Damage Detection in Polymer Matrix Composites by Analysis of Polymer-Water Interactions Using Near-Infrared Spectroscopy

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ABSTRACT:

Detection of early stage damage in polymer matrix composites (PMCs) is a challenge for current non-destructive examination (NDE) methods. New techniques based on sub-micron scale effects may enable identification and characterization of early, non-visible damage. Moisture, ubiquitous in most service environments and readily absorbed by PMCs, may present an opportunity for identifying and characterizing such damage. Water molecules absorbed naturally within PMCs exist either as 'bound water' (interacting with the polymer matrix via secondary bonding mechanisms), or as free water (having negligible external bonding interactions). Early-stage physical damage within a PMC takes the form of nano to micron scale free volume within the polymer matrix. This new free volume represents an opportunity for water to occupy and form clusters within the host polymer without directly interacting with the polymer matrix chemically or physically. Therefore, relative to a pristine region, a damaged region would contain a much higher concentration of free water. This altered spatial distribution of free water creates an opportunity for damage identification and characterization. This study explores this possibility by investigating the moisture state in undamaged and 3-joule impact-damaged 16-ply epoxy/glass fiber composite laminates. The specimens are exposed to moisture via immersion in deionized water to simulate long-term moisture exposure in a humid environment. The state of absorbed water is characterized quantitatively via near-infrared spectroscopy. Results show a significantly higher ratio of free-to-bound water in the 3-Joule damaged specimen when compared to the undamaged specimen at the same moisture content. This indicates the existence of free water within voids associated with matrix micro-cracks and delaminations created due to impact. Results from this study suggests that analysis of the nature of polymer-water interaction could be leveraged in developing a technique for damage detection even at very low damage levels in PMCs.

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INTRODUCTION

In polymer matrix composites, early stages of damage involve matrix cracking at and below the micron scale [1–3]. These cracks often develop into macroscale defects over time and may lead to sudden structural failure. Thus, the ability to detect damage at these early stages could prevent damage growth to the threshold of sudden in-service structural failure. Further, a better understanding of damage initiation and progression at the sub-micron scale may improve prediction of remaining useful life in critical load bearing structures [4]. The performance of several non-destructive examination methods have been reviewed in a number of previous studies [5–9]. While some success has been demonstrated over the years at the macroscale, damage detection at sub-micron scales remains a challenge [1,5]. In some cases, moisture which is absorbed naturally by in-service polymers may provide a way to address this challenge.

Studies have shown that water absorbed in polymer matrix composites may exist in one of two states: Free—without any polymer-moisture interaction, or Bound—having secondary bonding interactions with the polymer matrix [10–13]. These secondary bonding interactions may vary in strength and include highly restrictive hydrogen bonding between water molecules and polar functional groups within the polymer network, dipole-dipole attractions, and weak van der Waals attractions [14]. The fact that water exists in the free or bound states in a polymer network is well-known and widely recognized in a number of industries where moisture absorption tends to be problematic, e.g. food [15,16], pharmaceuticals [17], building & construction [18–20], cosmetics [21–23], aerospace radome [24,25], and biomedical industries [26,27].

A review of published literature shows that free and bound water has been characterized via several spectroscopic techniques and analysis methods. These techniques include gravimetric moisture uptake [28,29], nuclear magnetic resonance [19,23], infrared spectroscopy [11,30], dielectric spectroscopy [31], differential scanning calorimetry [26], and molecular dynamics simulations [32–34]. In previous studies, infrared spectroscopy has been applied in monitoring the effect of moisture uptake on an epoxy system. These studies primarily investigated the effect of moisture contamination on mechanical properties and glass transition temperature (T_g), concluding that bound water is responsible for degradation of mechanical properties and plasticization in epoxies—leading to reduction in T_g [11,30,35]. The effect of moisture on the distribution of free and bound water has also been studied using infrared spectroscopy, providing evidence of free water occupying micro-porosities and bound water interacting with the polymer matrix [11–13]. In studies by Musto et. al, methods were developed to perform quantitative analysis between the 6000 and 8000cm^{-1} region of the infrared spectra—within which O-H activity is prominent. These were applied successfully in estimating the relative concentration of free and bound water absorbed into an epoxy specimen [11].

Infrared spectroscopy is a well-developed and widely used technique that provides the ability to qualitatively and quantitatively characterize water in both of its possible states. Infrared spectroscopy involves the use of light between 780 and 50000nm (12800 – 200cm^{-1}) in the electromagnetic spectrum [36]. At specific frequencies within this range, inter-atomic bond vibrations absorb energy from incident light at their resonant frequencies. In spectroscopic applications, the infrared spectra is divided into ‘near’ and ‘mid’ (NIR and MIR) frequency/wavelength ranges. A number of bond pairs and functional groups have their fundamental vibrational frequencies in the mid-infrared (MIR) region ($<4000\text{cm}^{-1}$). Peaks at frequencies in the near-infrared region ($>4000\ \text{cm}^{-1}$) are usually overtones and combinations of fundamental frequencies in the mid-infrared range [11,37]. Although the existence of many overtones and combination bands of fundamental vibrations make identifying peaks more complicated, great progress has been made in understanding the NIR region and its application in qualitative and quantitative analysis. Further general details on infrared spectral analysis is outside the scope of this work but have been covered in a number of texts [38–40].

In the mid-infrared region, the influence of vibrations of O-H bonds resulting from symmetrical stretching, asymmetrical stretching, and bending, cover a wide band between 3800 and 2800cm^{-1} [11,41]. The wide frequency range results from the influence of secondary bonding interactions—primarily hydrogen bonding in water-water and water-polymer pairs. These interactions cause a downward shift in resonance frequency of the water molecule’s O-H bonds [11,41]. The magnitude of this shift is proportional to the strength of interaction, governed by the degree of electronegativity difference between atoms making up the polar functional groups involved in the hydrogen bond [41]. These groups could be polar functional groups within the polymer network which have significant hydrogen bonding effects, or other water molecules with less severe effects. In the near-infrared region between 8000 and 6000cm^{-1} peaks can be identified which are overtones or combinations of fundamental O-H vibrations in the mid-infrared region. However, in this region the peaks are more distinctly separated and easier to analyze, making NIR the preferred region for analysis of water state [11].

Physical damage in composite laminates typically involves matrix cracks and delaminations that create relatively large voids within the polymer matrix ranging from sub-micron scale to macroscale sizes [1]. Water molecules may reside within these voids, effectively isolated from the polymer network and therefore existing in the free state. This results in a locally higher ratio of free to bound water in the laminate at the damage site.

In prior work we have shown how changes in microwave frequency dielectric properties could be used to characterize the effect of damage on polymer-water interactions [42,43]. In this study, we further validate and explore these concepts by applying NIR spectroscopy. Established NIR spectral analysis techniques are applied in determining the effect of low levels of damage within a polymer composite laminate on the nature of moisture interaction with the polymer network. This is achieved by comparing changes in the free-to-bound water ratio in an undamaged laminate to similar changes in a laminate with barely-visible impact damage. The associated potential for applications in non-destructive examination is discussed.

MATERIALS AND METHODS

Materials

The test material used in experiments was a typical aerospace glass fiber/epoxy composite consisting of Hexcel F-161 resin with style 7781 8-harness satin weave reinforcement. The laminate was formed from 16 plies of 12 x 14 in. pre-preg and cured at a constant pressure of 56 psi (386 kPa) in a hot press while heating from room temperature at a rate of 10°C/min to 180°C. It was then held at 180°C for 120 minutes before pressure release. The formed laminate was allowed to cool to room temperature at a rate of 2°C/min. Circular pieces of 2.9 mm average thickness and 54 mm diameter were cut from the larger piece to form test specimens using a diamond-tipped hole saw. A resin burn-off in accordance with ASTM standards was performed to obtain laminate properties [44]. These properties are presented in Table I.

TABLE I. AVERAGE EPOXY/GLASS FIBER LAMINATE PROPERTIES

Property	Mean (%)	Standard Deviation (%)
Fiber volume fraction	62.3	1.5
Resin volume fraction	32.3	1.1
Voids	5.4	0.7

Sample Preparation and Moisture Contamination

The cut specimens were first dried in a vacuum oven at 65°C until a stable weight was achieved in accordance with ASTM standards [45]. After confirmation of their dry state, 4 of 8 specimen were left undamaged while barely-visible impact damage was induced in the remaining 4 specimens; this was to simulate the impact of low-velocity hail on an aircraft during flight. Using a drop tower equipped with a hemispherical impactor tip of radius 9.4mm, the impactor height was set to ensure 3 Joules of energy was applied to the specimens.

Dry specimen weights and NIR absorbance data were recorded before and after impact. Undamaged and damaged specimens were immersed in deionized water and maintained at 25°C using a temperature-controlled water bath. Moisture uptake was measured using a Mettler Toledo ML54 high-precision analytical balance. Specimens were immersed for a 6-month period while intermittently measuring moisture uptake and NIR absorbance. For each measurement, specimens were carefully dried using a lint-free cloth and exposed to ambient conditions for 20 minutes to ensure all surface moisture had been eliminated.

NIR Spectroscopy

The infrared spectrometer used was a FOSS 6500 NIR unit equipped with a spinning sample cup module, operating in reflectance mode, and capturing diffuse reflectance. The device scans over a range of 400 to 2500nm (25000 to 4000 cm^{-1}) with a resolution of 2nm. The device samples 32 random points within the aperture limits, which was estimated to be an area of approximately 20mm diameter. For each measurement, three consecutive scans were taken and an average absorbance was recorded for the specimen.

The obtained spectral response after subtraction of the spectral contributions of the dry composite was deconvoluted into component peaks by adopting a 3-peak model. Each peak was represented using a Gaussian-Lorentzian function given in Equation 1 [11].

$$f(v) = (1 - L)\, H \exp[-\left(\frac{v - v_o}{w}\right)^2 (4\, In\, 2)] + L \frac{H}{4\, (\frac{v - v_o}{w})^2 \; + \; 1} \tag{1}$$

where

v	is wavenumber (independent variable)
v_o	is peak mean location
H	is peak height
w	is full width at half height (FWHH)
L	is fraction of Lorentzian character

The 3-peak model spectra was fitted to the measured spectra by minimizing the sum of squared errors between the measured and model absorbance values. This was achieved by applying a minimization algorithm in which constraints could be applied on the parameters. A MATLAB® optimization function ‘fmincon’ was applied to determine the optimal combination of values for $v_o, H, w\ and\ L$ that gave the best fit to the measured spectra.

Areas under each peak were then calculated and used in computing the relative concentration of each water state by applying Equation 2. In previous literature [11], the three peaks at approximately 7100cm^{-1}, 6850cm^{-1}, and 6600cm^{-1} were representative of non-associated water molecules (S_0), self-associated water molecules (S_1) i.e. water-water hydrogen bonds, and the polymer-bounded water molecules (S_2) respectively.

$$\frac{C_x}{C_{total}} = \frac{A_x}{(A_0 + A_1) + \frac{a_x}{a_2} A_2} \tag{2}$$

where

x	No. of hydrogen atoms participating in hydrogen bonding (0, 1 or 2)
A_x	Peak area for S_x species
C_x	Concentration of S_x species
C_{total}	Concentration of all species
a_x	Integrated absorption coefficients for x species

For $x = 0$ and 1, Equation 2 can be applied as-is, while a similar expression can be obtained for $x = 2$.

RESULTS AND DISCUSSION

Gravimetric moisture uptake behavior for the undamaged and damaged specimens is compared in Figure 1 by plotting moisture uptake against the square root of immersion time. The plot shows a linear relationship for the undamaged specimens which is consistent with typical moisture uptake behavior for polymer matrix composite laminates [46,47]. The damaged specimens show non-linear

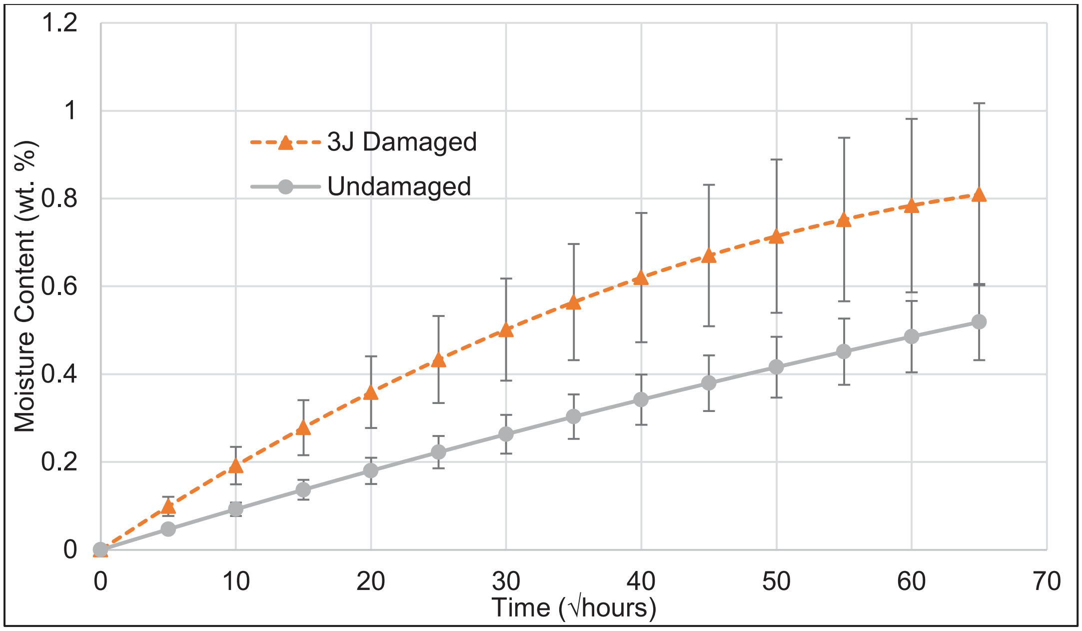

Figure 1. Moisture uptake vs square root of time.

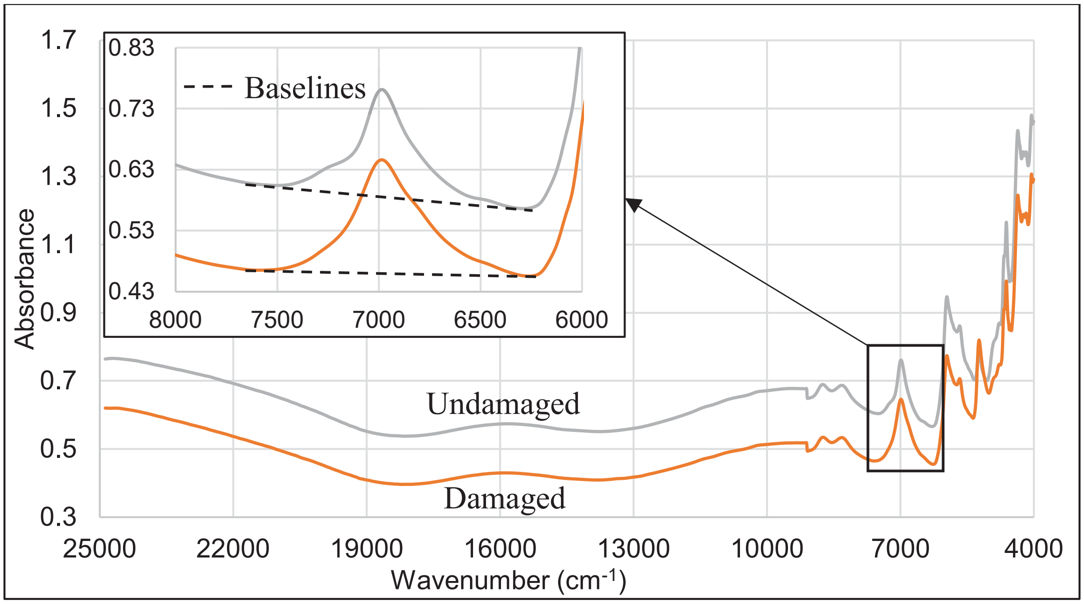

Figure 2. Full NIR spectra obtained for an undamaged and 3-Joule damaged specimen both at 0.19% moisture content.

behavior suggesting an initial higher rate of diffusion which reduces with time. This initially higher rate is likely driven by diffusion of water molecules into the matrix cracks and delaminations resulting from impact damage. The absorbed water molecules residing within these new voids would primarily exist in the free state. Error bars shown represent ± standard deviation when 2nd order lines of best fit for the 4 specimens are considered at the specified data point. The use of lines of best fit for each specimen rather than actual data points was necessary due to the fact that similar specimens absorbed moisture at slightly different rates.

A plot of the entire unprocessed NIR absorbance spectra acquired for a damaged and undamaged specimen is presented in Figure 2. The insert shows the range of interest containing information on the distribution of the different water states. The baselines shown are derived for each specimen using an objective baseline subtraction algorithm [48]. After subtracting these baselines from the absorbance spectra for different moisture contents, the curves in Figure 3 are obtained. The shape of the spectral curves indicate consistency with the 3-peak model, which is a combination of sharp peaks at approximately 7100 & 6850 cm^{-1} and a broad peak at 6600cm^{-1} [11]. The model is fitted to the measured spectra by the deconvolution process described in the Materials and Methods section. The resulting fitted model and component peaks are shown in Figure 4 (a) and (b). These represent the deconvoluted spectra for an undamaged and a damaged specimen respectively, containing the same amount of moisture (0.19%). Applying Equation 2, relative concentrations of each species of water molecule are calculated. Concentrations for S_0 and S_1 species represent the unassociated water (gas phase) and the water-water hydrogen bonded species (liquid phase); these are combined to obtain the total relative concentration of free water [11]. While for bound water the S_2 species involved in polymer-water hydrogen bonding is used [11]. Figure 5 (a) and (b) shows how both of these relative concentrations typically change with increasing moisture for an undamaged and damaged specimen respectively.

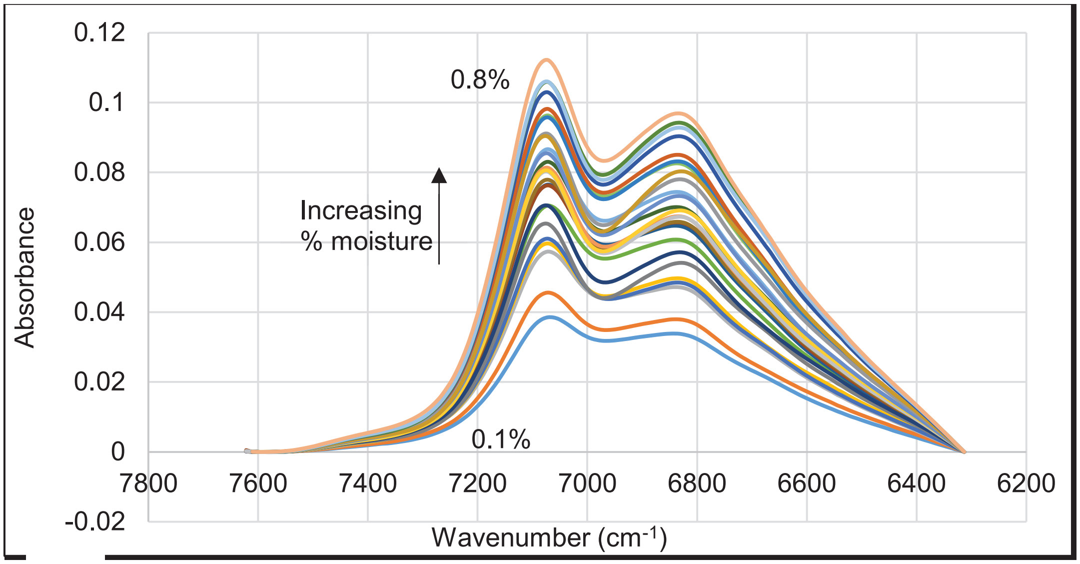

Figure 3. Response of NIR spectra to increasing moisture uptake for a 3-Joule damaged polymer matrix composite laminate.

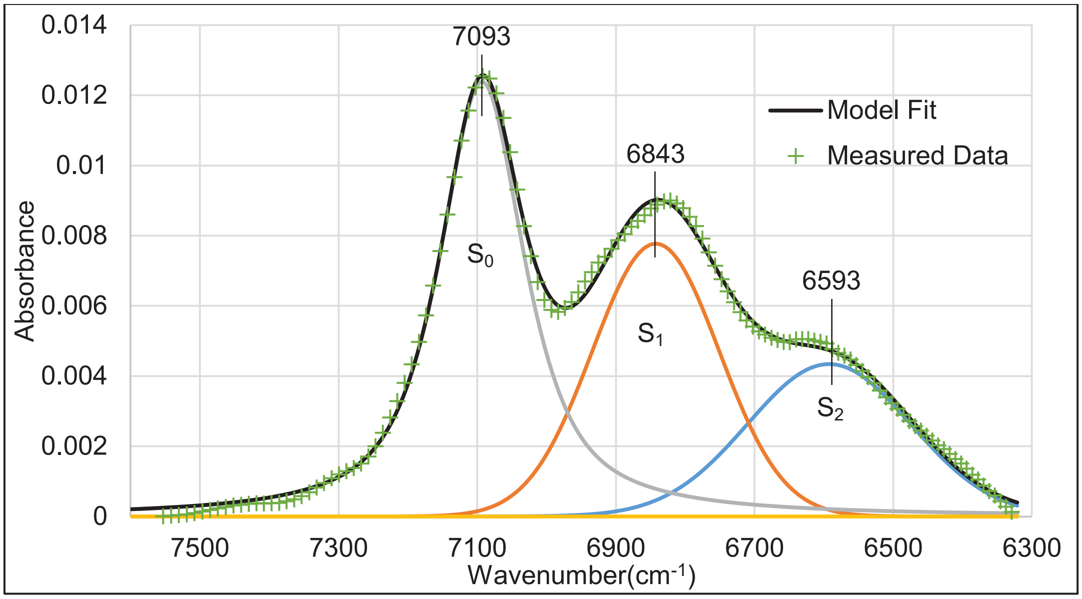

Figure 4 (a). Typical curve fitting for water spectra of an undamaged epoxy/glass fiber composite laminate at 0.19% moisture showing 3-peak model within spectral range 6250 to 7650cm^{-1}.

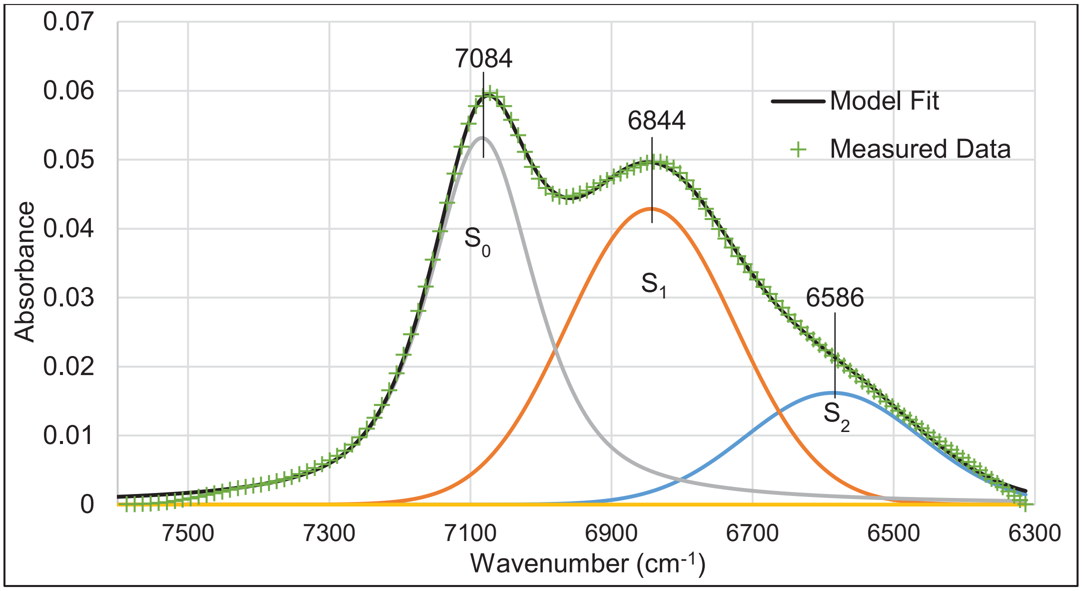

Figure 4 (b). Typical curve fitting for water spectra of a damaged epoxy/glass fiber composite laminate at 0.19% moisture showing 3-peak model within spectral range 6250 to 7650cm^{-1}.

To track changes in the state of water, we introduce a parameter ‘η’, which is defined as the free-to-bound water ratio [26]. This is calculated from trendlines for the fractions of total moisture content obtained in Figure 5 (a) and (b). Changes in η at various moisture contents for a damaged and undamaged laminate is shown in Figure 6. Results show a generally higher η for damaged specimens at all moisture levels— consistent with initial free water absorbed into the matrix cracks and delaminations. This initial free water results in a higher fraction of free water present at all subsequent moisture levels. Results also show a gradual decrease in η with increasing moisture for both the undamaged and damaged specimen, indicating a higher rate of increase in bound water compared to water in the free state as moisture content increases. This observation suggests a much higher activation energy for bound water compared to water in the free state, hence a much slower bonding process.

Results obtained for the undamaged specimens compare quite well to prior literature [11]. However, we note that here a 2nd order function is used to fit the data in Figure 5 (a) and (b), whereas a linear fit was used in previous studies. This was necessary to effectively incorporate the initially higher fraction of free water in damaged specimens at low moisture contents (<0.1%). Also, a difference exists when comparing moisture content with prior studies due to differences in test specimen material. In this study, composite laminates comprising epoxy and glass fibers were tested, unlike in the referenced study where neat epoxy was used [11]. With epoxy being the only active component interacting with water, the presence of glass fibers increases the specimen weight without any contributions to water interaction effects. Therefore, the amount of moisture per unit volume of epoxy would be a more comparable parameter. This means the responses shown in Figure 5 & 6 should be comparable to responses for significantly higher moisture contents in epoxy only systems.

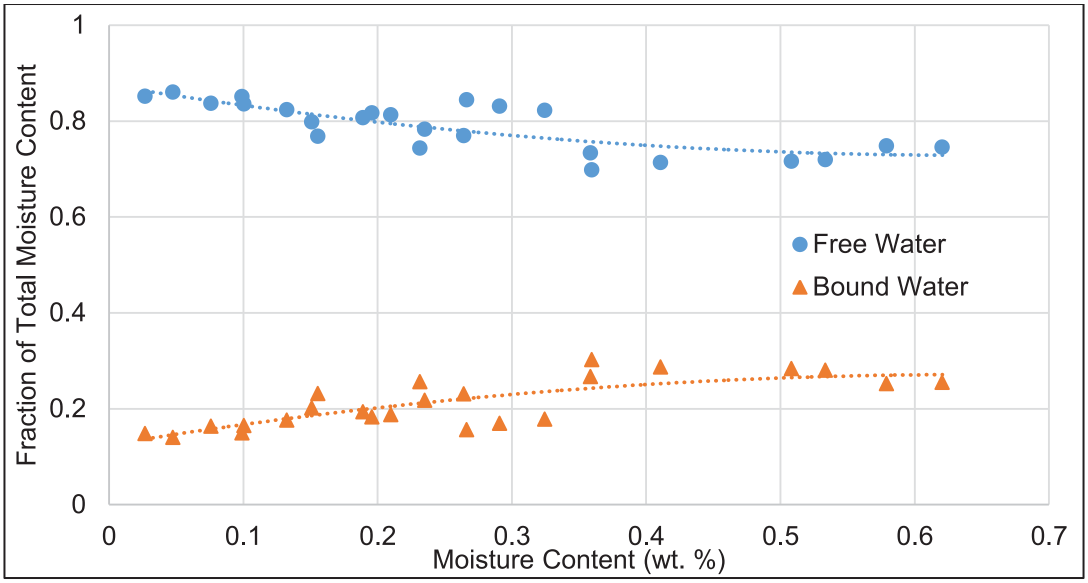

Figure 5(a). Free and bound water relative concentrations for an undamaged specimen as a function of total moisture content.

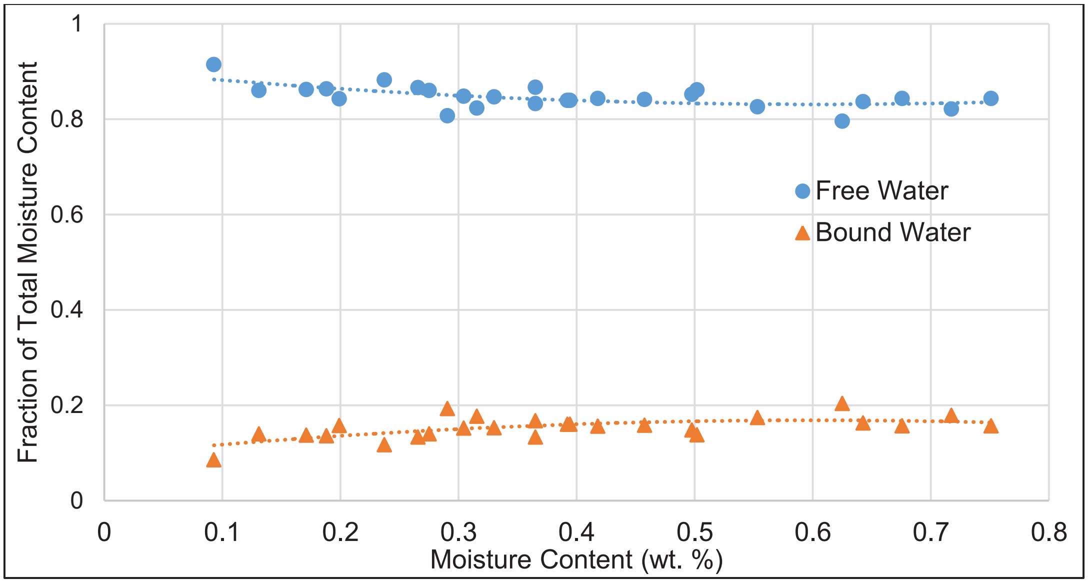

Figure 5(b). Free and bound water relative concentrations for a damaged specimen as a function of total moisture content.

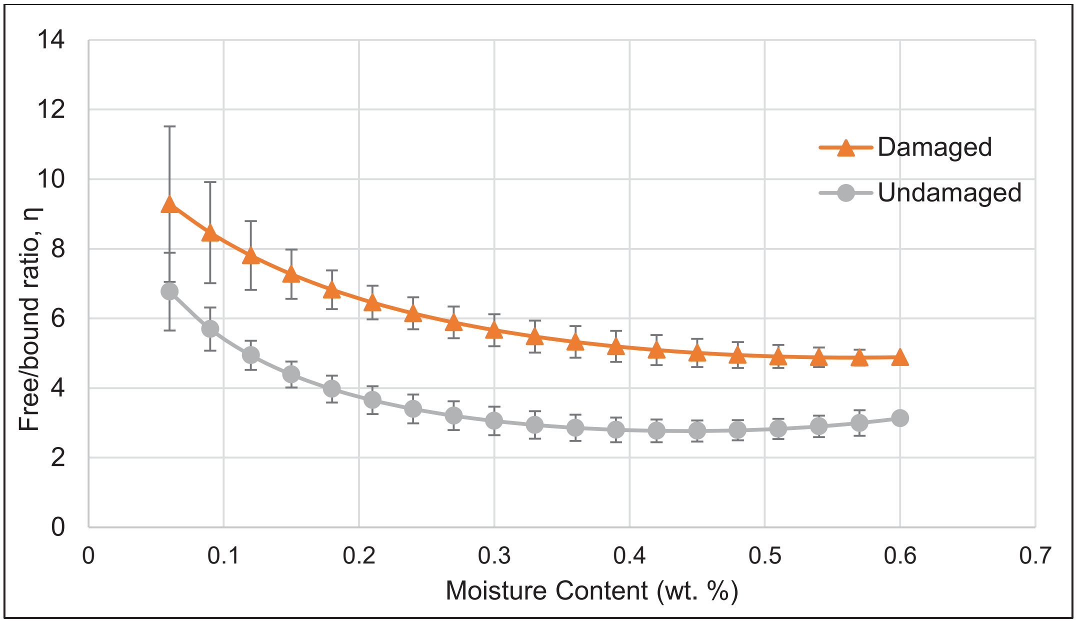

Figure 6. Plot of Free-to-bound water ratio vs moisture content (wt. %).

The curve for the free-to-bound water ratio for the undamaged case shown in Figure 6 indicates a gradual increase beyond 0.5% moisture content, indicating a higher rate of absorption for water in the free state. However, this could simply be an effect of applying a 2nd order polynomial fit to the data. This trend would require confirmation in future studies where additional data beyond 0.6% moisture content is available for the undamaged specimens.

Reliance on the natural process of moisture diffusion could pose some challenges in applying the method. Firstly, to ensure diffusion of moisture to the damaged region, a few hours or even up to a few days may be required before damage can be detected. However, damage is unlikely to accumulate to a significant degree at a faster rate than the required moisture content, so it is unlikely that this rate issue would pose a significant challenge. Secondly, variations in moisture content driven by changes in environmental conditions may affect the sensitivity of the proposed method. This has a greater effect on free water due to its relatively lower activation energy compared to bound water [49,50]. Hence, this may result in a decrease in sensitivity to damage within the polymer matrix composite. Strategies to accommodate for this variability are currently under investigation.

Infrared spectroscopy could be an attractive NDE tool for a number of reasons including minimal sample or surface preparation, ability to produce results in real-time, and the possibility of applying it in reflectance mode. Adopting reflectance mode enables flexibility for field use, with the ability to test parts which are accessible from one side only. However, we note that this feature is strongly dependent on the ability of the material to reflect infrared light in a diffuse manner. Therefore, for strongly absorbing materials such as carbon fiber, characterization depth may be significantly limited [51]. Infrared spectroscopy has been applied as an NDE tool for polymer matrix composites in detection of incipient thermal damage and damage resulting from exposure to ultraviolet radiation [52–54]. Analysis of polymer-water interactions could extend these capabilities to detection of early-stage mechanical damage by taking advantage of recent advances which combine atomic force microscopy (AFM) and infrared spectroscopy—AFM-IR. With these technological advances the spatial resolution of infrared spectroscopy has been drastically improved, exceeding conventional optical diffraction limits [55,56]. By combining this with polymer-water interactions, detection of sub-micron scale cracks and flaws at resolutions as low as 50nm may be possible [56].

CONCLUSION

This study investigated the potential of leveraging polymer-water interaction as a non-destructive examination (NDE) technique for polymer matrix composites by applying near infrared spectroscopy as a quantitative characterization tool. Experiments were presented which demonstrate the sensitivity of free-to-bound water ratio to low levels of mechanical damage at naturally occurring levels of moisture content. The results showed as much as 25% to 100% increase in free-to-bound water ratios when a 16-ply epoxy/glass fiber laminate is damaged by low energy (3-Joule) impact. A key benefit of this approach is the possibility of characterizing early-stage damage at sub-micron scales by utilizing molecular-level hydrogen bonding properties of water and the polymer matrix. Future work may include extending the method to 2-dimensional mapping of damage in polymer composite laminates.

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