SEA WATER EFFECTS ON ULTIMATE TENSILE AND FRACTURE STRENGTH OF CARBON FIBERS WITH NANO-TENSILE TESTING

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Abstract

It was recently demonstrated by authors that T700 sized carbon fibers under prolonged exposure to sea water and elevated temperature appeared to have degraded mechanical properties, specifically elastic modulus[1]. This utilized the unique mechanical characterization abilities of the MTS Nano-Bionix ultimate tensile machine as seen in Figure 1. This system uses small oscillatory vibrations in-situ to quasi-static tensile loading to determine simultaneous storage and loss modulus as a function of global strain. Expanding upon the previous study, the present work assesses the effect of ultimate tensile strength and fracture toughness of carbon fibers exposed to sea water and temperatures of 40 and 80C for 120 days with regular testing intervals.

1 Introduction

Globally, carbon fibers have seen significant interest for use in FRPs as lightweight replacement engineering materials. The Office of Naval Research (ONR) currently is exploring composite sandwich structures for use in sea worthy vessels. As a result, thorough testing and verification is needed to determine the integrity of these materials in the harsh sea water environment. Many authors have explored these topics, observing interfacial failures, specific phase chemical degradations, and global mechanical property changes from sea water exposure[2-4]. Relatively little work has been done exploring the single fiber mechanical properties of carbon fibers after sea water exposure. Carbon fibers are generally considered to be highly inert to most environments, noting resistance to acids, alkalis, salts and solvents[5]. However, initial work in sea water exposure of single carbon fibers prompted the authors to pursue this study.

A relatively new testing system, the MTS Nano Bionix or more recently the Agilent T150, has been used for single filament tensile testing for this work. (Although this system is currently commercially available as the Agilent T150, it will be referred to as the MTS Nano Bionix as this was the system used for this work.) Its high resolution load and displacement capabilities, and CDA, continuous dynamic analysis, testing option are uniquely suited for studying single fiber mechanical properties. This present study expands upon the author's previous demonstration of sea water effects on mechanical properties of carbon fibers by significantly increasing the quantity of fibers tested and duration with which fibers were exposed to sea water.

2 Experimental Procedure

Toray carbon fibers, type T700 taken from Devold LT650 woven fabric with apparent diameter of 7 microns, were soaked in simulated sea water, using Frontier™ Bulk Salt. The fiber cross-section was assumed to be round such that the cross sectional area could be calculated. These fibers are coated with sizing designed specifically for vinyl ester resin systems. Salt water baths were prepared and maintained at 40 and 80 degrees C with the salinity checked regularly. It was assumed and often expected for this work that elevated temperatures could increase the rate of aging effect. Tows were placed in vials of sea water which were then placed in sea water baths as in Figure 2. When testing occurred, a vial was removed, drained, and the sample was placed in desiccation for at least a day, at which point it was ready to be mounted for tensile testing. 10 fibers were mounted for each temperature at 1 month intervals. Single carbon fibers were mounted using a custom mounting procedure uniquely developed by the authors. Special care was taken in the design and implementation to avoid misalignments and compliance miscalculations. In general, suggestions from standards for single fiber tensile testing, ASTM and ISO, were followed[6, 7]. It was decided that the most repeatable data could be obtained with highly repeatable mounting procedures and materials. Hence, a reusable metal template was designed as is seen in Figure 3. Only the end of gripping portion of the template was needed to be used repeatedly and critical for test quality, thus the template arms were still constructed from disposable plastic or in this case Nylon 6/6. To construct the template or frame with which individual fibers were gripped, the metal template tabs were placed in grooved slots, as in Figure 5, that held them in place for template construction, whereby plastic arms were glued on, and accurately aligned them such that fibers could be also glued on to the metal templates along the fiduciary alignment mark, seen in Figure 3. Fibers were aligned and held in place with tape for application of epoxy, West System®, which finally mounted them to the template tab.

The complete template frame with the arms attached is seen in Figure 4 mated to the UTM. Three holes were precisely drilled into each template tab. The two outer holes mated to dowels on the grips attached to the UTM. The center hole held a screw that threaded into the grip. This screw was not overly torqued, but applied nominal normal force and kept the template from sliding on the dowels during testing. This grip system proved to be highly reliable, repeatable, and robust, demonstrating noticeable improvement over previously reported mounting techniques of single fibers. Single Fiber fracture specimens were prepared using FIB, focused ion beam, to mill an edge notche into a single fiber [9]. Figure 6 is a typical result of such an applied notch. T700 carbon fiber samples for fracture toughness measurements were mounted in identically the same way as that for tensile experiments. A similar mounting block previously described was made to fit inside the chamber of a FIB, such that as little manipulation of the fibers was necessary. The notch produced a stress concentration from which the fibers fracture strength was calculated according LEFM as in equation 1.

$$K_{IC} = \sigma_f Y \sqrt{\pi a_c} \qquad (1)$$

Here, σ_f is the far field stress at sample failure, Y is the dimensionless intensity factor, and a_c is the critical crack size. Special attention was given to develop a milling procedure that would produce a repeatable notch geomotry in the fiber. The ideal geometry was a beam width line, which after some trial and error was very nearly accomplished as seen in Figure 5. After the fracture test on single edge notched fiber was completed, the size of the notch was confirmed with SEM images of the fracture surface at high magnifications.

As previously stated the MTS Nano Bionix has been used for tensile experiments in this work. This system has the CDA capability, which continuously monitors stiffness as a function of global strain. To accomplish this, the Nano Bionix does not use a typical load cell to determine to force on a specimen, but rather a unique device called the NMAT or nano-mechanical actuating transducer, as shown earlier in Figure 1. A description of how this system operates with performance specifications has previously been reported by authors[1].

Previously, the harmonic load was set to 5 mN, but for this work it has been reduced to 40 μN. It is thought that this smaller load would indicate more closely the molecular motions caused by introduced strain, while the larger load would tend to average out these small changes. This is not a trivial change due to repercussions that must be accounted for in the electronics of the testing system. A complete description of how this is done is out of the scope of this paper due to space, but will be presented in a future publication expanding on current result.

3 Results

Typical results for stress and storage modulus against strain can be seen in Figures 7 and 8 for harmonic loads of 5mN and 40 μN. Both Figures demonstrate increasing storage modulus or stiffening with strain, typical for carbon fibers[8]. However, a noticeable difference in smoothness is observed between storage modulus of 5 mN and 40 μN harmonic load modulation. Although the undulation in the 40 μN storage modulus may appear as noise, it does not show randomness from point to point, but rather demonstrates controlled change. It seems as though this small harmonic load, two orders of magnitude smaller than the 5 mN harmonic load, is demonstrating a stochastic molecular reorientation process of the carbon planes inside the fiber, which gives carbon its stiffening effect with strain, captured by both 5 mN and 40 µN harmonic loads.

Previous work indicated that PAN T700 carbon fibers were susceptible to sea water induced mechanical degradation as demonstrated by the modulus drop associated with higher temperatures in Figure 9[1]. This was a preliminary study that motivated the authors to significantly increase the scope of this work and to incorporate failure stress analysis as well. However, the same trend was not seen to occur and in fact, the same samples under identical conditions exhibited no clear mechanical losses from exposure to sea water. Figure 10 gives the storage modulus taken at a strain level of 0.005 for ambient, 40C water bath, and 80C for a four month time period, but no clear indication of mechanical degradation is seen. Because carbon fiber modulus changes with strain level, comparing the modulus of multiple fibers is only relevant if a specific strain level is defined. Furthermore, Figure 11 demonstrates no noticeable change in failure stress, given the large scatter in failure stress measurements due to structure variations among individual fibers, with respect to sea water exposure and time. Exploration of the data to understand why the previous batch indicated mechanical losses and the current batch did not, revealed a specific relationship between the derivative of storage modulus with respect to strain and the storage modulus itself at a specific strain level. If this approach is applied to the previously reported storage modulus data, which demonstrated significant mechanical degradation with sea water exposure, a clear trend is seen in Figure 12. One can notice that samples corresponding to 80C had relatively low values of the derivative of storage modulus with strain (values less than 5,000) and seem to have degraded much more significantly with sea water exposure. Essentially, this trend is that stiffer fibers tend to also have a higher rate of change of modulus with strain. This indicates significant structural variation is being measured from fiber to fiber. Applying this understanding to the current batch of fibers, the same trend is noticed in Figure 13. If the reported slope of storage modulus variation with strain is a fundamental indication of fiber structure, then one can use it to evaluate relative effects of sea water on those fibers with similar value ranges of this parameter to reduce fiber to fiber variations. However, when we attempted this approach to extract data for those fibers that have a dSM/dε value of 5000-5500, shown in Figure 13 and a significant reduction in scatter is noticed for variations of storage modulus at 0.5% tensile strain, but still did not show clear trend in reduction in mechanical properties (Fig. 14).

For virgin fibers (not exposed to sea water), K_{IC} fiber fracture toughness was measured for PAN T700 fibers using the FIB notch technique. Reported here is the fracture toughness assuming isotropic properties, using various FEM based dimensionless intensity factors for edge crack of a long cylinder under tension [9-11]. The fracture toughness results are plotted against notch depth in Figure 15. It is concluded that for carbon fibers with surface defects, it is reasonable to use a value of K_{IC} 1 to 2.0, a suggested average value of 1.5. Future studies are planned to evaluate the mode I fracture behaviour of fibers which are long-term soaked in sea water.

4 Conclusion

A novel nano tensile testing system and advance mounting techniques using a metal-polymer template have been used for performing highly accurate tensile testing of small diameter (100 nm to 100 microns) fibers and demonstrated by measuring properties of individual 7 micron T700 Toray carbon fibers which are of significant interest to US Navy. The dependence of modulus with applied axial strain is carefully quantified using both static stress-strain curves and dynamic contact stiffness approach. Average failures stress values of 3 to 5 GPa and storage modulus values of 230 to 250 GPa were obtained from multiple samples of single carbon fibers. Procedures have also been developed to introduce sharp edge cracks of controlled length using FIB-SEM. Using edge notched fibers, mode 1 fracture behavior was determined for single carbon fibers for notch lengths in the range of 0.1 to 1.2 microns on a nominal 7 micron diameter carbon fiber. It is concluded that for carbon fibers with surface defects, it is reasonable to use a value of K_{IC} 1 to 2.0, a suggested average value of 1.5 for practitioners. Based on limited experimental data to date, the fibers soaked with sea water did not show a clear trend of variation in measured properties such as failure stress and modulus variation with strain as a function of exposure conditions, and the potential degradation seems to occur for those fibers with poor mechanical properties quantified by a valued corresponding to the slope of storage modulus with respect to axial strain.

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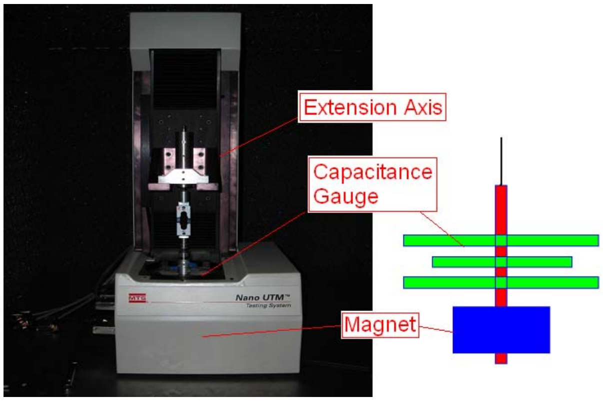

Fig.1.MTS Nano Bionix Testing system (left) and cartoon of NMAT loading sensing system (right)

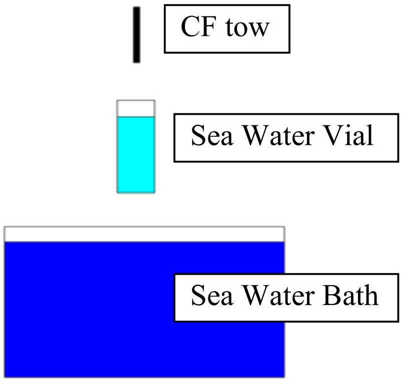

Fig.2.Carbon fiber soaking procedure

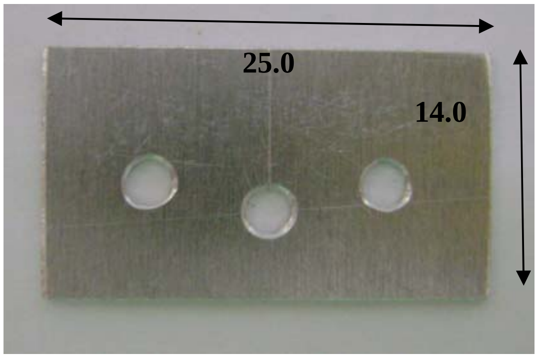

Fig.3.Custom aluminum template for single filament tensile testing

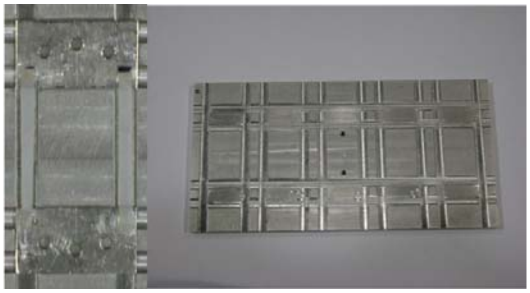

Fig.4. Template on mounting block with tabs placed in grooved slots and Nylon 6/6 template arms

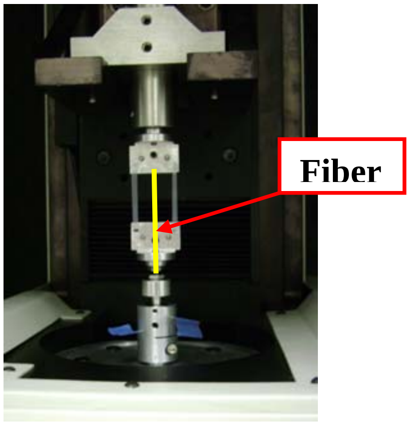

Fig.5.Template attached to nano-tensile testing system having double dowel grips

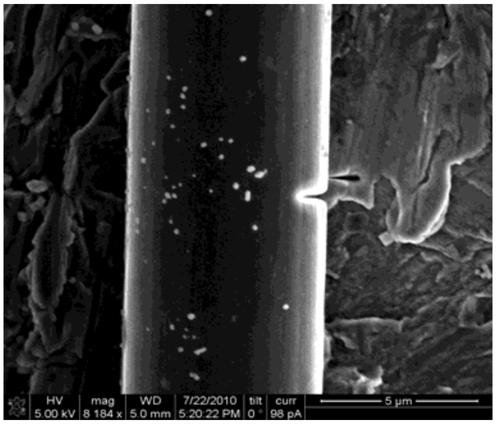

Fig.6.Single Edge notch in carbon fiber milled with FIB

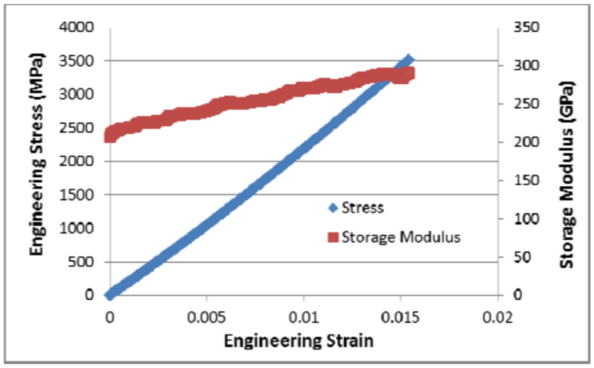

Fig.7. Typical results for carbon fiber T700 stress vs. strain and storage modulus vs. strain for a harmonic load of 40 µN.

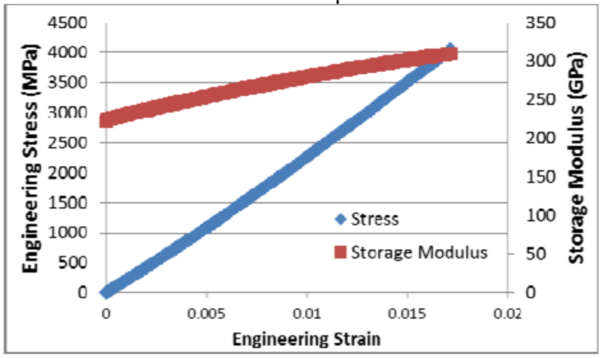

Fig.8. Typical results for carbon fiber T700 stress vs. strain and storage modulus vs. strain for a harmonic load of 5 mN.

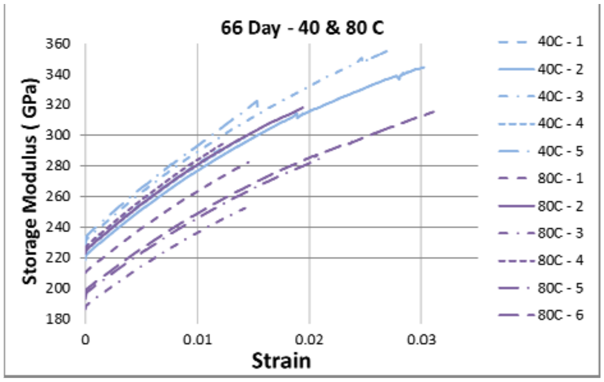

Fig.9. 66 Day Sea Water Exposure demonstrating clear distinction between 40Cand 80C

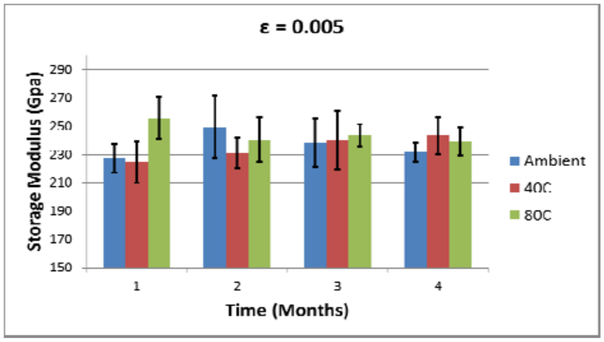

Fig.10. Storage modulus evaluated at a strain level of 0.005 for ambient and 40 and 80 C sea water bath exposures

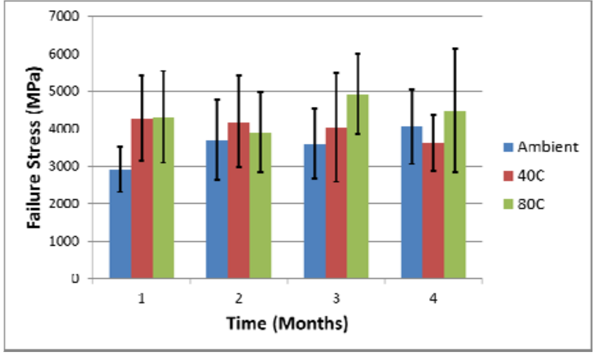

Fig.11. Failure stress of single carbon fibers exposed to ambient air and 40 and 80 C sea water baths demonstrating no clear trend from sample exposure.

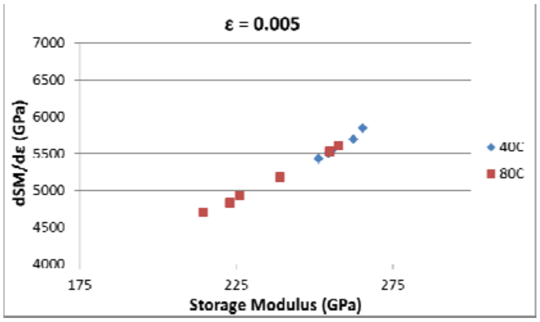

Fig.12.The derivative of storage modulus with strain against the value of storage modulus at 0.005 strain for the samples in Figure 11

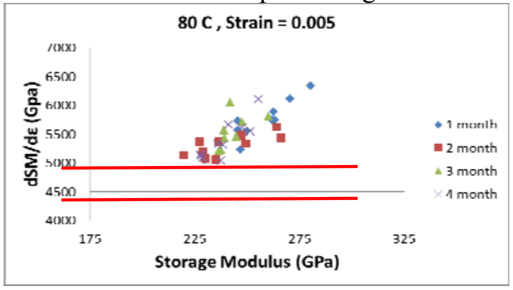

Fig.13. The derivative of storage modulus with strain against the value of storage modulus at 0.005 strain for the samples in Figure 12. The red lines represent the extracted range of data

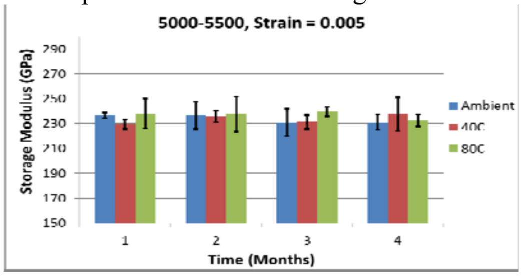

Fig.14. Storage modulus of fibers in the dSM/dε range of 5000-5500 from Figure 13 in between the red lines

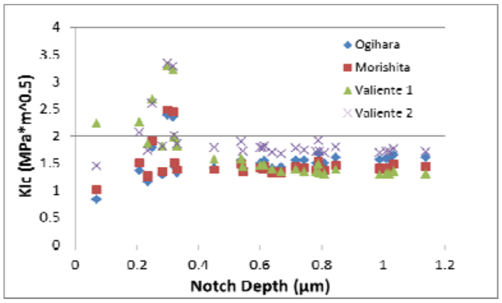

Fig.15. KIC fracture toughness using different dimensionless stress intensity factors[9-11].

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