Vitrimer carbon fiber composites for rotorcrafts components with fatigue reversal ability

Mithil Kamble
kamblm@rpi.edu
PhD Candidate
RPI
Troy, New York, USA

Sikharin Pranompont
pranos@rpi.edu
PhD Candidate
RPI
Troy, New York, USA

Catalin Picu
picuc@rpi.edu
Professor
RPI
Troy, New York, USA

Nikhil Koratkar
koratn@rpi.edu
Professor
RPI
Troy, New York, USA

ABSTRACT

As rotorcrafts enter new generation of their design, they are expected to be subjected to more stringent performance requirement, Increased loads and operational frequency necessitates use of structural components with higher fatigue life. Carbon fiber reinforced polymer composites (CFRP) are popular as structural material due to their superior performance while being lightweight. However, fatigue originating in weaker polymer limits their fatigue life, moreover the fatigue damage introduced accumulated irreversibly resulting in catastrophic failure. The damage is irreversible due to permanent crosslinked nature of thermoset polymers used in CFRP. If the crosslinks are made dynamic i.e. reversibly crosslinked, the fatigue damage may be reversed imparting ultra-high fatigue life to the components. Vitrimers are such epoxy based networks which may be ideal candidate for this application as they possess ability to dynamic crosslinking at elevated characteristic temperature. Here we report a vitrimer based CFRP i..e., vCFRP which has properties comparable to conventional CFRP which has ability to retain its original properties in fatigue tests when they are subjected to periodic heating. The fractographic analysis suggests that periodic heating serves dual purpose of enabling dynamic crosslinking as well as repairing small scale fiber-matrix interface failure. Thus, rotorcraft components made with vCFRP may have very high fatigue life compared to conventional CFRP components.

INTRODUCTION

Rotorcrafts are increasingly being subjected to higher loads and higher operational frequency. Consequently, the materials which are used in the rotorcrafts must reevaluated against increased performance demands. Rotorcrafts typically employ carbon fiber reinforced polymeric composites (CFRP) as structural components due to their superior strength to weight ratio. In CFRP systems polymeric matrix provides structural integrity whereas carbon fibers are the primary load carriers. Fatigue remains a critical design constraint in the design of CFRP components and must be addressed as the new generation of rotorcrafts must operate in more challenging operating conditions.

Fatigue in CFRP systems typically originates in the weaker polymeric matrix in form of incipient flaws which grow from inherent heterogeneities. The incipient cracks grow from stable regime to exponentially increasing crack growth rates which results in catastrophic failure [1,2]. Epoxy is the matrix material of choice in CFRP systems due to its high strength and stiffness. Its superior mechanical properties are result of permanent crosslinking of molecular chains introduced during the curing process. The rupture of crosslinks during operational loading leads to inception of irreversible damage. Efforts have been directed towards adding nanofillers to epoxy which create interactions with small scale cracks and extend the fatigue life [3–5]. However, since the crosslinks are permanent, the damage induced by their rupture is irreversible. Moreover, the crosslinking imparts strength to the material hence networks without crosslinking i.e., thermoplastics, tend to be weaker and hence unsuitable for structural applications.

If the crosslinking of the network is made reversible, it may retain its mechanical properties while being able to heal during normal operation. Such networks with reversible crosslinking ability are called covalent adaptable networks (CAN). Polymer scientists have been exploring CAN for several decades, however, historically, they were chemically complex, unstable, and tended to depolymerize over time[6,7]. A breakthrough in this direction was achieved when Liebler et al discovered epoxy-based networks called vitrimers which have reversible crosslinking capability which is activated by heating the material to a characteristic temperature [8] (Figure 1). Vitrimers exhibit a characteristic temperature apart from the glass transition temperature (T_g) called topology freezing temperature (T_v) above which the reversible crosslinking proceeds rapidly[9].

Presented at the Vertical Flight Society's 78th Annual Forum & Technology Display, Ft. Worth, Texas, USA, May 10-12, 2022.

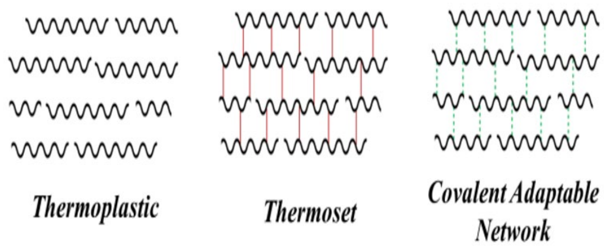

Figure 1.Covalent adaptable networks: Thermoplastics are not crosslinked so are reprocess able but weaker, thermosets are permanently crosslink and hence strong but prone to irreversible damage. CAN combines the two by having reversible crosslinks.

While vitrimers are being explored heavily, their fatigue characterization remains to be explored. In this work we report vitrimeric system which undergoes healing through periodic heating. A carbon fiber composite made from the vitrimer exhibits similar behavior in fatigue as well which may pave way for CFRP with ultra-high fatigue life. These composites made with vitrimers can be used in rotorcraft components for better endurance and reliability.

MATERIAL DETAILS

Vitrimer preparation

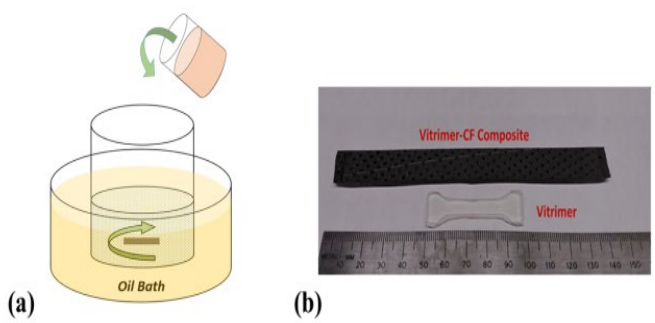

Figure 2. Vitrimer fabrication: (a) Epoxy resin and adipic acid are mixed in oil bath at 160C in presence of catalyst TBD (b) Vitrimer dogbone and vCFRP samples created using vitrimer as matrix material

Vitrimers are fabricated by replacing amine-based hardeners in epoxy chemistry with a carboxylic acid and the curing reaction is carried out in presence of a base catalyst. The epoxy resin i.e., Diglycidyl Ether of Bisphenol-A resin (DER 332) and adipic acid were purchased from sigma Aldrich. The base catalyst, 1,5,7 Triazabicyclo-[4,4,0]-decene (TBD, 98%) was purchased from J&K. Resin and acid were mixed in 1:1 molar ratio in oil bath at 160°C. Base catalyst (2.5 mol% to the COOH) was then added while continuous stirring. The catalyst initiated rapid curing reaction, hence the mixture is then rapidly poured in PTFE dogbone molds and cured under pressure for 6 hours at 160°C (Figure 2a).

vCFRP Fabrication

High strength aerospace grade woven carbon fabrics (Toho-Tenax Japan, HTS40-3K, basis weight of 200 g/m^2) were used to fabricate the composite. The vitrimer carbon fiber polymer composite (vCFRP) was created by rapidly pouring just mixed vitrimer onto a single layer of carbon fiber fabric and kept under 2MPa pressure for 15 minutes. Eight such layers were stacked and pressed under 10MPa for 6 hours at 160°C to get final vCFRP. The final plate was cut into rectangular samples of 10×75 mm^2 for testing (Figure 2b).

TESTING DETAILS

Static Testing

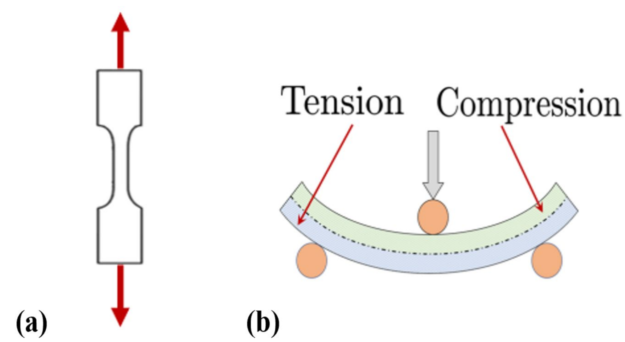

Figure 3. Mechanical testing details: (a) Vitrimer dogbone samples are loaded statically to get strength and stiffness (b) vCFRP samples are subjected to three point bend test, this test tests performance under tension and compression simultaneously

Mechanical testing of vitrimer dogbone samples was performed on an MTS 858 servo hydraulic testing machine. The tensile loading test was performed according to ASTM D638 with strain rate of 0.05 ε sec^{-1}. The tests were also carried out at rates 10 times higher and lower than the initial test to assess the rate sensitivity of the material (Figure 3a).

The vCFRP samples were loaded in flexural i.e., thre-point bending setuo. The test was carried out in accordance with the ASTM790 standard and displacement rate of 1 mm/min. This mode of testing was selected so that the sample is subjected to compression and tension simultaneously as depicted in the figure (Figure 3b). The maximum force recorded was used to calculate ultimate failure stress σ_u.

Fatigue Testing

vCFRP specimen were loaded in three- point bending setup in accordance with ASTM standard. The flexural fatigue test was carried out in accordance with ASTM D774 in force control mode at the frequency of 1 Hz and peak stress of $\sigma_u/2$. Initially the vCFRP sample was fatigue till failure and number of cycles to failure was recorded. Healing experiment was carried out by repeating the fatigue test with intermittent healing at 150°C for 1 hour and cooling to ambient. The fatigue test was run in force control mode. However, for healing experiment, the cut-off was displacement based i.e. the test was interrupted when the displacement increased by more than 10% compared to initial displacement. This strategy was adopted to ensure that accumulated damage is controlled.

RESULTS AND DISCUSSION

Static Testing

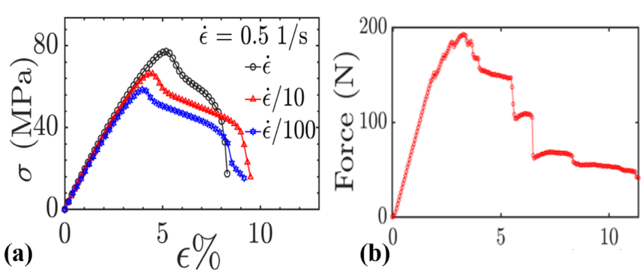

Figure 4. Static testing results: (a) Vitrimer tensile tests reveal rate sensitive nature of vitrimer, the stiffness is around 2GPa and strength is ~60-80MPa depending on loading rate (b) vCFRP loaded in three-point bending exhibit a peak in the force followed by stepwise drop indicating failures in different layers.

The vitrimer samples subjected to tensile testing indicate stiffness of 1.8 ±0.2 GPa and ultimate stress if 58MPa to 78 MPa. The strain to failure was around 9%. The stress to failure increased by ~33% when the strain rate was increased by two orders of magnitude (Figure 4a). This indicates that vitrimers are rate sensitive materials, this observation is supported by previous reports as well. It is worth noting that the strength and stiffness of vitrimer system is comparable to conventional industrial epoxy systems[10,11]. Hence these materials are indeed a suitable candidate for structural applications in various fields including rotorcraft components.

The static testing of vCFRP exhibited a typical carbon fiber response where, as applied displacement increases, the force increases to a critical value followed by a stepped drop in the force. The stepwise drop indicated progressive failure post peak force in individual carbon fiber plies. The peak force can be used to calculate ultimate failure stress σ_u of the composite using bending theory. The ultimate stress observed was 448.47 ± 52.8 MPa. The calculated value is comparable to previously reported CFRP and even higher than some of the other reported vCFRP systems[4,12].

Fatigue Without Healing

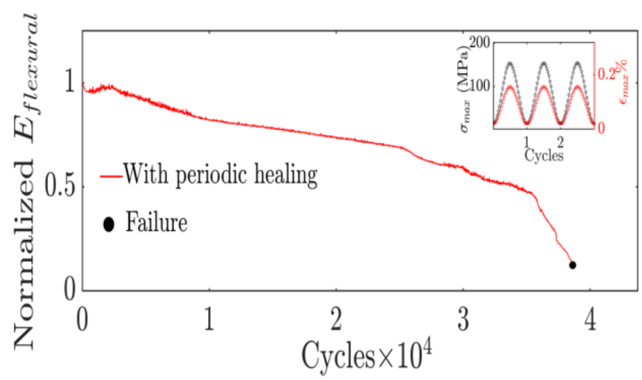

Figure 5. vCFRP cycles is fatigued in force-controlled mode with sinusoidal force input (inset) and normalized flexural modulus is plotted for each loading cycle

In the next stage, vCFRP sample is subjected to sinusoidal force cycle with load ratio R of 0.1. The maximum force is selected such that maximum stress at the peak of cycle is $\sigma_u/2$ (Figure 5, inset). The flexural modulsu calculated using force dispalcement plot extracted from each cycle. Figure 5 shows the normalized flexural modulus plot. As the test is force controlled, the dispalcement peak in each cycle increases i.e. the sample becomes more comliant. This is reflected as the drop in the flexural modulus. As seen in Figure 5, around 40,000 cycles the flexural moduls drops to 10% of the original value and sample fails completely.

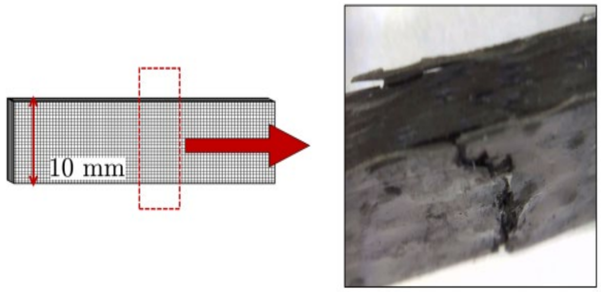

Figure 6. Optical image of the vCFRP sample fatigued without healing, a macroscopic failure is evident.

To emphasize on the extent of the damage in the sample, an optical image of the center section of specimen is provided (Figure 6). A through crack is visible across the width of the sample. Pervasive fiber-matrix interface failure is also present on the sample.

Fatigue With Healing

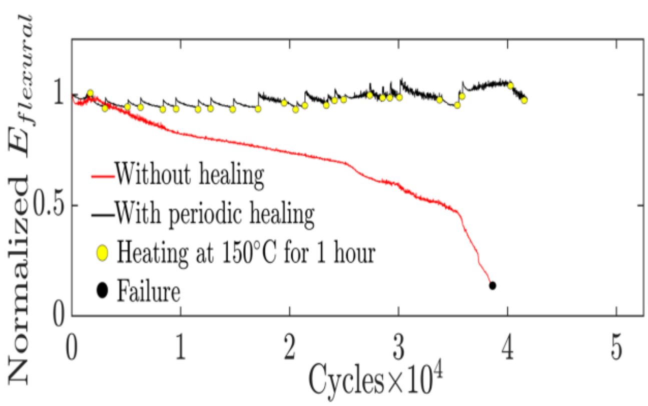

Figure 7. vCFRP cycles is fatigued in similar manner with intermittent heating to 150°C, the sample retains its flexural modulus when subjected to periodic healing

To demonstrate fatigue reversal in vCFRP sample, a force-controlled experiment with displacement-based cutoff was designed. A pristine sample was subjected to the same loading parameters as the previous section. However, this time the test was stopped when the displacement increased by 10% compared to the original displacement. The specimen was then put in an over preheated to 150°C for 1 hour under 200 kPa pressure. Then it was allowed to cool down to the ambient, mounted in the loading fixture and the test was resumed. As done in previous section, flexural modulus is extracted from each cycle. We observe that after 25 heating cycles, the sample retains the original flexural modulus, and it has already exceeded the number of cycles to failure observed without failing (Figure 7).

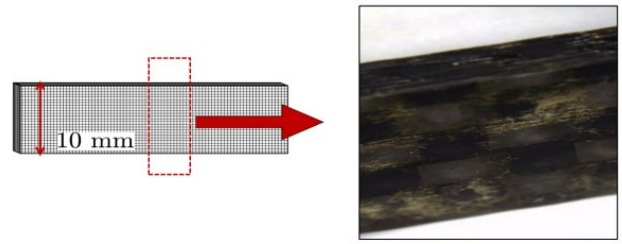

Figure 8. Optical image of the vCFRP sample fatigued with healing, the sample retains its structural integrity.

An optical image of the central span of the healed sample shows structural integrity of the sample (Figure 8). Despite being subjected to similar loading conditions and for similar duration, the sample dies not exhibit any macroscopic flaws. This suggests that the vCFRP subjected to periodic healing may undergo reversal in small scale fatigue damage. Thus, components fabricated with vCFRP may have ultra high fatigue life.

Fractography of Specimen

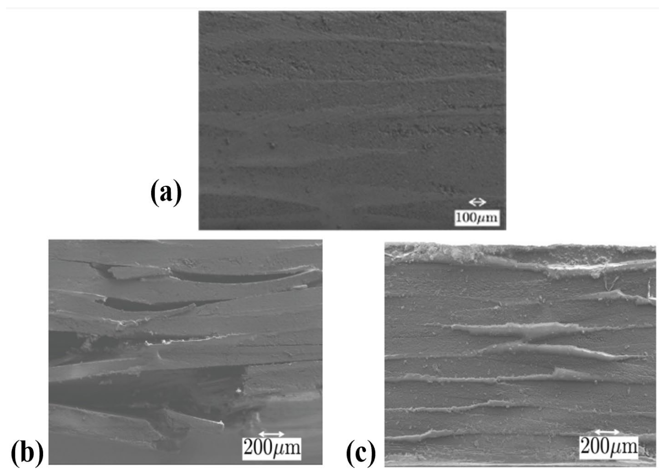

Figure 9. vCFRP fractography: (a)Pristine sample (b)Sample fatigued without healing (c)Sample fatigued with healing

The fractography of the fatigued vCFRP specimen was performed through SEM imaging. The pristine vCFRP sample (Figure 9a) shows no signs of damage or delamination as expected. Fractography of the specimen which is fatigued without healing (Figure 9b) shows clear indication of widespread failure. Along with the fiber rupture, interfacial failure at the fiber-matrix interface is clearly visible as well. However, the specimen fatigued with healing (Figure 9c) does not exhibit any microscopic failure in fibers and interface. Moreover, it appears akin to the pristine specimen. As the specimen is heated under pressure during healing, the vitrimer can potentially egress from the sides of the specimen, as seen in the SEM. Hence, the fractography further confirms that intermittent healing may reverse small scale fatigue damage in composites.

Comment on Healing Mechanism and Strategy

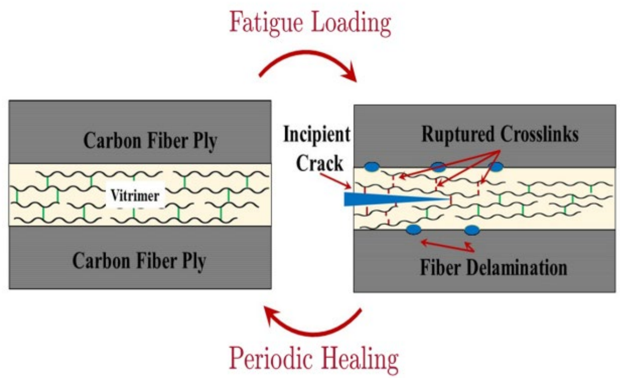

Figure 20. vCFRP healing mechanism: The intermittent healing enables reversible crosslinking healing and in addition, the flow induced by healing may repair small scale fiber-matrix interface damage, returning component to near pristine condition

As the fractography suggests, fatigue damage in carbon fiber composites may involve matrix failure as well as interfacial failure. We subject vCFRP to heating to 150°C which may induce some flow in the vitrimer. This flow can potentially help repair the interfacial failure as well. Therefore, heating in vCFRP system serves the dual purpose of repairing matrix damage and interface failure. Hence, if we subject specimen to repeated healing protocol they may be returned to near pristine condition if the fatigue damage is small scale (Figure 20).

CONCLUSIONS

In this study we have demonstrated that-

1. Reaction of DGEB-A and Adipic Acid in presence of TBD creates a vitrimer.
2. Vitrimer shows rate sensitive behavior and has mechanical properties comparable to epoxy.
3. Small scale fatigue in vCFRP may be reversed by intermittent heating to a high temperature.
4. Fractography suggests the healing protocol may reverse fatigue damage in matrix as well as damage to the interface.

Author contact: Nikhil Koratkar koratn@rpi.edu

REFERENCES

1. Tserpes KI, Papanikos P, Labeas G, Pantelakis S. Fatigue damage accumulation and residual strength assessment of CFRP laminates. *Compos Struct.* 2004 Feb 1;63(2):219–30.

2. Degrieck J, Van Paepegem W. Fatigue damage modeling of fibre-reinforced composite materials: Review. *Appl Mech Rev.* 2001;54(4):279–300.

3. Kamble M, Lakhnot AS, Koratkar N, Picu CR. Heterogeneity-induced mesoscale toughening in polymer nanocomposites. *Materialia.* 2020 Jun 1;11:100673.

4. Yavari F, Rafiee MA, Rafiee J, Yu ZZ, Koratkar N. Dramatic increase in fatigue life in hierarchical graphene composites. *ACS Appl Mater Interfaces.* 2010 Oct 27;2(10):2738–43.

5. Rafiee MA, Rafiee J, Srivastava I, Wang Z, Song H, Yu ZZ, et al. Fracture and fatigue in graphene nanocomposites. *Small*. 2010 Jan 18;6(2):179–83.

6. Krishnakumar B, Sanka RVSP, Binder WH, Parthasarthy V, Rana S, Karak N. Vitrimers: Associative dynamic covalent adaptive networks in thermoset polymers. *Chem Eng J* https://doi.org/10.1016/j.cej.2019.123820

7. Van Zee NJ, Nicolaÿ R. Vitrimer Chemistry and Applications. *Macromolecular Engineering*. 2022. 1–38 p.

8. Montarnal D, Capelot M, Tournilhac F, Leibler L. Silica-like malleable materials from permanent organic networks. *Science* (80-). 2011;334(6058):965–8.

9. Ciarella S, Biezemans RA, Janssen LMC. Understanding, predicting, and tuning the fragility of vitrimeric polymers. *PNAS* 2019;10(50):25013–22.

10. Picu CR, Krawczyk KK, Wang Z, Pishvazadeh-moghaddam H, Sieberer M, Lassnig A, et al. Toughening in nanosilica-reinforced epoxy with tunable fi ller-matrix interface properties. *Compos Sci Technol* doi.org/10.1016/j.compscitech.2019.107799

11. Jajam KC, Tippur H V. Quasi-static and dynamic fracture behavior of particulate polymer composites: A study of nano- vs. micro-size filler and loading-rate effects. *Compos Part B Eng.* 2012 Dec;43(8):3467–81.

12. Kamble M, Lakhnot AS, Bartolucci SF, Littlefield AG, Picu CR, Koratkar N. Improvement in fatigue life of carbon fibre reinforced polymer composites via a Nano-Silica Modified Matrix. Vol. 170,

Carbon. 2020. p. 220–4.

13. Chabert E, Vial J, Cauchois JP, Mihaluta M, Tournilhac F. Multiple welding of long fiber epoxy vitrimer composites. *Soft Matter*. 2016;12(21):4838–45.