A Dielectric Resonant Cavity Method for Monitoring of Damage Progression in Moisture-contaminated Composites

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ABSTRACT

A method for monitoring of damage progression due to combined mechanical and hygroscopic loading in polymer composite materials is presented. Polymer-based materials have a tendency to absorb moisture from their operating environment. Dielectric properties of these materials are significantly affected by the total amount of absorbed moisture and the degree of its interaction with the host polymer. Bound water molecules which are restricted in their ability to rotate with an applied electromagnetic field contribute less to the bulk relative permittivity. 'Free' water molecules rotate without impediment and are therefore associated with a higher relative permittivity. The bulk relative permittivity as a function of total water content of a contaminated composite is a unique function of the internal physical and chemical characteristics of the specimen. Holding chemical contributions constant, physical characteristics dominate. Thus, relative permittivity provides insight into the physical state of composite, including amount of free space from processing-induced voids or, critically, the presence of physical damage such as cracks and voids across multiple length scales. Here, we demonstrate a method for leveraging this phenomenon to provide insight into the initiation and accumulation of physical damage in moisture-contaminated composites. This is accomplished using a split-post dielectric resonant technique operating in the low GHz frequency range, where dipolar contributions to relative permittivity dominate. Further, continuous and non-contact monitoring of relative permittivity is achieved by integrating a resonant cavity with a fatigue loading frame. Preliminary experimental assessment of this test method is supportive of its potential in damage tracking. Water-contaminated 12-ply bismaleimide (BMI) / quartz laminate specimens were tested in impact and flexural fatigue, while a 4-ply glass/epoxy laminate was tested in tensile fatigue while changes in relative permittivity were recorded. The results show a distinct rise in relative permittivity consistent with the expected magnitude and progression of damage in all cases.

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INTRODUCTION

Polymers and their composites are increasingly used in aerospace, automobile, industrial, and marine applications, where environmental factors play a large role in material performance and longevity. Water contamination is among the leading contributors to polymer composite degradation due to the ubiquitous nature of water and the tendency of polymers to absorb measurable moisture even in hot, dry environments [1]. The deleterious effects of water contamination rarely act independently; instead acting in concert with mechanical loading and other environmental factors to degrade material properties over the life span of a polymer composite structure. As polymer composites become more prevalent as an economically viable replacement for metals, predicting the onset and progression of this degradation is increasingly important. Accurate characterization of damage and its progression is a prerequisite to both the development of damage prediction methods and their validation. Achieving both accuracy and applicability to in-service composites will require that environmental and mechanical loading are considered independently and in tandem to capture complex and important synergistic effects.

Several damage characterization methods for polymer composites have been developed based on different theories; Jolly and colleagues [2] highlighted seven of these methods. These include visual inspection, ultrasonic testing, thermography testing, radiographic testing, electromagnetic testing, acoustic emission, acousto-ultrasonic testing and shearography testing. Other, more complex methods have also been introduced, such as a fiber-optic laser-ultrasound scanner [3]. These have proven moderately successful in characterizing damage in polymer composites, each with its own limitations, but generally they lack the ability to capture combined environmental-mechanical effects, characterize damage below the micro-scale, or capture the chemical changes that act as precursors to physical damage during the early stages of damage initiation and progression.

The dielectric resonant cavity method presented here has only recently been developed, but has shown significant potential in this area. This method relies on high-accuracy measurement of the complex relative permittivity of a polymer composite. There are a number of resonant cavity methods, including the split cylinder method, ASTM D2520 cavity perturbation method, and split post dielectric resonator (SPDR) method. These methods are generally used to determine single-frequency complex relative permittivity of pristine dielectrics for use in the electronics industry. To the best of our knowledge, single-frequency resonant cavity methods have not previously been used to track damage evolution in polymer composites. Of the resonant cavity methods, the split post version is chosen in this study due to its high accuracy [4] and ability to detect subtle changes in relative permittivity. The SPDR method utilizes low loss dielectric materials in its construction which enables the device to resonate at a specific frequency with a very high quality factor (Q-factor). On insertion of the material under test into the device, the resonant frequency undergoes a measurable shift. This shift is measured using a vector network analyzer (VNA) and is then used to determine the relative permittivity of the sample. Fig. 1 and 2 show a cross-section of the SPDR schematic and the as-fabricated SPDR, respectively.

In moisture-contaminated polymer composites, the effective relative permittivity of the material is a function of the dielectric properties of both the dry, pristine composite and the absorbed moisture [5]. The contribution of absorbed moisture to the effective relative permittivity of these materials is affected by both the amount of moisture absorbed and the nature of its chemical and physical interaction with the polymer network. The degree of restriction imposed by these interactions impedes the ability of the molecular water dipole to rotate and polarize with an applied electromagnetic field. This ability to rotate in an applied electromagnetic field directly contributes to the effective relative permittivity. The more firmly bound water molecules rotate less than the loosely bound molecules, while free molecules in voids rotate unimpeded in an electromagnetic field. The latter of these two water states has a much higher relative permittivity than bound water, similar to the permittivity of ice (~3) versus bulk liquid water (~80) [6]. Chemically, moisture interacts with the polymer network in various ways; from firmly-bound direct hydrogen bonding to multi-layer bonds to less restrictive interactions resulting from van der Waals forces (see Fig. 3). Unrestricted bulk water also exists as free unbound water in micro-voids within the polymer network. Physical interaction of water molecules with the polymer network, such as at interfaces where water molecules are physically constrained by the polymer network while bounded to other water molecules, also imposes some degree of restriction to dipolar rotation in an electromagnetic field.

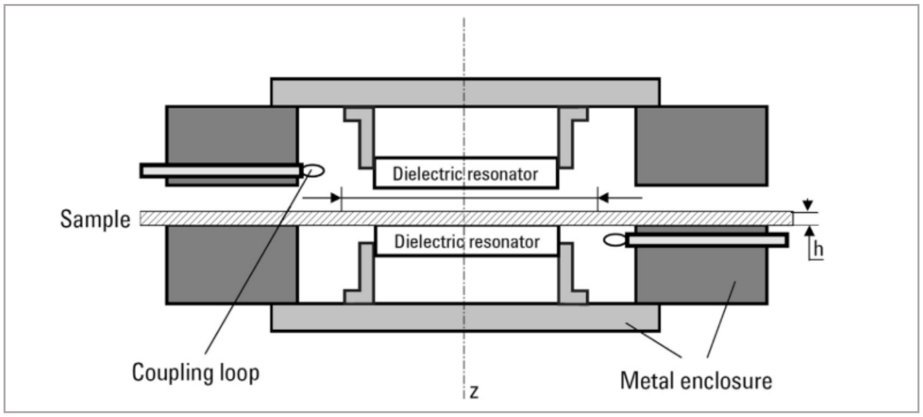

Figure 1. Cross-section of split post dielectric resonator.

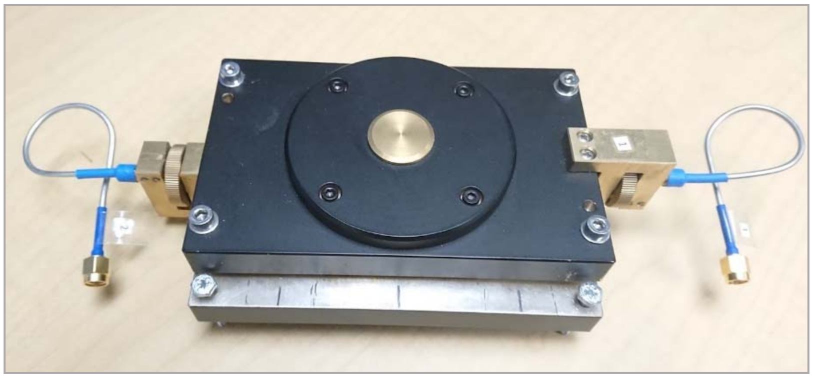

Figure 2. Image of a split post dielectric resonator.

The operating hypothesis of this study is that damage evolution in a polymer is accompanied by a shift in the relative distribution of water states arising from chemical and physical changes to the host polymer and, further, that this shift can be tracked by accurately measuring subtle changes in relative permittivity throughout damage accumulation. The intent of this work is to present results to date in support of this hypothesis. This includes relative permittivity changes resulting from flexural fatigue of a water-contaminated laminate, as well as significant progress in the in situ measurement of damage accumulation through relative permittivity monitoring in tensile fatigue of the same.

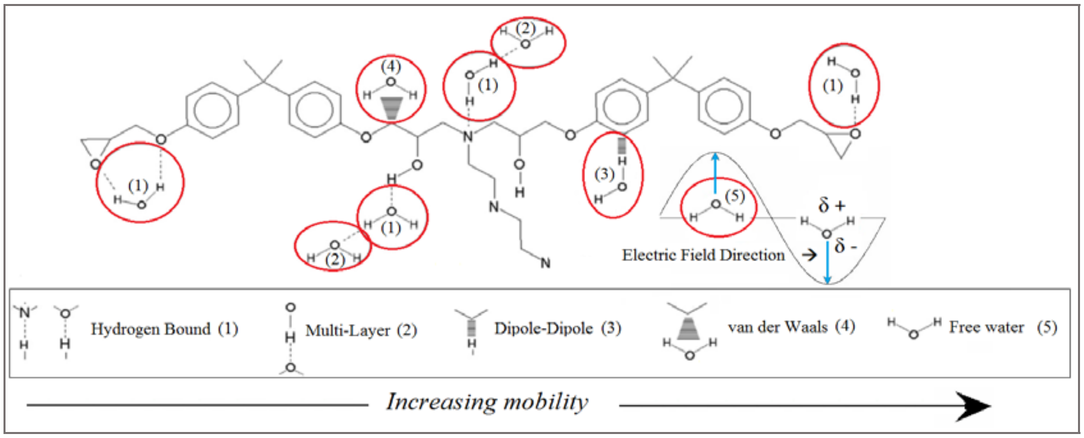

Figure 3. Levels of restriction of water molecules [7].

1. MATERIALS AND METHODS

Sample Material

A 12-ply bismaleimide (BMI) / quartz fiber laminate representative of an in-service aerospace composite was tested. The laminate is a bismaleimide resin, trade name HexPly® F650, reinforced with an eight-harness satin weave quartz fabric. A 12-ply test panel was fabricated with dimensions of 36 inches square. The test panel was cured in an autoclave at 190°C (375°F) and 85 psi for four hours, followed by an eight-hour post-cure at 232°C (450°F) according to the manufacturer's recommendations. Individual 75 x 50 mm test specimens were cut from the larger panel using a wet diamond saw. The laminate properties were obtained by means of resin burn-off in a high-temperature furnace maintained at 800°C until elimination of all bismaleimide residue. Pre- and post-burn weight measurements allowed the accurate determination of resin, void, and fiber content. In order to ensure accuracy, 15 samples from various locations within the 36-inch square panel were used. Each sample weighed approximately 5 grams prior to burn off. The average laminate properties were; fiber volume fraction 59.41% (0.149 standard deviation), resin volume fraction 40.27% (0.144 standard deviation), voids 0.323% (0.045 standard deviation).

Moisture Contamination

Using a vacuum oven, specimens were heated to and maintained at 50˚C until considered dry according to ASTM D5229. These where weighed using an analytical balance before immersion, and weighed periodically after immersion to monitor weight gain due to water absorption. Using a water bath set at a fixed temperature of 25˚C, BMI test specimens were immersed in distilled water for a period of 3 months.

Experimental Setup

To accurately measure dielectric properties at GHz frequencies, the split post dielectric resonator (SPDR) is coupled with a vector network analyzer (VNA). A 2.45 GHz SPDR is connected to a 2-port VNA via high precision coaxial cables. The final connection to the SPDR is via a pair of semi-rigid coaxial cables to minimize effects of external physical disturbances on the signal (see Fig. 4). The S-parameters (S11, S22, and S21) of the SPDR are adjusted manually by locating the coupling loops within the resonant cavity until S11 and S22 are equal and S21 is -40db (see Fig. 5). For -3bd bandwidth calculation, values for resonant frequency and quality factor of the empty resonator are recorded. The material specimen to be tested is then inserted centrally into the SPDR. The presence of the sample shifts the resonant frequency and reduces the quality factor. This shift in resonant frequency and Q-factor are used along with specimen thickness to calculate the relative permittivity according to Eq. 1 [8].

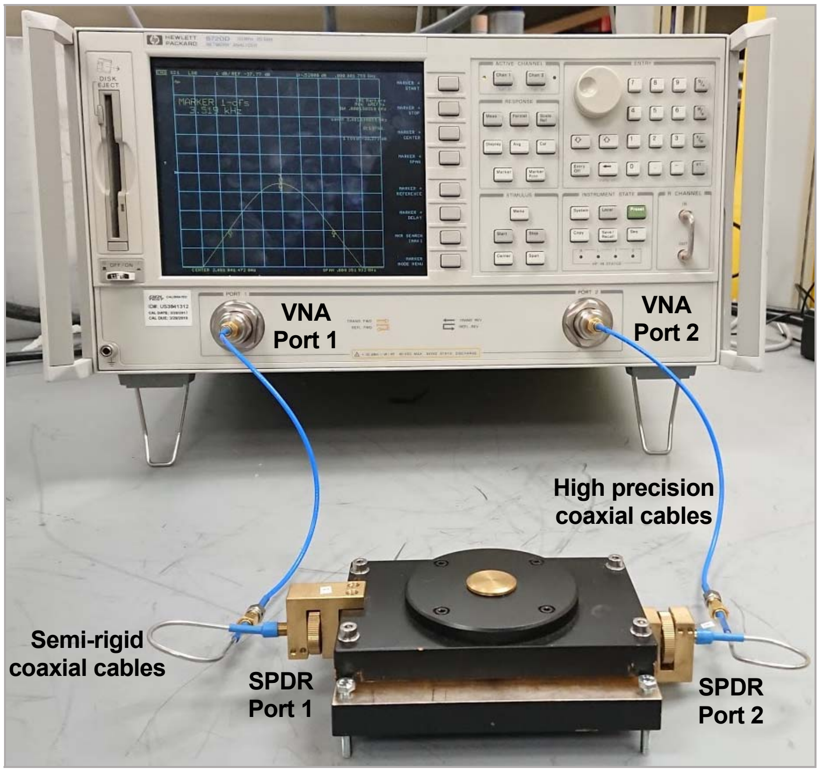

Figure 4. SPDR connection to Vector Network Analyzer.

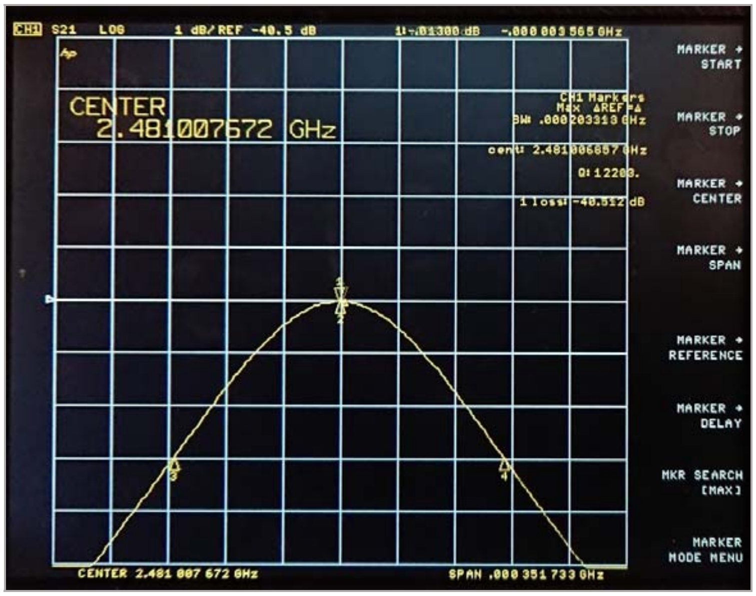

Figure 5. S-21 Measurement on Vector Network Analyzer.

$$\varepsilon'_r = \frac{1 + f_0 - f_s}{h\, f_0\, K_\varepsilon(\varepsilon'_r, h)} \tag{1}$$

Where h is the sample thickness, f_0 is the resonant frequency of the empty SPDR, f_s is the resonant frequency of the SPDR containing a specimen, K_s is a function of the specimen's dielectric constant and thickness. The function K_s is computed and tabulated for each SPDR after fabrication.

Damage Methods

Impact: Specimens were impacted at 3, 6, 9 and 12 J to simulate non-visible (internal) hail damage and then immersed in water for a period of 15 days while weight and relative permittivity were measured intermittently. Twelve samples were originally impacted using a drop tower, with three samples impacted at each energy level. The height from which the impactor was dropped was varied to create each energy level. The impactor used on the drop tower had a hemispherical striker tip.

Flexural Fatigue: Flexural fatigue was performed using a 10kN static/5kN dynamic load cell installed on an Instron 8502 servo-hydraulic load frame. Load was applied on the specimens in the form of a sinusoidal wave with a frequency of 1 Hz. To simulate the effect of 30% and 40% ultimate load applied, a sinusoidal load with average peaks of 670N and troughs of 350N, and 920N and 440N, respectively, was applied on the specimen in a typical 3-point bend setup in accordance with ASTM D7774.

2. RESULTS AND DISCUSSIONS

The primary challenge of this method of using water as a type of "imaging agent" to track damage via relative permittivity changes is separating the effects of water loss and water state changes; both can produce relative permittivity changes, but only the latter is meaningful in the context of damage. These trends are, to date, in the opposite direction; water loss drives a decrease in permittivity while damage accumulation drives an increase due to a shift toward a higher percentage of "free" water occupying new free volume. Compensating for water loss is straightforward in cases where the test can be stopped and the sample weighed for accurate gravimetric determination of water loss. In these cases, a known relationship between relative permittivity and water content, which is linear for all cases investigated thus far, can be employed to remove the effect of water loss. In previous investigations using 12-ply BMI specimens, permittivity is shown to reduce by 0.212 per percent water lost. Two investigations of this type were performed; in the first, the effect of varying levels of impact damage on the relative permittivity of water-contaminated 12-ply BMI laminates was studied, and in the second, the effect of flexural fatigue was measured.

We have recently reported on the effect of impact damage in detail in Ref. [9]. In this study, relative permittivity of 12-ply BMI/quartz laminate was measured before and after damage from both impact and moisture contamination. In the most significant case, a 12 J impact and a 0.79 % increase in water content by weight resulted in a 10.3 % increase in relative permittivity compared to the dry, impacted state and a 6.1 % increase compared to the unimpacted samples at the same water concentration.

One of the most important results from this study is the direct correlation between impact energy and relative permittivity, even at equivalent water content. This is illustrated in Fig. 6. For example, at 0.77% water content, the 9 J impact caused a 9.6 % increase in permittivity while unimpacted samples showed only a 5.2 % increase at the same moisture content. This trend is consistent throughout all iterations of this study; increased damage due to higher energy impact resulted in higher relative permittivity even at equivalent absorbed water content. Put simply, this strongly suggests that relative permittivity is heavily influenced by internal damage, independent of water content.

The effect of flexural fatigue on the same 12-ply BMI/quartz laminates was also investigated, at 30 and 40% ultimate load. A plot of results obtained show a continuous increase in relative permittivity with increasing load cycles as well as magnitude of imposed load (see Fig. 7). Experimental results show an increase of 0.67% in relative permittivity over a range of 30,000 load cycles, when 30% of ultimate load is applied to the specimen. When 40% of ultimate load is applied, an increase of 0.85% is observed in relative permittivity over the same range of load cycles.

The gradual accumulation of physical damage within the polymer matrix due to fatigue is a well-reported phenomenon [10]. Further, the application of higher ultimate loads are expected to drive more rapid and significant damage accumulation [10]. The results reported here are consistent with this behavior, and with the expected behavior of molecular water in response to the increasing internal free volume in the form of cracks and voids of multiple length scales. The dielectric response of the specimens undergoing flexural fatigue suggests that some water molecules previously existing in

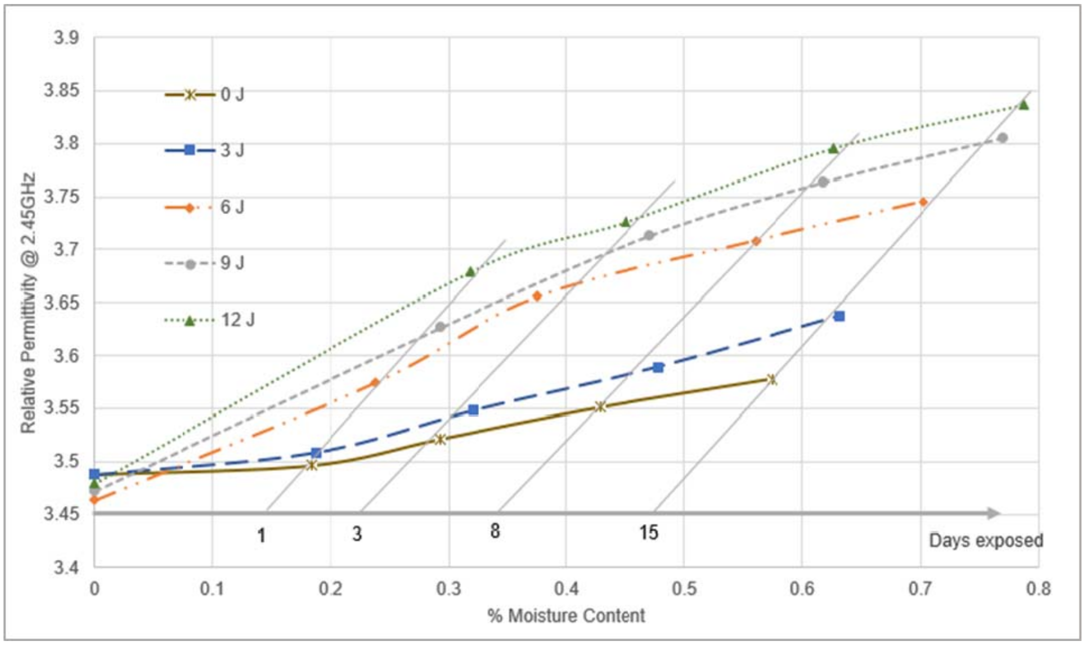

Figure 6. Effect of impact damage and moisture exposure on relative permittivity.

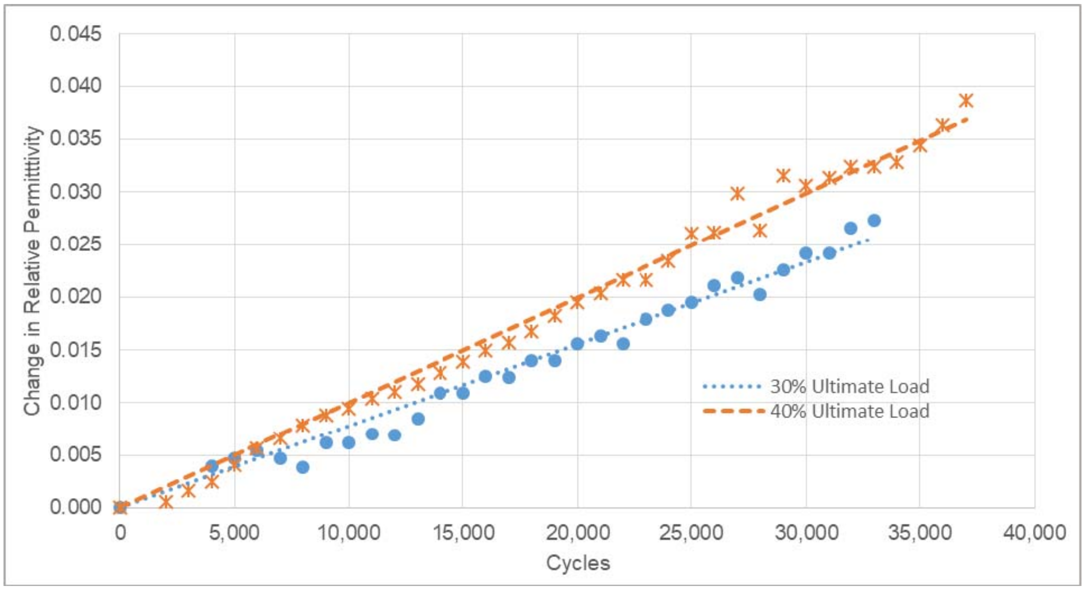

Figure 7. Plot of change in relative permittivity against no of flexural fatigue load cycles.

various bound states within the polymer network preferentially migrate to form clusters of bulk water in new free space. Essentially, this results in a redistribution of bound and free water molecules, and the ratio of bound to free molecules, within the polymer matrix. Bulk water in the new free volume exists in the free state and rotates unimpeded with an electromagnetic field, hence resulting in a higher relative permittivity as well as higher contribution to the bulk relative permittivity of the composite.

Definitive confirmation of the hypothesis – that damage results in a shift in free/bound water states that are measurable via the SPDR method – will require further and more exhaustive investigation. However, the theoretical support derived from the literature and all results to date are indicative of its validity. There is little doubt that absorbed molecular water will react to early-stage chemical and physical changes within the polymer network. Monitoring this reaction has the potential to provide valuable insight into the mechanisms governing these early changes associated with initiation and progression of damage. Questions regarding sensitivity of the method, and at what stage of damage we can reliably discern any changes, are among several important questions that remain to be answered. Despite these challenges, the test method holds substantial promise; particularly if we can adapt the method to in situ monitoring of water state redistribution and the associated damage accumulation.

3. PROGRESS TOWARD *IN SITU* TESTING

Continuous monitoring of relative permittivity during tensile quasi-static and fatigue loading has been achieved by integrating the resonant cavity with a load frame as in Fig. 8. The specimen is secured and loaded in tension according to standard protocols but passes through the resonant cavity between the specimen grips, without contacting the SPDR. By employing the instrument control function of Matlab software and built-in remote control capabilities of the VNA, a Matlab script running on a Windows PC and containing instructions that duplicate the manual operation of the VNA was developed. Automating the process enabled triggering the SPDR and recording dielectric data at much faster rates, producing results with much higher resolution.

Derivation of dielectric properties relies not on the magnitude but on the *shift* in resonant frequency and Q-factor with and without the sample present in the cavity. In the impact and flexural fatigue investigations, these values for the empty resonator were obtained each time before inserting the test specimen, which eliminates the effects of changes in the dielectric properties of air within the resonant cavity as a result of varying environmental conditions such as temperature and humidity (see Fig. 9). This poses a challenge for an in situ method, as environmental conditions may change considerably with time and location, without the ability to remove the specimen and reset the empty resonator values prior to each measurement. To mitigate this problem, relationships between temperature and humidity and resonant frequency and Q-factor (without a sample inserted) were developed based on experimental data collected for the specific SPDR and incorporated into the automated data collection.

Data in Fig. 9 show that over a temperature rise of 1˚C within the testing temperature range, the resonant frequency of the 10Ghz SPDR decreases by an average of approximately 0.37 MHz in the high humidity (≥ 95%) or “humid” case and 0.72 MHz in the low humidity (≤12%) or “dry” case. While with temperature fixed, an increase in relative humidity by approximately 80% (from dry to humid) results in an average increase in resonant frequency of approx. 10.6 MHz. These have a significant influence on accuracy of the measured relative permittivity and highlight the necessity of compensating for humidity and temperature in cases where relative permittivity is measured continuously without specimen removal.

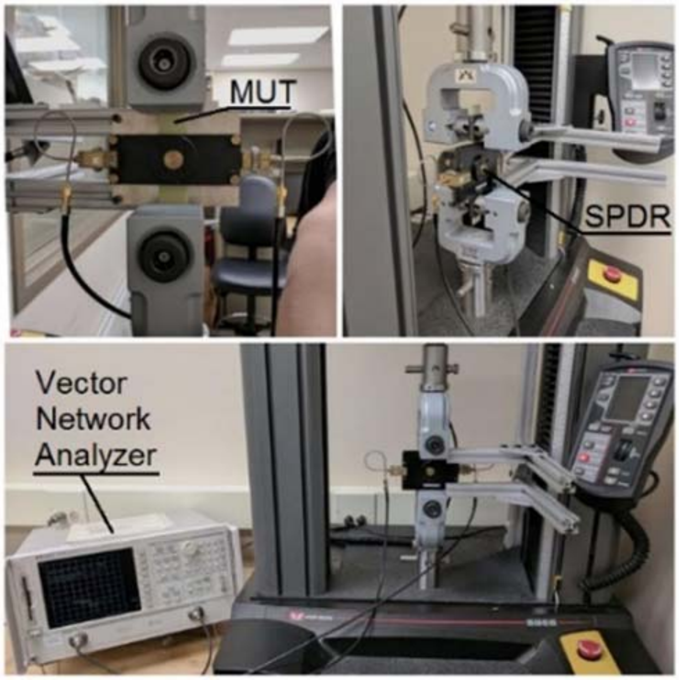

Figure 8. Setup for in-situ monitoring.

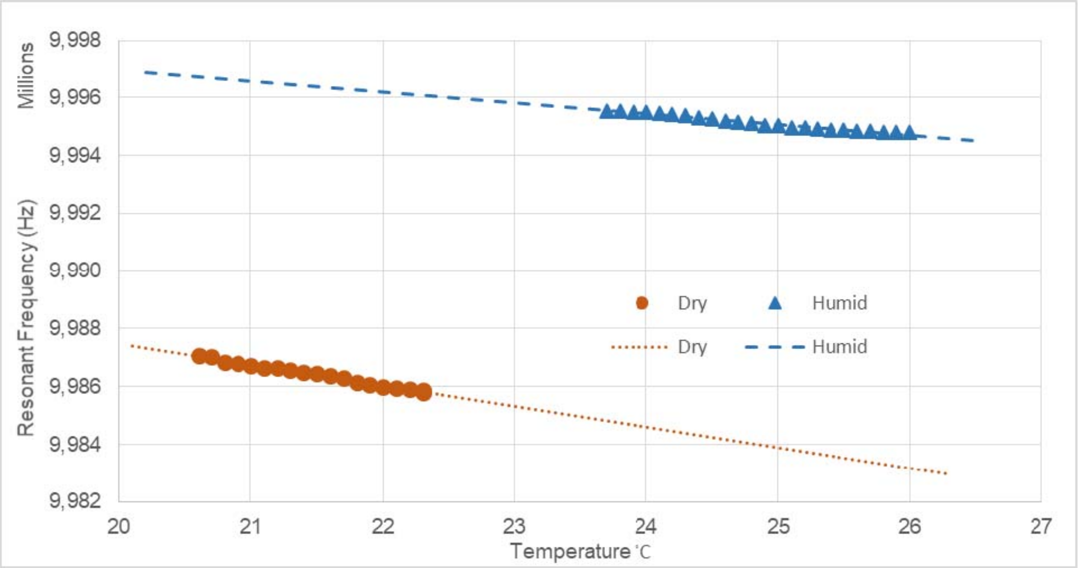

Figure 9. Variation of resonant frequency with temperature and humidity for an empty SPDR.

Initial investigations of the feasibility of in situ monitoring have focused on tensile fatigue of a moisture-contaminated, 4-ply, Style 4180 glass fiber/epoxy laminate equivalent to an in service military aircraft component. As-cured panels were cut into test specimens of size 50 x 185 mm. Specimens were loaded under tension in the servo-hydraulic load frame while passing through the integrated 10 GHz resonant cavity. Specimens were tested in their dry and moisture contaminated (0.8% water by weight) states while dielectric properties were continuously recorded. As expected, the fully dry specimen showed nearly constant relative permittivity over 100,000 load cycles when tested in a low humidity chamber. The moisture contaminated specimen, however, showed a modest increase in relative permittivity in an uncontrolled chamber despite water desorption throughout the test. In other words, the effect of bound water shifting toward free water was more significant than water loss. After compensating for permittivity changes due to water loss during testing, the increase in permittivity over 100,000 cycles becomes much more significant.

Fig. 10 compares changes in relative permittivity between two similar specimens, one dry and one wet, which are loaded in equivalent tensile fatigue conditions for 100,000 cycles. The relative permittivity of the dry sample remained approximately constant throughout the test, while relative permittivity of the wet specimen increased continuously with load cycles as predicted.

The test setup generates a sinusoidal pattern between the start of test and approximately 60,000 cycles due to variations in the programmed sinusoidal loading frequency of the servo-hydraulic load frame. This then causes the SPDR to be triggered when the specimen is at slightly different states of strain in the sinusoidal load cycle, detecting slightly lower permittivity at lower strains and slightly higher permittivity at higher strains, consistent with investigations on the effect of strain on relative permittivity in quasi-static conditions. During this period, trigger time of the SPDR remains constant at 10 seconds, hence the effect is clearly visible in data collected. Beyond 60,000 cycles, the trigger time begins to drift (See Fig 11); this immediately degrades the uniform pattern, thereby making the data points more random, i.e. relative permittivity is captured at random strain states.

As a result of sinusoidal variations in permittivity described above, a moving average trend line with window size of 1000 seconds was plotted for the two cases. This clearly shows the constant permittivity of the dry specimen and continuously increasing relative permittivity of the wet specimen. (See Fig. 10).

Results to date are promising, though significant effort remains to validate and improve this potential method of in situ damage progression monitoring. Of particular concern, as mentioned, is distinguishing between water loss and water state redistribution given the inability to monitor water loss gravimetrically while undergoing fatigue loading. Previous studies have shown a linear trend in both absorption versus relative permittivity and desorption versus relative permittivity curves. As such, sample weight before and after fatigue loading may provide a useful approximation. However, a complication exists in the eventual total failure of the specimen, potentially resulting in material loss that would confound any attempt to approximate water loss during the test gravimetrically. Efforts are underway to eliminate or control this and other potentially confounding variables.

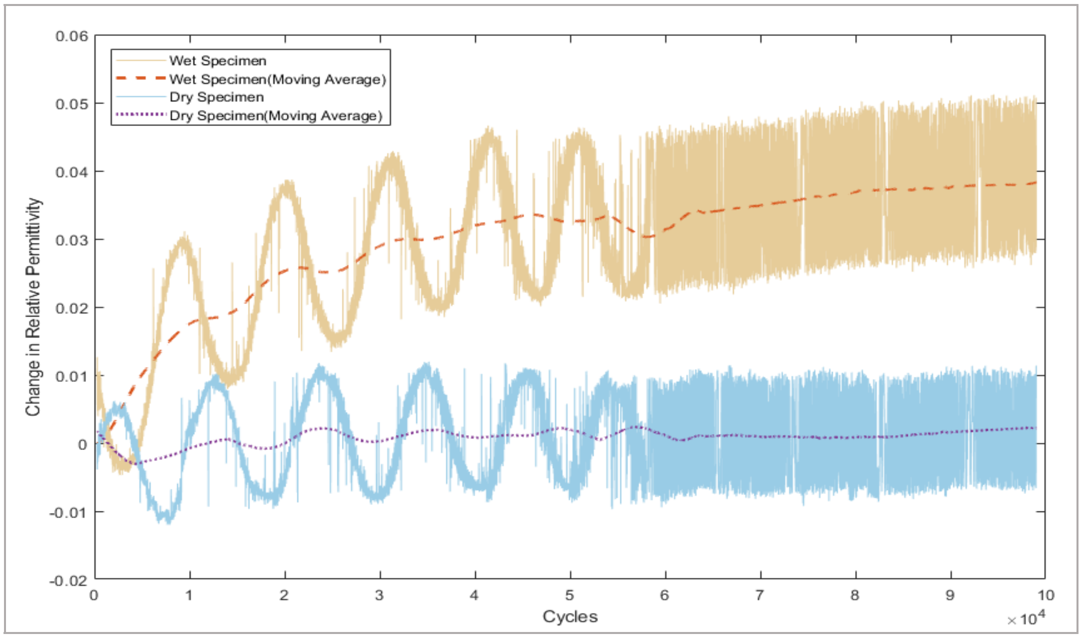

Figure 10. Plot showing change in relative permittivity with fatigue load cycles for dry and wet specimens.

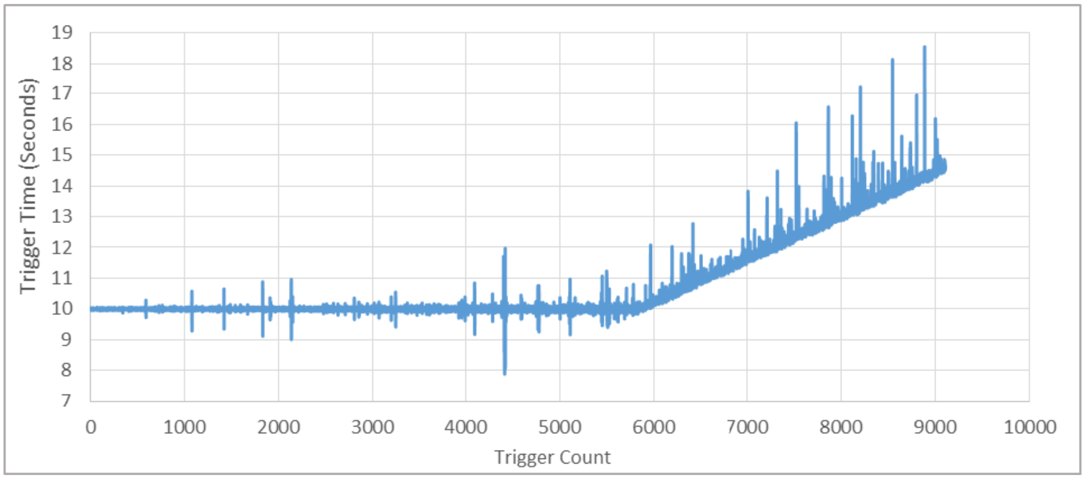

Figure 11. Variation of SPDR trigger time with trigger count during fatigue testing.

4. CONCLUSION

The study has shown that monitoring the bulk relative permittivity of a water-contaminated polymer composite material using the high accuracy split post dielectric resonant cavity method can be used to detect changes in the states of water within a polymer network as damage accumulates. These changes can be used as a means of damage progression monitoring in moisture contaminated composites. Damage due to impact and fatigue, representative of typical in-service damage, were evaluated using the method. Results indicate significant increases in the relative permittivity of damaged moisture-contaminated specimens compared to those without damage and also indicates sensitivity to the magnitude of accumulated damage. The method was further extended to continuous monitoring by presenting preliminary results which showed potential in the method to be a viable means for in situ tracking of damage progression.

5. ACKNOWLEDGMENTS

This material is based upon work partially supported by the National Science Foundation under Grant No. CMMI-175482.

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