series of isothermal temperatures ranging from 170 - 210 °C. Nominal sample dimensions were 50 mm x 10 mm x 2 mm with gauge length of 40 mm when loaded into the torsional fixture. After a 15-minute equilibration at the target temperature, a 0.5 % shear strain step was applied and held for the duration of the test while recording the resultant shear stress, which was normalized by the initial stress for comparison between tests. A -0.5 N tensile normal force was also applied for the duration of the test to maintain straightness.

3 Results

3.1 Thermal Characterization

Results from TGA and DSC of the thermoset and vitrimer material are summarized in Table 1, which reports the 1 wt% and 5 wt% degradation onset temperatures (DOT) as well as the glass transition temperature (Tg) for these materials. A final column also reports the percentage change of the vitrimer material relative to the commercial thermoset. Thermal properties obtained for the thermoset were in good agreement with the supplier's technical data sheet for the given cure cycle, which states a glass transition temperature of 133 - 138 °C [12]. In comparison, the thermal properties of the vitrimer all seemed to decrease by approximately 5 - 14% relative to the thermoset.

Table 1. Thermal properties of the thermoset and vitrimer materials.

Property	Thermoset	Vitrimer	% Change
1 wt% DOT (Air) [°C]	296	280	-5.4
1 wt% DOT (Nitrogen) [°C]	302	282	-6.5
5 wt% DOT (Air) [°C]	357	327	-8.4
5 wt% DOT (Nitrogen) [°C]	360	326	-9.4
Tg [°C]	132	114	-14.0

This property reduction of the vitrimer was expected, and can most likely be attributed due to the reduction in crosslinks as the quantity of hardener (relative to the epoxy resin) was halved. The reason for this change in resin:hardener stoichiometry is ultimately due to the nature of the vitrimer dynamic bond chemistry, which relies on the transesterification reaction that occurs between an ester and alcohol. As most epoxy-anhydride thermosets are formulated to have near stoichiometric amounts of epoxide and anhydride to ensure complete reaction, halving of the anhydride ensures that there is an abundance of unreacted hydroxyl groups available to participate in the transesterification [5,6,10]. Though this change in stoichiometry for the vitrimer formulation reduced the overall crosslink density of the material, the overall change in thermal properties was not significant.

3.2 Thermomechanical Characterization

The stress relaxation behaviour of the thermoset and vitrimer materials at 210 °C is presented in Figure 1. At this temperature, the vitrimer showed rapid stress relaxation, relaxing over 90% of the initial stress by the 100-minute mark. In contrast, the thermoset showed little relaxation (less than 19%) by the same time point. This difference in stress relaxation behaviour can most likely be attributed to the type of covalent bonds between the two materials. Whereas the relaxation of the thermoset polymer appears to be restricted by its irreversible covalent crosslinks, the dynamic reversible bonds present in the vitrimer enabled rapid stress relaxation at elevated temperature.

By characterizing the stress relaxation behaviour of the vitrimer at various isothermal temperatures, it can be seen that the rate of relaxation is a function of temperature (Figure 1, right). As the temperature is increased from 170 °C - 210 °C, the rate at which the relaxation occurs increases and the initial stress is relaxed in a shorter timespan. This temperature-dependent relaxation time (τ) follows an Arrhenius-type relationship (Equation 1), where E_a is the apparent activation energy, R the universal gas constant, and τ_0 a pre-exponential factor. In this equation, the activation energy is of specific interest as it is known to be influenced by the dynamic bond exchange rate, which in turn is dependent on the vitrimer chemistry [5]. By determining the characteristic relaxation time (the time to relax to ~37%, 1/e of the initial stress) at each temperature, one can perform a linear fit to obtain an activation energy of 54.10 kJ/mol (Figure 1, right inset). This is relatively close to that which has been reported in literature for similar transesterification-based vitrimers (~88 kJ/mol [6]), however the discrepancy between these two values can potentially be explained by specific differences in the polymer composition and structure [5].
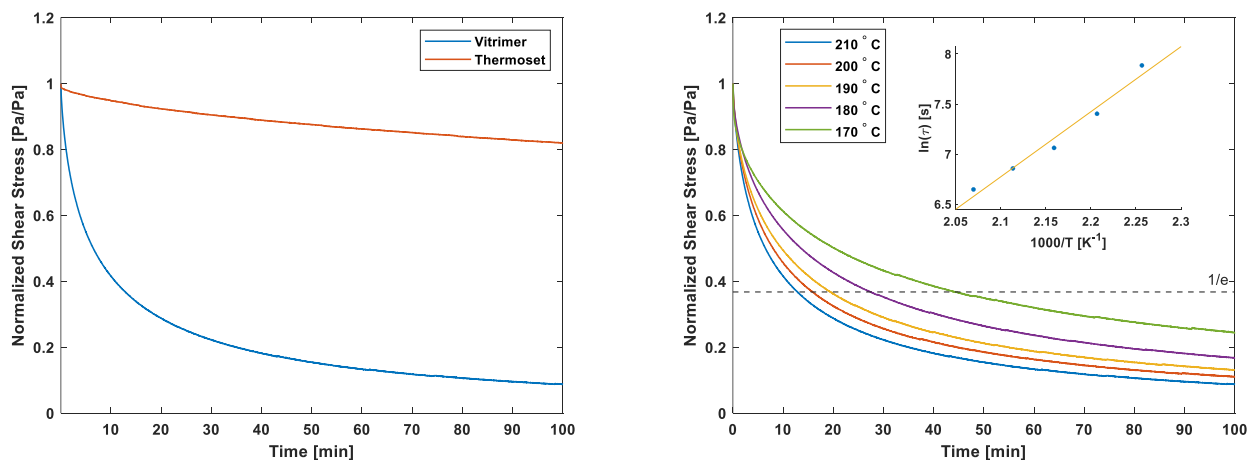

Figure 1. (Left) Stress relaxation of the thermoset and vitrimer materials at 210 °C. (Right) Stress relaxation of the vitrimer at various temperatures. (Right inset) Linear fit of the characteristic relaxation times.

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{RT}\right) \tag{1}$$

3.3 Vitrimer Reprocessability Maps

Using the data acquired through TGA, DSC, and stress relaxation experiments, a thermal reprocessability map for the vitrimer material can be constructed to predict the time required to relax stress at a given temperature (Figure 2). First, the Arrhenius relationship is plotted using the values obtained previously, which delineates the threshold at which 63% of the initial stress has been relaxed. As mentioned by [11], it is useful to note that though this value is used by convention, other values could be used to represent more practical thresholds (e.g. 75%, 95%). Then, TGA and DSC data is then used to establish upper and lower constraints for processing, in which above, degradation may occur, and below, there is no molecular mobility to facilitate dynamic bond exchange.

This diagram can be used to estimate the time required for the material to relax an initial stress based on the selected temperature profile. For example, starting at an isothermal temperature of 170 °C, a neat resin part can relax ~63% of it's initial stress in approximately 45 mins (Figure 2). The part is first heated up to the processing temperature ("A" in Figure 2) before applying the deformation (i.e. initial stress), after which this temperature and deformation are held for the required time ("B" in Figure 2). Higher or lower temperatures may be used to shorten or lengthen the necessary reprocessing time respectively, however the T_g dictates the lower limit and T_{DOT} the upper limit to reprocessing temperatures. However, one aspect not covered by this map is the potential for degradation that may occur at sustained high temperatures (even if below the static upper limit), and as such further investigation into thermal degradation kinetics is needed [11]. Furthermore, this reprocessability map is based on a relatively thin neat resin part, and as such thickness effects or the impact of fibre reinforcement are not considered [11]. Notwithstanding these potential improvements, the constructed reprocessability map offers an initial approach to predicting reprocessability of vitrimer materials at their end-of-life.
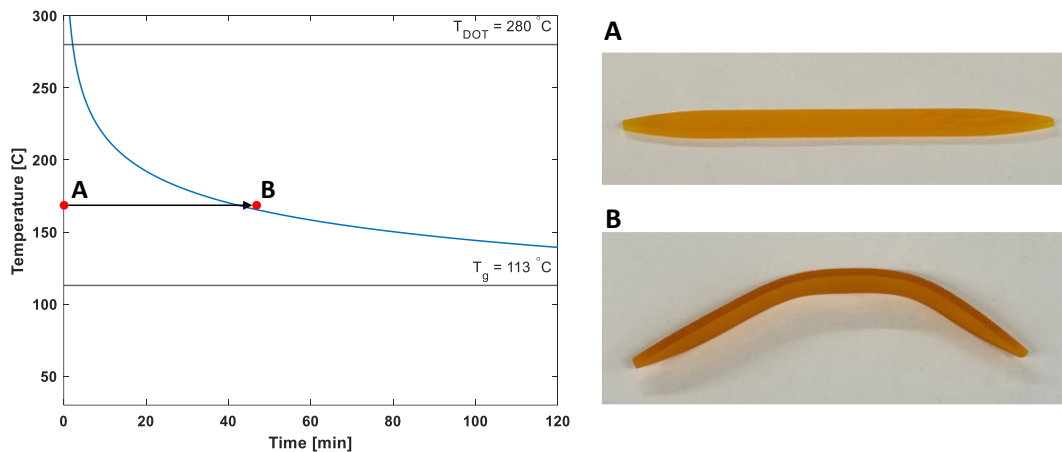

Figure 2. Thermal reprocessability map for the vitrimer polymer.

4 Conclusions

Though vitrimers are still relatively new and unknown to the composites industry, there is great potential for them to be used in the next generation of sustainable composites due to their thermoset properties and thermoplastic

reprocessability. Despite this potential, there exists a technological gap to their adoption, with few commercial products currently available. To bridge this gap, a simple method to prepare a vitrimer polymer using a commercially available thermoset system was investigated, in which only minor changes were required to the overall manufacturing process. Thermomechanical properties of the vitrimer produced were compared to that of the original thermoset, where it was shown that thermal reprocessability could be imparted due to the presence of dynamic covalent bonds with minimal negative effects on the thermal properties (<15% reduction). Building on these results, a map to predict the reprocessing time for the material at a given temperature was then presented, which may serve as a useful tool to streamline processing. Ultimately, by demonstrating the ability for vitrimers to be straightforwardly incorporated into current composite materials and processes, future studies may look to employ these materials on the quest towards composite circularity.

5   Acknowledgements

6   REFERENCES

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