Vitrimer composites for rotorcraft components

Mithil Kamble
kamblm@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

Carbon fiber reinforced composites (CFRP) are frequently used in rotorcraft components due to their high strength to weight ratio. Carbon fibers are the principal load carriers whereas polymer matrix provides structural integrity to the CFRP components. Fatigue failure originating in the matrix pose a design constraint on CFRP components. The fatigue failure originates in form of small scale sub-critical cracks which eventually grow into macroscopic cracks/shear localization resulting in eventual failure. Research efforts have been directed at improving fracture and fatigue performance of polymeric matrix by arresting incipient cracks. Thermoset polymers are widely used as matrix material as they posses superior strength due to high crosslinking density. However, since no self-healing mechanism operates in thermosets, damage is irreversibly accumulated over the life cycle of components. A new class of materials called vitrimers provide a novel approach to develop fatigue resistant CFRP. Vitrimers are associative covalent adaptive networks (CAN) which have reversible crosslinking reactions which can be activated by external energy stimulus like heat. As the crosslinked network is reversible, the incipient damage can be 'healed' by application of heat. In this work we explore the self-healing properties of vitrimer fabricated by the reaction of adipic acid and epoxy resin. The vitrimer is initially tested in static tests to probe mechanical properties, followed by fatigue experiments. The vitrimer is then used to make a vitrimeric CFRP (vCFRP) composite and is tested for its static and fatigue performance.

INTRODUCTION

New generations of rotorcrafts will be expected to perform under severe operating conditions due to increased load carrying capacity, speed and frequent operation. The structural components of rotorcrafts will be subjected to higher mechanical loads over longer duration. Fatigue is a principal cause of failure in these components which also adds to the maintenance cost of rotorcrafts. This necessitates development of new structural materials with superior fatigue properties.

Since the rotorcraft components are constrained by their weight, carbon fiber reinforced polymer composites (CFRP) are most widely used. CFRP have the advantage of having high strength to weight ratio. In CFRP system, the primary load carriers are carbon fibers which can be oriented in the desired direction to get optimal directional strength. Polymeric matrix holds the carbon fibers together and gives the composites its structural integrity. Epoxy, a thermoset polymer, is used as the matrix material due to its superior strength and stiffness relative to other polymers. The superior strength is a result of permanent crosslinking of the molecular network which is formed during the curing process. The fatigue failure in CFRP typically originates in the weaker matrix material where the sub-critical cracks originate due to the breaking of crosslinks. Initially, the sub-critical cracks grow in at very slow rates. However, as the component goes through repeated loading, the cracks enter steady state crack growth which is followed by a rapid catastrophic failure (Ref. 1).

Nanocomposites have been explored in the past to enhance fatigue life of CFRP where nano-additives interact with small scale cracks to retard crack growth (Ref. 2-6). However, since a thermoset polymer is irreversibly crosslinked, once the damage is introduced, the cracks would eventually grow sufficiently to cause catastrophic failure. If crosslinks in the network are somehow made reversible such that they can reform during service, it could potentially lead to the development of composites which would show improved fatigue performance (Ref. 7). The reversible crosslinking reaction can be induced either thermally or photochemically (Ref. 8,9). Such networks with dynamic reversible reactions have been explored for some time and called covalent adaptable networks (CAN) (Ref. 10). However, initial CAN were chemically complex with a tendency to degrade over time. Additionally, they had strength and stiffness one order of magnitude lower than conventional epoxy. A breakthrough was achieved in 2011 when Liebler et al developed an epoxy-acid based network which could undergo reversible

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crosslinking reaction under application of heat (Ref. 11). These novel materials were termed vitrimers. Apart from glass transition temperature T_g, vitrimers networks have a characteristic temperature called vitrimeric temperature T_v where the rate of reversible reaction is sufficiently high to allow for dynamic healing of the polymer (Ref. 12).

Invention of vitrimers has spurred growing research activity to investigate self-healing composites. While several chemistries have been proposed to create vitrimer networks, their fatigue properties remain largely unexplored. In this work we investigate a vitrimer network based on epoxy resin and adipic acid and show that it possesses mechanical properties comparable to epoxy. We demonstrate dramatic fatigue life improvement in the network under application of periodic heating. In future, we will be making vitrimeric CFRP composites and test them in fatigue.

MATERIAL DETAILS

Vitrimer preparation

The conventional epoxy (Diglycidyl Ether of Bisphenol-A) resin was initially crosslinked with industrial hardener to prepare baseline samples. To make vitrimer, DGEBA was reacted with adipic acid in presence of 1,5,7 Triazabicyclo-[4,4,0]-decene (TBD, 98%). TBD acts as a transesterification catalyst. The resulting samples was cut in dogbone specimen.

vCFRP Fabrication

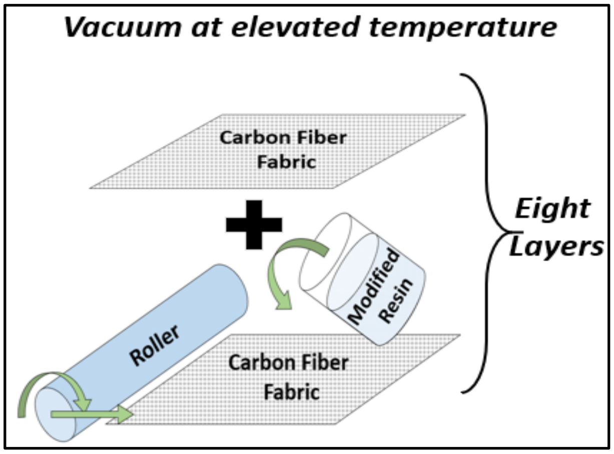

Figure 1. Wet layup procedure to make vCFRP plates.

The vCFRP composite is fabricated using the wet layup procedure (Fig. 1). The carbon fiber sheets of 0^o-90^o orientation were obtained from Toho-Tenax (TSK 300). The vitrimer resin was applied to individual sheets and eight such sheets were stacked. The resulting composite was put under vacuum to eliminate air pockets and then it was cured at 90^o under vacuum. The vCFRP plate is eventually cut in rectangular specimen of 10X70 mm for testing in flexural mode.

TESTING DETAILS

Thermomechanical analysis

Vitrimer samples were subjected to thermomechanical analysis to determine the characteristic properties of the network. Differential calorimetric analysis (DSCwas performed with the heating rate of 10 °C/min.Next the sample were subjected to dilatometric analysis. The experiment probes axial strain changes to the sample subjected to pre-load as the temperature is increased gradually. The samples were subjected to pre-stress of 25 KPa and then heated at 2.5 C/min. The changes to volumetric strain with temperature change reveal transformation to the network structure as it absorbs heat and mobility of the cross-linked network increases. The strain evolution of material with temperature is used to infer topology freezing or vitrimeric temperature (T_v).

Static testing and healing experiment

After establishing the thermomechanical properties, vitrimer dogbone samples were subjected to uniaxial tensile testing at three different loading rates of 8.3×10^{-5}, 8.3×10^{-4} and 8.3×10^{-3} to probe the stiffness and strength of the material as well as to analyze the rate sensitivity of vitrimer.

It is important to establish the healing performance of the vitrimer in static testing before studying the fracture. To study this, samples were first heated to 80^o C to eliminate the pre-stresses developed in the fabrication process. The annealed samples are then statically loaded to 2.5% strain at 1mm/min do induce damage in the sample. The peak force drops around 5% after five loading cycles. The damaged sample is then heated to 80^o C for one hour, allowed to cool for 15 minutes and loaded again in the same manner to determine the peak force. The failure surface of the vitrimer sample is imaged with scanning electron microscope (SEM) to understand the failure mode of the sample. To analyze the static performance of vCFRP samples they are loaded in 3 point bending mode at loading rate of 1 mm/min.

Fatigue and healing experiment

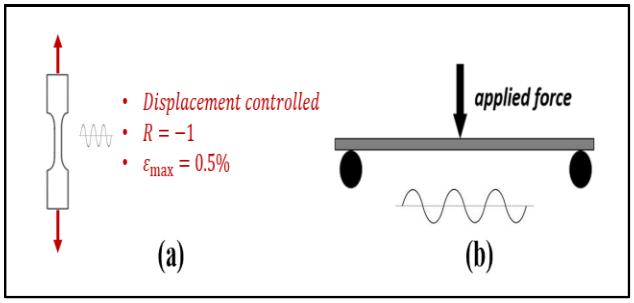

Figure 2. (a) Wet layup procedure to make vCFRP plates.

To study the fatigue performance vitrimer samples are loaded in cyclic tension, with sinusoidal strain of 0.5% at 2 Hz (Fig.

2a). The loading ratio R of -1 is selected to eliminate the effect of ratcheting. The sample was loaded till failure and the stiffness of the sample was monitored through the test along with number of cycles for failure (N_f). After the initial failure, another sample is loaded in similar manner for $0.5*N_f$ cycles. The sample is then removed and heated to 80°C for 1 hour and allowed to cool for 15 minutes. The sample is again loaded for $0.5*N_f$ cycles and the test is stopped for heating the sample. This sequence is repeated 10 times.

RESULTS AND DISCUSSION

Thermomechanical analysis

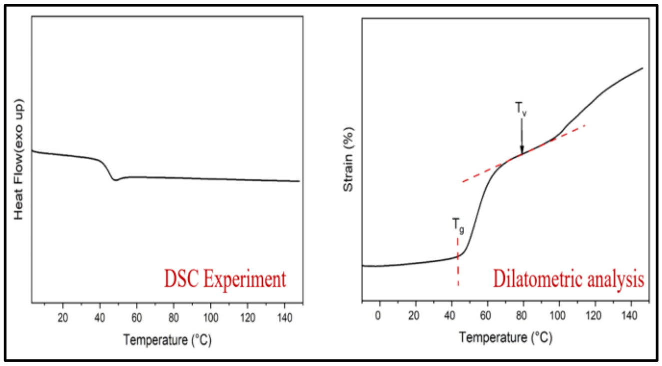

Figure 3. (a) DSC analysis (b) Dilatomeric analysis

The DSC plot indicates heat release at 40°C (Fig. 3a). This defines the glass transition temperature, T_g. In dialatometric analysis, three distinct regions. Initially, the strain remains approximately constant at low temperatures below ~40°C (Fig. 3b). The rapid increase of the strain at 40°C confirms the glass transition observed in calorimetry at this temperature (Fig. 3a).

In the rubbery regime after T_g, the strain growth slows down before increasing again. This is a characteristic of vitrimer networks where the flow of the network is controlled by the transesterification (reversible crosslinking) reaction. At temperatures between Tg and a material-specific temperature, Tv, the network behaves as a viscoplastic solid. At temperatures higher than T_v, the material becomes a viscoelastic liquid. . Importantly for the present discussion, the reversible crosslinking reaction enables the network to heal the damage that may occur during loading.

Static testing and healing experiment

The tensile tests reveal the rate sensitive nature of vitrimer network (Fig. 4). The strength of the material increased from 58 MPa to 67 MPa and 78 MPa as the strain rate was increased from 8.3×10^{-5} by factor of 10 and 100 respectively. The stiffness of the material however is insensitive to the strain rate. The stiffness was measured to be around 2 GPa which is comparable to industrial epoxy network.

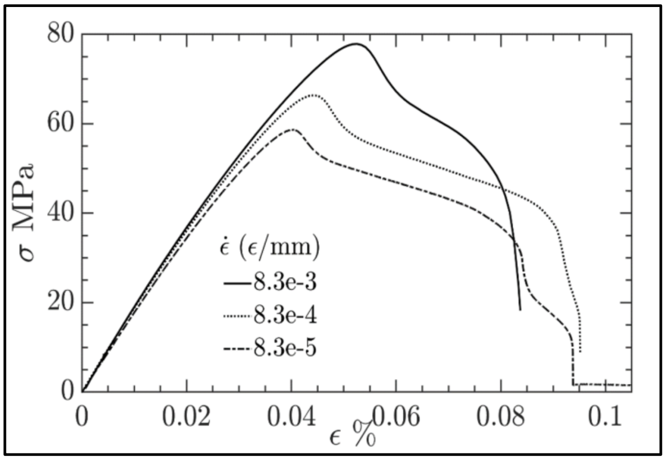

Figure 4. Stress-strain plots obtained from tensile testing

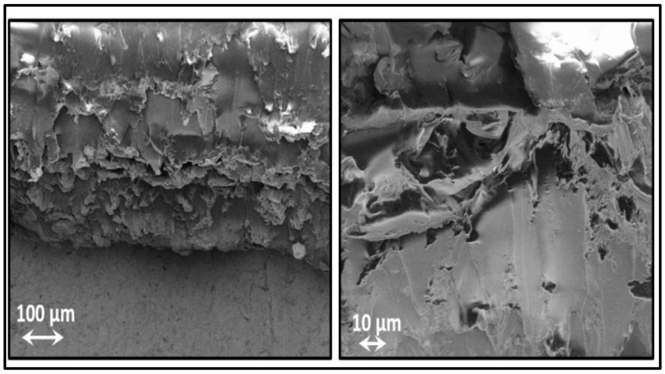

Figure 5. SEM of failed vitrimer sample

The fracture surface of the failed vitrimer sample was imaged using SUPRA SEM 500. The fracture surface revealed microfibrils on the fracture surface (Fig. 5). This indicates that fracture initiated in form of micro-voids which eventually grew and the microfibrils are formed which fail at critical load. This is a typical ductile failure mode in viscoelastic solids and is different from brittle fracture observed in epoxy networks. This further underscores the distinct viscoelastic nature of vitrimer networks even when they are derived from conventional DEGB-A resin. Viscoelasticity in vitrimers have been observed in earlier studies as well (Ref. 13, 14).

In static healing experiments, the sample was loaded in tension till the load begins to plateau with increasing displacement. This plateau is a result of accumulated damage as crosslinks begin to break. The loading was repeated five times to see sufficient small scale damage which can be observed in the test. The peak load where the load begins to plateau was observed to drop by 5% after five loading cycles, indicated by black and yellow plots (Fig. 6). After this, the sample was heated at 80°C which is close to the T_v of this vitrimer. If the small scale damage is healed by reversible crosslinking reaction which is accelerated by heating, the original response would be recovered. This is confirmed by the tensile loading tests performed after heating cycle. The red curve obtained from the last loading is virtually identical to

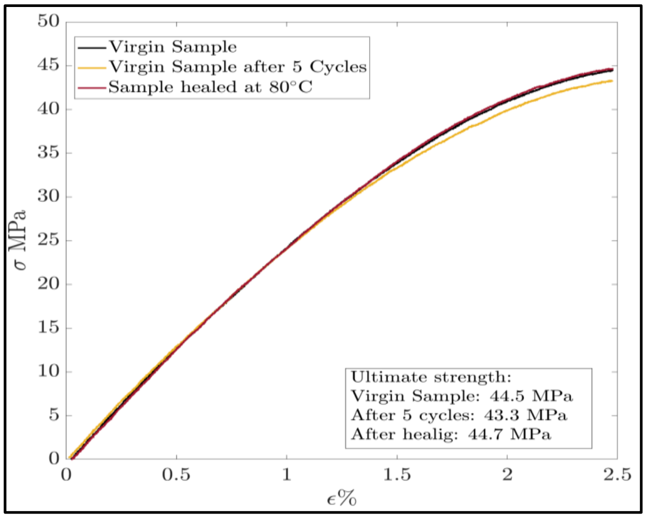

Figure 6 . Healing plot in static test

the initial response of the sample. This healing experiment conforms that the vitrimer is able to self-heal when subjected to sufficiently high temperature..

Fatigue healing experiment

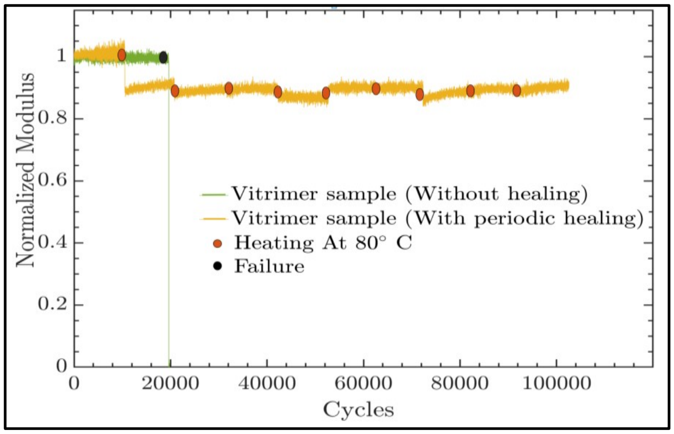

Figure 7 . Healing plot in static test

In the initial fatigue testing, the vitrimer sample failed around 20000 cycles. The stiffness was calculated from the loading branch of each cycle. The stiffness was found to remain constant throughout fatigue loading before dropping to zero at failure (Fig. 7). This indicates that the damage slowly accumulates in the sample as it is cycles. However, since stiffness is a macroscopic property, the accumulated damage is not reflected in the stiffness of the sample.

For the fatigue healing test, the next sample is cycled for 10,000 cycles only and taken out for heating at 80°C. After heating the sample for 1 hour and cooling it to room temperature, another loading regime of 10,000 cycles is applied. The stiffness of the sample drops after first heating. However, as the fatigue-heating cycles are repeated consequently, no drop in the stiffness is observed. Hence the initial drop in the stiffness is potentially a result of prestress being relieved during the first thermal treatment.

We observed that, the sample did not fail even after ten fatigue-heating cycles. The life of the sample was effectively extended by 5 times by introducing periodic heating of the sample. This indicates that vitrimers hold great promise for the purpose of fatigue resistant composites which can have considerably higher fatigue life than conventional composite.

In the next stage, we will be testing vCFRP samples in similar manner to assess their fatigue performance. Demonstrating dramatic fatigue life improvement in vCFRP would be of great interest for rotorcraft structural applications.

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. Vitrimer which is damaged can be healed by thermal treatment at temperatures close to Tv.
4. Periodic heating may be applied during fatigue loading to increase fatigue life significantly.

Author contact: Nikhil Koratkar koratn@rpi.edu

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