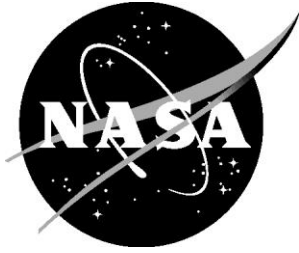


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Epoxy Resins with Reduced Viscoelastic Relaxation

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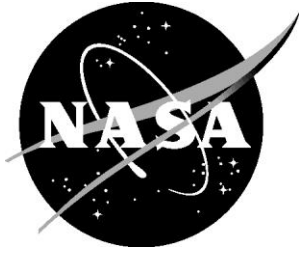
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Abstract

The payloads of current space launch systems, e.g. rockets, are constrained to a small size due to aerodynamic, weight, and cost limitations. Deployable structures allow for a folded or stowed configuration during launch and deployment at the mission location. Polymer composites have shown both high weight savings over current metallic structure, as well as improved specific mechanical strengths overall. One issue encountered with polymer composite deployables, however, is stress relaxation of the polymer matrix in the stowed configuration. In this study, a range of different epoxy formulations were evaluated as potential matrix resins for deployable composites. A new multifunctional epoxy resin with a fortifying additive is predicted to show 70% less stress relaxation after 1 year as compared to a state-of-the-art aerospace epoxy matrix.

Nomenclature

Symbols

T_g	glass transition temperature
E_a	activation energy
a_T	time-temperature shift factor
RM_{1yr}	percent reduction in relaxation modulus at 1 year

Acronyms

TRAC	Triangular Rollable And Collapsible
CTM	Collapsible Tubular Mast
TTS	Time Temperature Superposition
DMA	Dynamic Mechanical Analyzer
TGDDM	4,4'-Methylenebis(<i>N,N</i> -diglycidylaniline)
DDS	4-Aminophenyl sulfone
DGEBA	Bisphenol A diglycidyl ether
HAA	4-hydroxyacetanilide
VCD	vinyl cyclohexane diepoxide
SOA	state-of-the-art
PMT	Patz Materials and Technology

1. Introduction

Deployable structures for space applications have the benefit of being compact during launch and expandable on orbit or at the mission location. Examples are expandable habitats, trusses, booms, solar sails and other large structures [1]. The goal of these technologies is to build increasingly large space structures with the same or reduced launch costs; the easiest way to accomplish this is to use lighter materials. Carbon fiber reinforced polymer composite materials have played an increased role in aerospace vehicles and components due to their high specific strengths and stiffnesses [2,3].

The focus in this report is composite booms due to the current interest in them for solar sail and other NASA missions [4,5]. These booms are composite versions of the Triangular Rollable And Collapsible (TRAC) boom and Collapsible Tubular Mast (CTM), shown below in Figure 1.

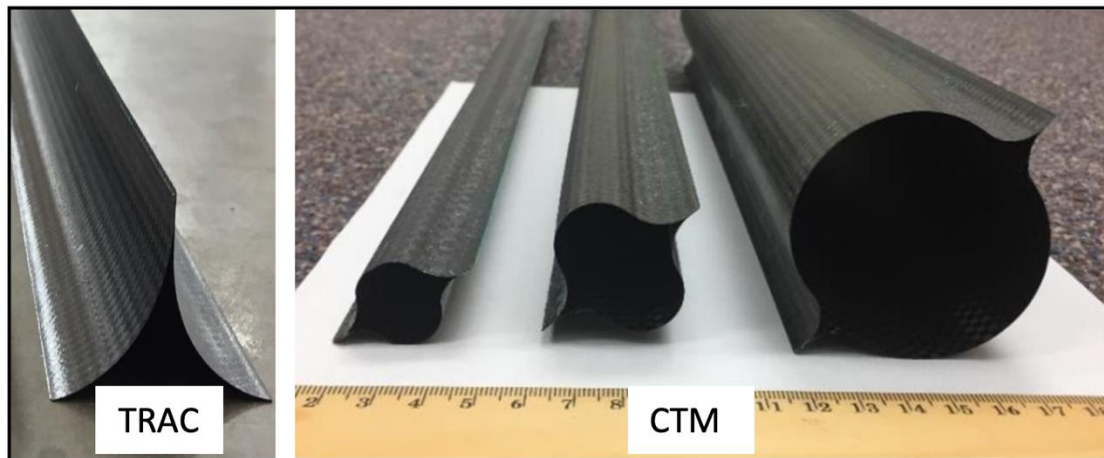


Figure 1. Different deployable composite boom designs shown. Images are sourced from reference [4].

During stowage, each boom is flattened and rolled around a center spool. Satellites and other payloads may be stored for up to one year before launch or eventual deployment. Permanent deformation via stress relaxation may result as a consequence of this long-term storage [6]. The example in Figure 2 shows the reduction in a CTM boom cross section after 1-month of storage at room temperature. The area moment of inertia of a hollow cylinder depends on its radius to the fourth power, so a 25% reduction in radius could result in a loss of 68% in buckling strength. This decrease in buckling strength could lead to failure of the boom assembly.

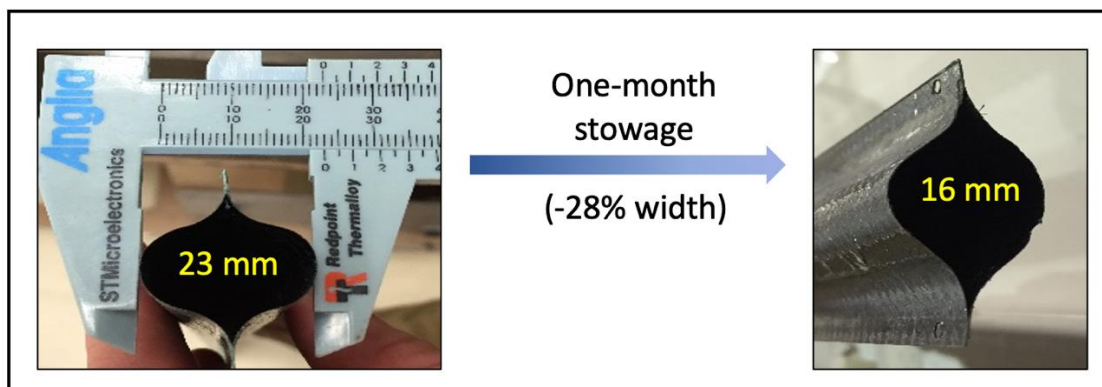


Figure 2. Reduction in boom width due to relaxation during storage. Images sourced from Fernandez, et al. [7]

In this report, a tetra-functional neat epoxy resin is formulated. It and its modifications are characterized using Dynamic Mechanical Analysis (DMA). The effects on stress relaxation from changes in stoichiometry and of antiplasticizing additives (“fortifiers”) are examined. The primary figure of merit was the percent decrease of relaxation modulus at 1 year (RM_{1yr}), extrapolated from master curves generated using time-temperature superposition (TTS).

2. Experimental Procedure

2.1 Materials

The baseline material, F7, was obtained from Patz industries. According to Peterson [8], it is primarily a trifunctional epoxy toughened with core-shell rubber particles. Although Peterson described a formulation that also contained 10% nano-silica, thermogravimetric analysis of our batch showed essentially no inorganic residue.

Fortifiers [9] were prepared from monomers purchased from Sigma-Aldrich. These monomers are shown in Figure 3. The DGEBA-HAA fortifier (DGEBA) was produced by stirring HAA into liquid DGEBA (1:1 mole ratio) at 140 °C for approximately 15 minutes. A partially reacted fortifier was desired. The VCD fortifier was prepared similarly using VCD and HAA in a 1:1 molar ratio. The VCD was heated to 110 °C and the HAA powder was stirred in until a transparent solution was obtained, approximately 15 minutes.

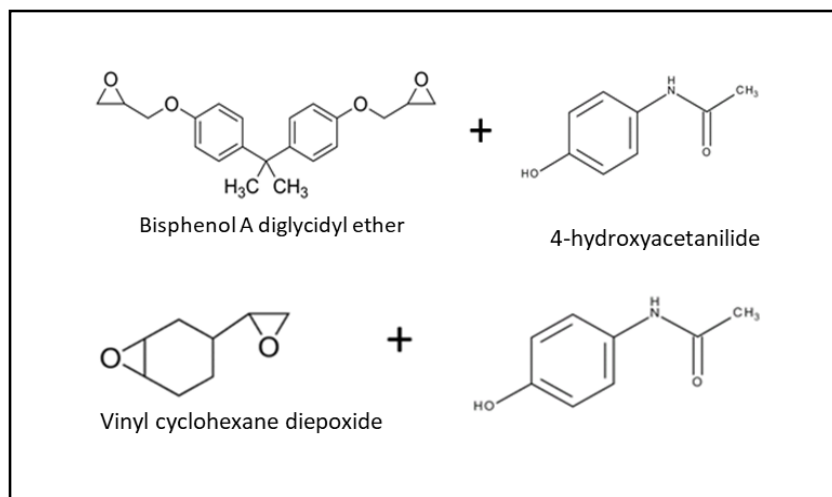


Figure 3. Components of fortifiers: Bisphenol A diglycidyl ether (DGEBA), vinylcyclohexane diepoxide (VCD), and 4-hydroxyacetanilide (HAA).

TGDDM and DDS (Figure 3) were purchased from Sigma Aldrich and used as received. The tetra-functional epoxy was cured with diaminodiphenyl sulfone using a method supplied by the manufacturer [10], but with slight variations in stoichiometry. If fortifier was to be added, it was stirred into the warm mixture after the DDS. Fortifier concentrations are denoted in phr, that is, weight in grams per hundred grams of epoxy+amine. A total of 8 different epoxy resin formulations were prepared. The epoxy was heated to 110 °C in a sand bath and the DDS powder was stirred in. Once it was clear and homogenous, the solution was vacuum degassed at 115 °C and 30 inHg for approximately 15 minutes. After degassing, the resin was cast into dry preheated silicone molds. The cure and post-cure cycles are shown in Figure 4.

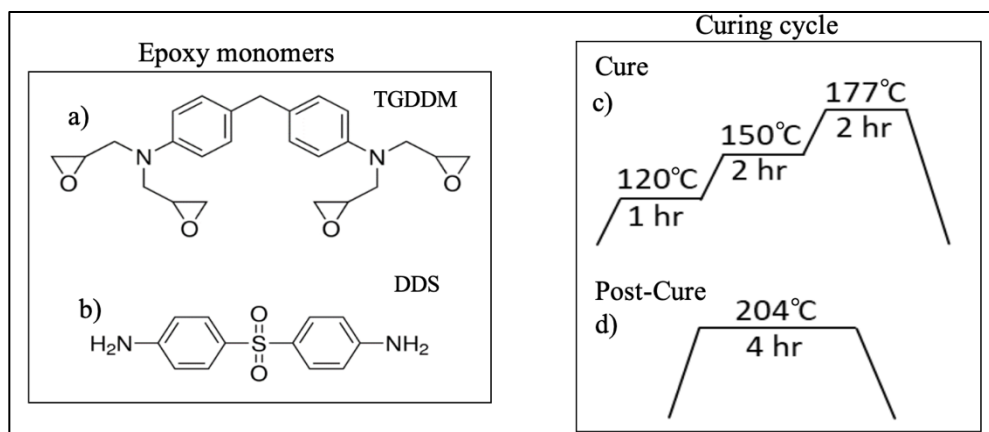


Figure 4. Epoxy monomers: (a) 4,4'-Methylenebis(*N,N*-diglycidylaniline) (TGDDM), (b) 4-Aminophenyl sulfone (DDS). (c) Cure and (d) post cure cycles in a convection oven, air atmosphere with a 3 °C/min ramp rate.

2.2 Specimen preparation

Once demolded, the castings were ground flat and sectioned into rectangular strips, 60 mm long, for DMA testing. Surface effects from oxidation are assumed to be negligible due to the exterior surfaces being ground off. All specimens were vacuum dried at 110 °C overnight after sectioning and then stored in a desiccator cabinet until testing to avoid water absorption.

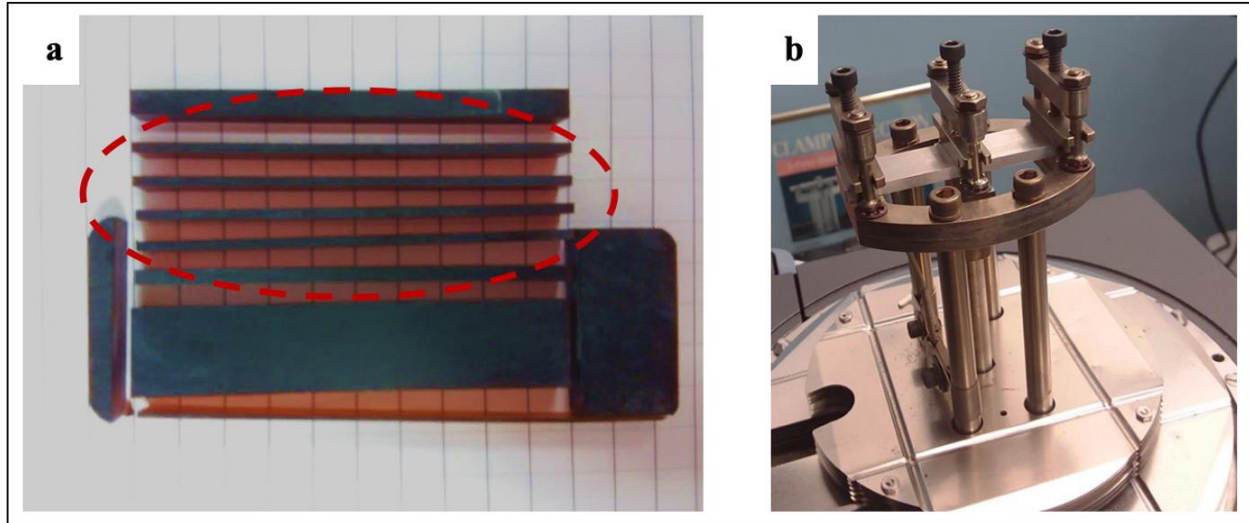


Figure 5. (a) Sectioned epoxy specimen after casting and grinding flat. Width is approximately 60 mm. Rectangular test specimens are indicated in the red dashed oval. (b) DMA test setup using dual cantilever clamp (steel calibration shim shown).

2.3 DMA testing and data reduction

Stress relaxation was tested in a TA Instruments[®] Q800 DMA equipped with a dual cantilever clamp (Figure 5). In a stress relaxation test, the DMA applies a constant strain to the material and records the decaying force at temperature. The initial and reference temperature for the stress relaxation data is 20 °C. Testing was performed from 20 °C to 160 °C. The full testing method is indicated in Table 1. Each test resulted in 14 isothermal, accelerated stress relaxation data sets where each data set was collected at an increasing temperature as the experiment progressed. The results were plotted in log-linear space and manually shifted to generate a master TTS curve. Figure 6, below, shows an example. At each temperature, the applied time-temperature shift factor shifts that specific data set to the right, overlapping the data to produce a continuous curve— a master curve. Past experiments have shown agreement between master curves and actual long-term creep tests; Scott, et al. [6] provide an excellent summary of accelerated experimental procedures and their accuracy. RM_{1yr} , the percent relaxation in one year, is calculated for each master curve from the ratio of the initial modulus to the modulus at one year.

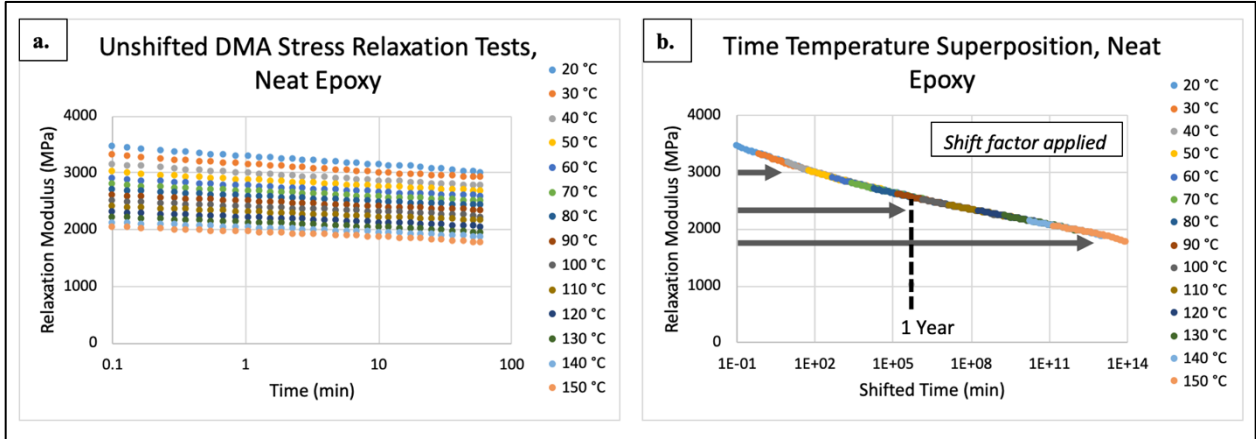


Figure 6. (a) Individual stress relaxation data sets at different temperatures. (b) The individual relaxation curves in Figure 6a have been horizontally shifted using time-temperature superposition. The resulting master curve enables RM_{1yr} prediction.

3. Results and Discussion

Figure 7 below shows the effect of stoichiometric variations of the neat epoxy on the master curves. Small increases in the initial relaxation modulus were observed with an increasing amount of amine hardener. An increase in DDS from 1:0.38 ratio to 1:0.44 ratio (by weight) reduced the predicted RM_{1yr} from 34% to 27%. It should be noted that the neat epoxy 1:0.38 resin was prepared and tested at different conditions and used a reference temperature of 35 °C.

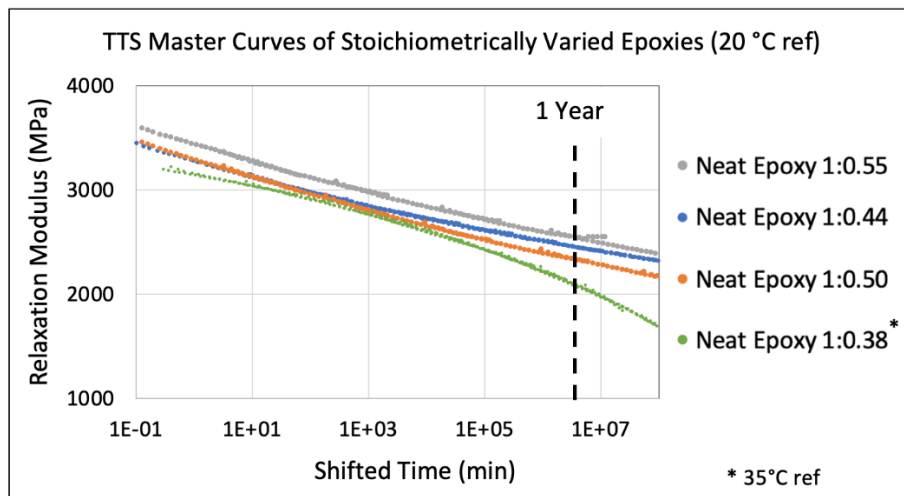


Figure 7. TTS master curve comparison of neat epoxies with TGDDM:DDS stoichiometric variance.

Higher stoichiometric ratios of DDS:TGDDM did not yield any further improvement in relaxation properties. This is in agreement with other studies which find that an epoxy excess can suppress β -relaxations [11,12].

The addition of small molecules, called anti-plasticizers or fortifiers, into the matrix can increase the room temperature modulus while maintaining ductility [13, 14]. While their exact mode of action is not understood, it is thought that they occupy free volume within the network and exert a local steric hindrance to chain mobility below T_g [13-15]. One manifestation of this is suppression of the sub- T_g beta relaxation observed in DMA, as shown in Figure 8.

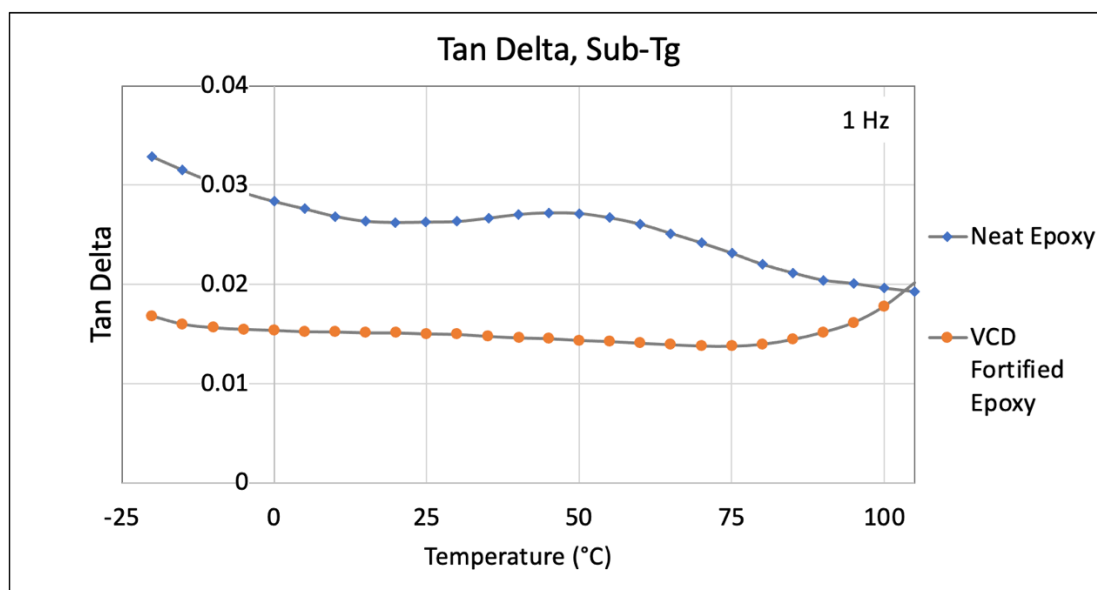


Figure 8. Tan delta as a function of temperature at 0.1 Hz for neat tetra-functional epoxy and VCD fortified epoxy. Notice “bump” at around 50 °C; this β -relaxation is associated with local molecular motions [16]. This data was not collected for DGEBA fortified epoxy.

The addition of small fortifier molecules was shown to increase the initial elastic modulus and decrease sub- T_g relaxation in epoxies. Additionally, fortifiers are typically reactive with the main epoxy-amine network and can sterically hinder chain motion and increase the activation energy for β -relaxations [10, 17]. On this basis, it is reasonable to expect that fortifiers might decrease stress relaxation.

TTS curves for all fortified epoxies are shown below in Figure 9. Of the two fortifiers tested, VCD gave the larger reincrease in relaxation modulus and had a larger impact on the relaxation properties. The DGEBA fortifier also decreased relaxation, but to a lesser extent. The resin fortified with VCD at 35 phr concentration exhibited the lowest RM_{1yr} at 15% in 1 year at 20°C. This value is 70% lower than that of state-of-the-art epoxy resin (Patz Materials & Technology, PMT-F7) that had been chosen for NASA’s Advanced Composite Solar Sail System (ACS3) project. While raising the concentration of VCD from 17.5 to 35 phr increased the initial

relaxation modulus, it did not have a large impact on the RM_{1yr} value. A summary of the results for all the formulations is shown in Table 2; further details on the time-temperature shift factors are given in the Appendix.

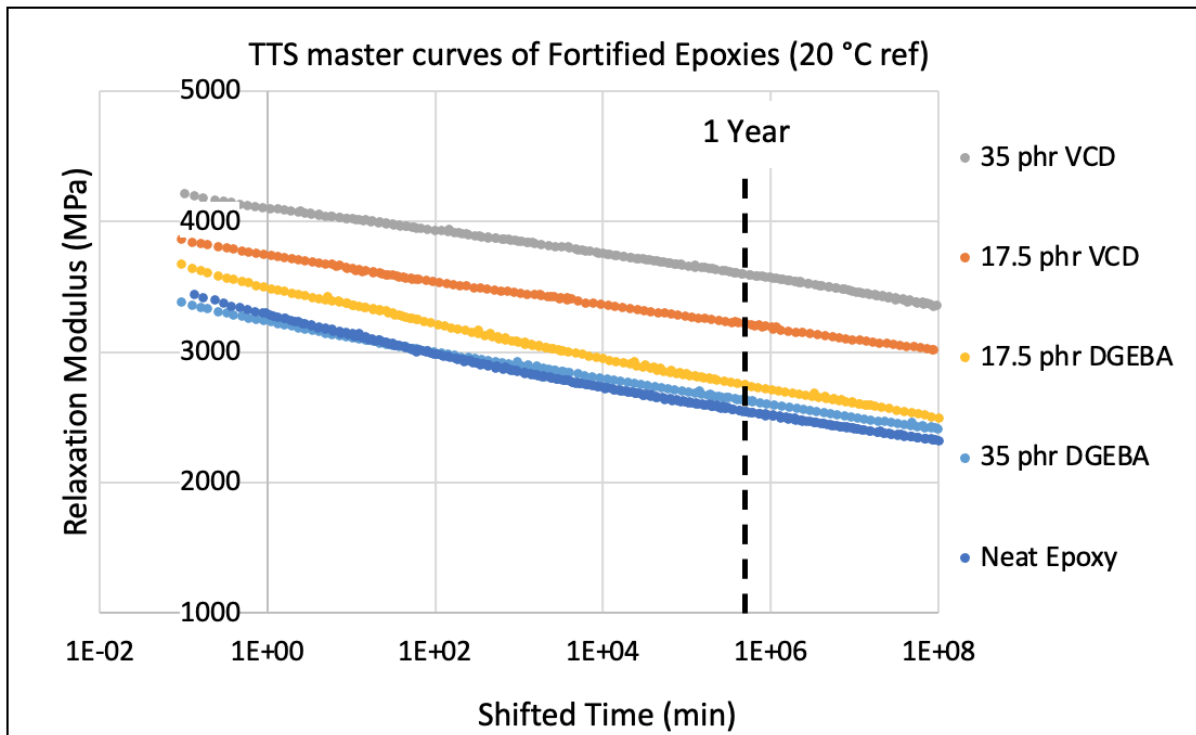


Figure 9. All fortified epoxy TTS master curves compared with neat epoxy. VCD had the most pronounced effect on both the slope and the initial relaxation modulus.

4. Conclusions

Starting from a tetra-functional epoxy resin, initial improvements in stress relaxation properties were observed when the amine hardener: epoxy ratio was increased; however further increases in hardener content did not yield significant changes to relaxation properties. The addition of small fortifying molecules was also observed to reduce relaxation and increase the initial elastic modulus of resins, as expected. An epoxy containing 35 phr of added VCD fortifier resulted in a RM_{1yr} value that is 70% lower than the state-of-the-art PMT-F7 resin in current booms. VCD appears to be a more effective fortifier than DGEBA in this tetra-functional epoxy.

Future work will include preparing carbon fiber composites infused with fortified epoxy resin to evaluate how the resin properties translate to the composites' stress relaxation. Other alternative low creep polymer matrices are also being evaluated, such as low creep polyimides. Even the most effective fortified epoxy resin tested in this study still had a relaxation modulus decrease of 15%, meaning there is still research to be done into further minimizing stress relaxation without embrittlement.

Table 1: TA-DMA Q800 Stress Relaxation Method.

STEP	PROCEDURE
1	Equilibrate at 20 °C
2	Isothermal for 20 min
3	Data storage On
4	Displace (0.1000%) 60 min, Recover 10 min
5	Data storage Off
6	Increment 10 °C
7	Repeat 3-6 until temperature equals 160 °C

Table 2: Epoxy Resin Formulations and Properties.

RESIN BATCH ID	EPOXY:AMINE WT. RATIO	ADDITIVE	$RM_{1yr} \pm 2$	INITIAL MODULUS (Gpa)	ACTIVATION ENERGY, E_a α -RELAX (kJ/mol)
SOA EPOXY (PMT F7)	N/A	Toughened with nano-silica and other company proprietary additives	49%	2.99 ¹	601
NEAT 1:0.38	1 : 0.38	-	35%	3.19	N/A
NEAT 1:0.50	1 : 0.50	-	31%	3.60	N/A
NEAT 1:0.55	1 : 0.55	-	28%	3.56	N/A
NEAT	1 : 0.44	-	27%	3.45	-
17.5 DGEBA	1 : 0.44	17.5 phr DGEBA-HAA	25%	3.68	N/A
35 DGEBA	1 : 0.44	35 phr DGEBA-HAA	22%	3.39	N/A
17.5 VCD	1 : 0.44	17.5 phr VCD-HAA	17%	3.87	656

1: Reported by Peterson, M. [18]

References

- [1] Sokolowski, W. M. and Tan, S. C. “Advanced Self-Deployable Structures for Space Applications” *Journal of Spacecraft and Rockets*, Vol. 44, No. 4 (2007).
- [2] Kang, J. H., Cano, R. J., Ratcliffe, J. G., Luong, H., Grimsley, B. W. and Siochi, E.J., “Multifunctional Hybrid Carbon Nanotube/Carbon Fiber Polymer Composite” SAMPE Technical Conference, Long Beach, CA, May 23-26, 2016, Society for the Advancement of Material and Process Engineering, CD-ROM – 15 pp.
- [3] Gay, D. and Hoa, S. V. “Composite Materials” 2nd edition, CRC Press: Boca Raton, 2007.
- [4] Fernandez, J. M. “Advanced Deployable Shell-Based Composite Booms for Small Satellite Applications including Solar Sails” 4th *International Symposium on Solar Sailing*. Kyoto, Japan, (January 17-20, 2017).
- [5] Kang, J. H.; Hinkley, J.; Gordon, K.; Thibeault, S.; Bryant, R.; Fernandez, J.; Wilkie, W.; Peterson, R.; Brandenburg, C.; Hill, E.; Arcot, N.; Diaz Moralez, H.; and McGruder, D. “Viscoelastic Characterization of Polymers for Deployable Composite Booms” 5th *International Symposium on Solar Sailing*, Aachen, Germany, July 30 – August 2, 2019.
- [6] Scott, D. W.; Lai, J. S.; and Zureick A-H. “Creep Behavior of Fiber-Reinforced Polymeric Composites: A Review of the Technical Literature” *Journal of Reinforced Plastics and Composites*, Vol. 14 (1995).
- [7] Fernandez, J. M.; Rose, G. K.; Younger, C. J.; Dean, G.D.; Warren, J. E.; Stohlman, O. R.; and Wilkie, W.K. “NASA’s Advanced Solar Sail Propulsion System for Low-Cost Deep Space Exploration and Science Missions that Use High Performance Rollable Composite Booms” (March 2017) <https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20170001556.pdf>.
- [8] Peterson, M. E. and Murphey, T. W. “Large Deformation Bending of Thin Composite Tape Spring Laminates” 54th *AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference*, Boston, MA (2013).
- [9] Garton, Andrew “The Use of ‘Epoxy Fortifiers’ in Adhesives Applications” DTIC Accession Number ADA205202, 26 Jan 1989. <https://apps.dtic.mil/dtic/tr/fulltext/u2/a205202.pdf>.
- [10] Huntsman Advanced Materials, “Araldite® MY 720 Resin, Technical Datasheet” (2015) <https://azelisamericascase.com/midwest/wp-content/uploads/2018/09/Araldite-MY-720.pdf>.
- [11] Pandini, S.; Bignotti, F.; Baldi, F.; Sartore, L.; Consolati, G.; and Panzarasa, G. “Thermomechanical and Large Deformation Behaviors of Antiplasticized Epoxy Resins: Effect of Material Formulation and Network Architecture” *Polymer Engineering and Science* 57, pp. 553-565 (2017).
- [12] Munz, M.; Sturm, H.; and Stark, W. “Mechanical Gradient Interphase by Interdiffusion and Antiplasticisation Effect—Study of an Epoxy/Thermoplastic System” *Polymer*, vol. 46, pp. 9097-9112 (2005).
- [13] McLean, P. D.; Garton, A.; and Scott, R. F. *Canadian Patents and Development Ltd No. US4480082A*. Ottawa, Canada. National Research Council (1987).

- [14] Rana, D.; Sauvant, V.; and Halary, J. L. "Molecular Analysis of Yielding in Pure and Antiplasticized Epoxy-Amine Thermosets" *Materials Science*, vol. 37, pp. 5267-5274 (2002).
- [15] Venditti, R. A.; Gillham, J. K.; Jean, Y. C.; and Lou, Y. "Free Volume After Cure vs Fractional Conversion for a High-Tg Epoxy/Amine Thermosetting System" *Journal of Applied Polymer Science*, Vol. 56, pp. 1207-1220 (1995).
- [16] Yee, A. F. and Smith, S. A. "Molecular Structure Effects on the Dynamic Mechanical Spectra of Polycarbonates" *Macromolecules*, vol. 14, no. 1, pp. 54-64 (1981).
- [17] Cuikerman, S.; Halary J.; and Monnerie, L. "Dynamic Mechanical Response of Model Epoxy Network in the Glassy State" *Polymer Engineering Science*, vol. 31, pp. 1476-1482 (1991).
- [18] Peterson, M. "High Shear Strain Characterization of Plain Weave Fiber Reinforced Lamina", MS Thesis (2015). https://digitalrepository.unm.edu/ce_etds/102 (2015), p. 32.
- [19] Li, R. "Time-Temperature Superposition Method for Glass Transition Temperature of Plastic Materials" *Materials Science and Engineering A-Struct*, vol. 278, pp. 36-45 (2000).
- [20] Goertzen, W. K. and Kessler M. R. "Creep Behavior of Carbon Fiber/Epoxy Matrix Composites" *Mat. Sci. & Eng. A*, vol 421, pp. 217-225 (2006).

Appendix

Based on the assumption of thermorheological simplicity, viscoelastic properties for an amorphous polymer well away from its T_g follow an Arrhenius relationship. This allows for the calculation of the horizontal time-temperature shift factors via Eq. 1, [19, 20]:

$$\ln(a_T) = \frac{E_a}{k} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \quad (1)$$

where a_T is the shift factor, E_a is activation energy, k is the Boltzmann constant, T_{ref} is the reference temperature, and T is the temperature of the curve being shifted. By plotting the natural log of the empirically determined shift factors versus $1/T$, it is possible to verify the Arrhenius relationship and improve confidence in the shift factor legitimacy.

As a result of the linear form of Eq. 1, a linear plot would support the Arrhenius relationship. The plot in Figure A.1 of $\ln(a_T)$ versus $1/T$ shows these relationships for all DMA data. The linearity of the data indicates that the shift factors follow a roughly Arrhenius relationship. Differences in slopes of the curves are due to differences in activation energies of relaxations for different resin compositions. Calculated activation energies, E_a , were listed in Table 2. Neat epoxy (1:0.44) showed an abnormally large activation energy – over 1000 kJ/mol – and has been omitted. Activation energies that have not yet been characterized are denoted by “N/A”.

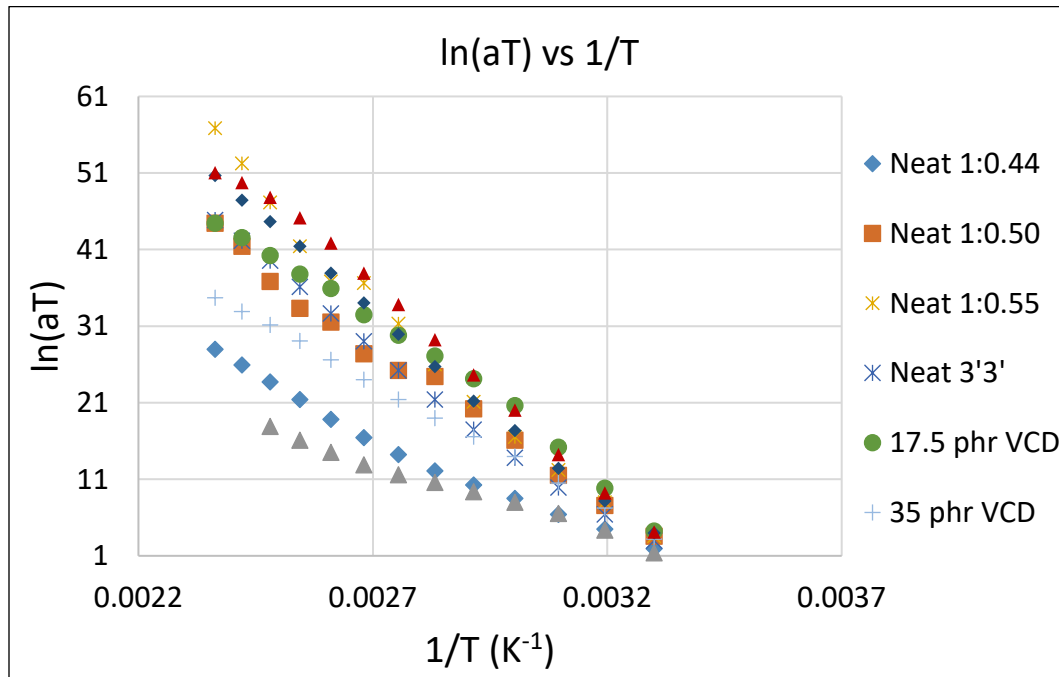


Figure A.1. Semi-log plot of $\log(a_T)$ versus $1/T$ for all TTS master curves. Linear trendlines for all data sets have $R^2 > 0.98$.