



# Hygrothermal aging effects on fatigue of glass fiber/polydicyclopentadiene composites

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## Abstract:

We investigated the effects of hygrothermal aging on the tension–tension fatigue behavior of unidirectional (UD) glass/polydicyclopentadiene (pDPCPD) composites. Samples were immersed in deionized (DI) water and salt water, and glass/epoxy composites were used as a benchmark for comparison. Composites of pDPCPD showed less water uptake and superior fatigue performance compared to similarly aged epoxy composites, a distinction attributed to the intrinsic hydrophobicity of the pDPCPD resin. Superior fiber-matrix interface adhesion in pDPCPD composites accounted for the greater strength retention after aging. Degradation of fiber and interface were coupled but not synchronous: glass fiber degradation was determined by aging time, while interface degradation depended primarily on moisture level. Salt water influenced the amount of water absorption, but no salt water corrosion was observed for either composite.

Key words: Polymer-matrix composites (PMCs); Environmental degradation; Fatigue; Acoustic emission



## 1. Introduction

The use of polymer matrix composites (PMCs) is expanding to civilian infrastructure, energy, and marine applications. Despite the significant performance advantages of PMCs compared to traditional materials, long-term durability remains a major concern in such applications, particularly those where materials are expected to provide decades of outdoor service with minimal inspection and maintenance. For example, wind power turbine blades require resistance to long-term humidity, cyclic temperatures and loads, UV radiation and seawater aging, especially in offshore installations, where inspection and monitoring of structural health pose challenges.

Studies of moisture aging of PMCs have shown that hygrothermal exposure can affect fibers, matrix and interfaces in different ways [1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11],[12], [13], [14], [15], [16] and [17]. For example, carbon fibers are reportedly inert to humid environments [12], while glass fibers are sensitive to moisture exposure [11]. The strength decrease of glass fiber is typically a result of surface corrosion through an ion exchange mechanism [18]. Similarly, polymers and interfaces exhibit a wide range of responses to hygrothermal exposure that reflects the diversity of chemical and structural effects.

Hygrothermal aging of polymer matrices often involves multiple chemical and physical mechanisms operating concurrently, and thus presents complex challenges. Water molecules typically diffuse into polymer networks and act as a plasticizer when they exist in a free state. Plasticization softens the matrix and decreases the observed glass transition temperature ( $T_g$ ), modulus and strength [19]. On the other hand, moderate plasticization also can enhance fracture toughness by impeding crack propagation [20]. In most cases, water-based plasticization is reversible after drying. On the other

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hand, during long-term aging of some thermosets [21], water molecules can bond strongly with polymer chains and cause additional cross-linking, *increasing*  $T_g$  and strength.

Additional aging processes can occur with or without the presence of moisture. For example, physical aging is an important issue for polymers during extended high-temperature exposure. In the structural recovery (relaxation) process, free volume decreases and polymer chains become more densely packed, which results in strengthening and shrinkage. Darkening after aging arises from chemical changes in the resin, such as oxidation. Oxidation can occur during aging, although in water immersion, and is generally limited to a thin surface layer (diffusion limited oxidation, DLO) if no surface cracking occurs and thus has negligible influence on overall mechanical properties. Physical aging and oxidation are generally considered irreversible.

Hygrothermal aging of the fiber-matrix interface reportedly causes fatigue strength degradation of PMCs [13] and [15]. Matrix swelling is generally detrimental to the interface due to the resulting normal tensile stress that facilitates interface separation. Interface debonding is often observed after water immersion [14], reducing the load transfer capability between fiber and matrix. The debonded interfaces retain water (“wicking”) and become capillary diffusion pathways, which in return accelerate the aging process.

Multiple studies of the effects of hygrothermal aging on the fatigue behavior of PMCs have been reported [10], [11], [12], [13], [14], [15], [16] and [17]. However, further investigation is warranted, particularly for PMCs based on non-crimp fabrics, often used for wind blades. Polydicyclopentadiene (pDCPD) is a potential matrix material for wind turbine blades, offshore oil structures, and automotive parts because of the inherent hydrophobicity and the resistance to chemical corrosion [22], [23], [24] and [25]. Although the fatigue behavior of pre-aged pDCPD

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composites has been reported [26] and [27], the effect of hygrothermal aging on the fatigue behavior has not been systematically investigated. In this study, we report the effects of aging in deionized water and salt water environments on the tension–tension fatigue behavior of UD glass/pDCPD laminates. A conventional glass/epoxy composite is used as a reference material for comparison, and acoustic emission (AE) is employed to monitor damage evolution during fatigue tests. The evolution of fatigue behavior with aging time is described, and mechanisms involved in fatigue strength degradation are identified. Results showed that pDCPD composites absorbed less water than epoxy composites and exhibited superior fatigue resistance. This phenomenon was primarily attributed to the superior resistance of the hydrophobic pDCPD to water absorption. Both deionized water and salt water aging environments influenced the amount of water absorption, although no salt water corrosion effects were observed.

## 2. Experimental

### 2.1 Samples preparation

UD glass/pDCPD laminates and UD glass/epoxy laminates were produced by a commercial source (Materia, Inc., Pasadena, CA) using common vacuum infusion processing techniques. The pDCPD resin (Proxima™, Materia, Inc., Pasadena, CA) and the epoxy resin (Epikote™ MGS RIMR 135 resin with RIMH 137 hardener, Momentive, Inc.) were selected for composite matrices. The pDCPD was formulated using a ruthenium-based catalyst (Grubbs Catalyst™). This formulation shows favorable toughness, viscosity, and chemical resistance compared to traditional pDCPD formulations, but the long-term aging behavior is not yet well understood. The pDCPD laminates

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were cured at 30 °C for 2 h, and then post-cured at 100 °C for 30 min. The epoxy laminates were cured at 80 °C for 8 h. Table 1 shows basic properties of the two cured resins.

*Table 1. Basic properties of cured pDCPD and epoxy neat resin.*

	$T_g$ (°C)	Density (g/cm <sup>3</sup> )	Tensile modulus (GPa)	Ultimate tensile strength (MPa)	Tensile elongation
pDCPD	124	1.05	3.1	73	2.7%
epoxy	101	1.15	2.9	64	3.4%

The laminates were prepared using non-crimp fabric (E-LT 3500, Vectorply, Corp.) comprised of E-glass (94 wt% PPG Hybon<sup>®</sup> 2026 in the warp direction and 6 wt% PPG Hybon<sup>®</sup> 2002 in the weft direction). The properties of the glass fiber are modulus = 82.7 GPa, tensile strength = 2790 MPa, fiber diameter = 17 μm. The glass fibers featured a polyethylene terephthalate (PET) sizing, which coalesced in matrix-rich regions of the cured composites. Thus, the fiber sizing had a negligible effect on interface properties. Analysis of fiber sizing is included in the Appendix.

Two thicknesses of laminates were fabricated: 2-ply laminates were used for 0° testing and denoted as [0°]<sub>2</sub>, while 4-ply laminates were used for 90° testing and denoted as [90°]<sub>4</sub>. The thickness of [0°]<sub>2</sub> laminates was 1.6 mm, while the [90°]<sub>4</sub> laminate thickness was 3.2 mm. The fiber volume fraction for both laminates was ~58% (determined by burn-out method).



## 2.2. Water immersion aging

The two aging environments consisted of (1) deionized water at 60 °C and (2) 3.5 wt% NaCl solution at 60 °C. The former will be referred as “DI water” and the latter as “salt water.” Laminate panels were cut to (200 × 200) mm plates and immersed for aging. The plate edges were not sealed during aging, allowing accelerated diffusion through fiber-matrix interface. Neat resin samples were also aged for comparison. Temperature and salinity were monitored and kept constant. Samples were removed periodically to measure weight change.

## 2.3. Static tension

Quasi-static tensile tests were conducted following ASTM D3039. The dimensions of test coupons were (200 × 25) mm (*length* × *width*), and tabs were used on the two ends of the sample (50 mm long and 1.6 mm thick). Thus the gauge length of the sample was 100 mm. Fiberglass tabs were bonded to the specimen using epoxy adhesive. Specimens were pulled to fracture on a load frame (Instron 5567) at a loading rate of 2 mm/min. An extensometer was used to determine tensile strain values.

## 2.4. Tension–tension fatigue

Tension–tension fatigue tests were conducted in air in a well-ventilated room on a hydraulic load frame (Instron 8500R-1331) in accordance with ASTM D3479 (for testing) and ASTM E739 (for data processing). Samples were the same as for static tensile tests. Load control was implemented using a stress ratio of  $R = 0.1$ , a loading frequency of 10 Hz, and a run-out cycle of  $10^6$ .

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Considering the possible effect of sample heating during fatigue tests, which is sensitive to loading frequency [28], fatigue tests of 10 Hz were compared with 5 Hz at different load levels using a group of pre-aged samples. No difference was observed in fatigue life. A temperature rise was observed only when extensive damage occurred near final rupture, and the maximum temperature rise was less than 3 °C for both frequencies. Fatigue fracture surfaces of  $[90^\circ]_4$  samples were examined by scanning electron microscopy (JEOL JSM-6610), after sputtering gold on the sample surface.

## 2.5. Acoustic emission

Acoustic signals generated by internal damage during fatigue tests were recorded using an acoustic emission collection system (Physical Acoustics, PCI-2 based AE systems). Two sensors were attached at the two ends of the gauge length of the sample using a hot glue gun. The piezoelectric sensors detect transient acoustic waves generated from a release of localized damage event, recorded as a hit signal. The sensors also can be used to measure the wave energy and the position of the event, calculated from the difference in arrival time between each sensor. Acoustic emission is a useful nondestructive testing (NDT) technique for composites, as the energy of signals can be correlated to different damage mechanisms.

Noise from the fatigue testing system was removed using a filter in the AE software. Thresholds of 70 dB and 60 dB were used for  $0^\circ$  and for  $90^\circ$  fatigue test, respectively. (The load level in  $0^\circ$  tests was greater and introduced higher noise levels.) Therefore, some low energy signals, e.g., from matrix and interface cracking below the threshold, were not captured.

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### 3. Results and discussion

#### 3.1. Effect of moisture uptake on fatigue properties

Fig. 1 shows the weight change of 4-ply pDCPD and epoxy laminates after aging. The pDCPD composites showed less water uptake than epoxy composites after aging, as expected. The pDCPD composites showed a roughly linear increase, while epoxy composites showed a Fickian approach to saturation with accelerated kinetics in salt water. (Differences between aging in DI water and salt water will be discussed in Section 3.3.) The intrinsic hydrophobicity of pDCPD resin can be explained on a molecular level: pDCPD polymer chains lack hydrophilic groups, while epoxy polymer chains contain hydrophilic groups such as hydroxyls, fostering water uptake [24].

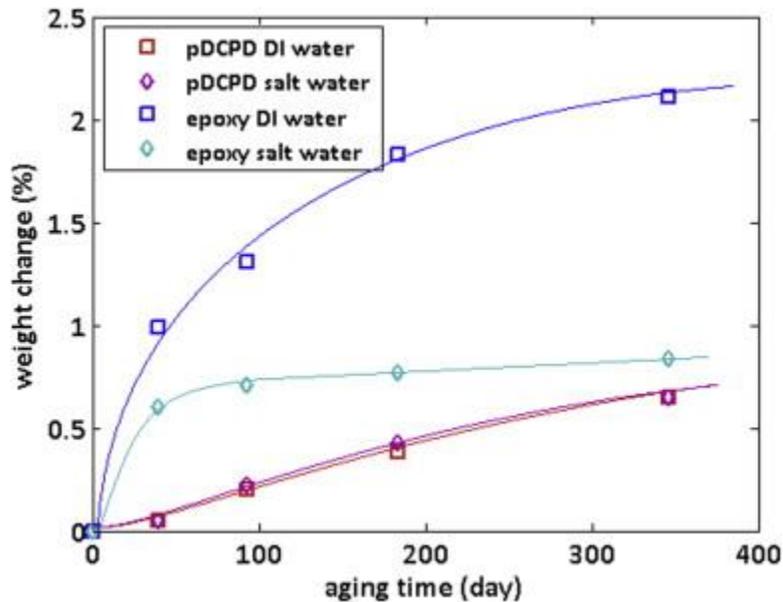


Fig. 1. Weight change after aging.

Fig. 2 shows the  $S-N$  curves of the two composites after aging in salt water.  $S$  indicates maximum cyclic stress while  $N$  represents cycles to failure. Data points with arrows at  $N = 10^6$  cycles indicate



run-out samples. The load levels used are 40%–80% of the ultimate tensile strength (UTS) for the given aging condition. (Static tensile properties will be discussed in Section 3.2). For both loading directions, the pDCPD composites showed greater fatigue strength, and the slope of the  $S-N$  curve decreased with aging time, indicating a greater influence of aging on low-cycle fatigue than on high-cycle fatigue. Standard deviations of aged samples were generally greater than that of pre-aged, indicating a greater scatter in mechanical properties from sample to sample after aging.

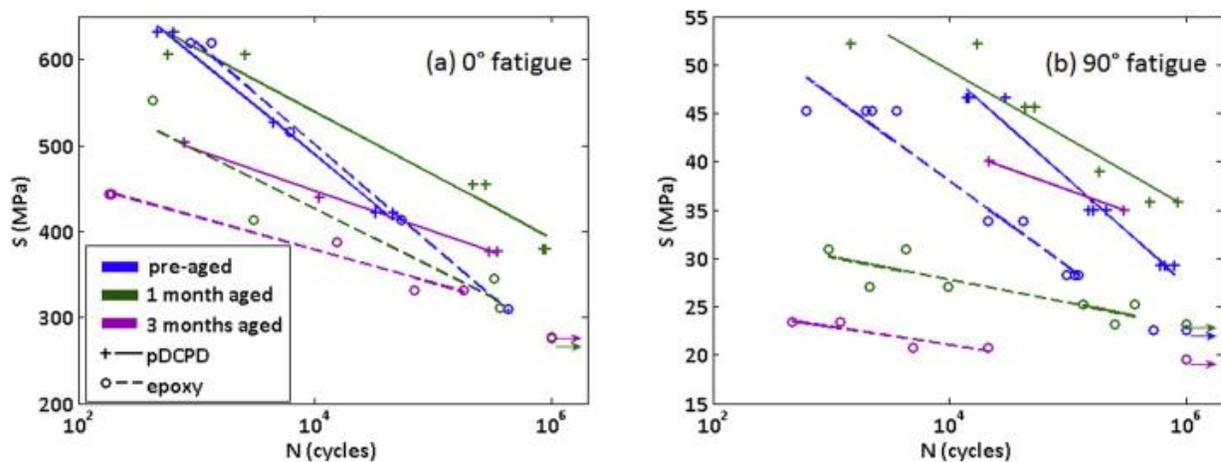


Fig. 2.  $S-N$  curves evolution after aging.

Fig. 2a shows the 0° tension–tension fatigue property evolution. In the pre-aged condition, pDCPD and epoxy composites displayed similar fatigue properties. However, after one month of aging, for pDCPD composites, the high-cycle fatigue life *increased*, a phenomenon attributed to post-curing and/or physical aging of the matrix. In contrast, for epoxy composites, the low-cycle fatigue life decreased, attributed to fiber strength decrease, matrix plasticization, and interface degradation. After three months of aging, both composites showed fatigue life decrease at all load levels, although pDCPD composites showed superior strength retention relative to epoxy composites.

Fig. 2b shows the evolution of fatigue behavior for 90° tension–tension. For the pre-aged condition, pDCPD composites showed greater fatigue strength than epoxy composites, indicating superior



interface adhesion and/or matrix strength, since fiber strength has negligible influence on 90° failure. Because the static tensile strength of pDCPD and epoxy are similar (from dogbone tensile tests per ASTM D638), the superior fatigue behavior of pDCPD composites is attributed primarily to the superior interface adhesion. The superior interface adhesion is partly caused by the lower viscosity of the DCPD resin during manufacture, which facilitates infiltration and promotes fiber-matrix contact. The trend in *S-N* curves for 90° direction followed the same trend as 0° fatigue, suggesting similar damage mechanisms were involved.

The superior post-aging adhesion of interfaces in pDCPD composites compared to epoxy composites also is apparent from SEM fractography of 90° fatigue samples. Fig. 3 shows the fracture surface of 90° fatigue samples at different aging conditions. Note that the fracture morphologies shown in Fig. 3 were consistent over the entire fracture surface and thus are representative for the corresponding aging condition. Furthermore, the fractography was consistent for all load levels for each aging condition. The epoxy composites (Fig. 3b, d, f) showed identical fractography throughout six months of aging. Bare fiber surfaces were common, while matrix failure was rare, indicating relatively weak interface adhesion to the matrix cohesive strength.

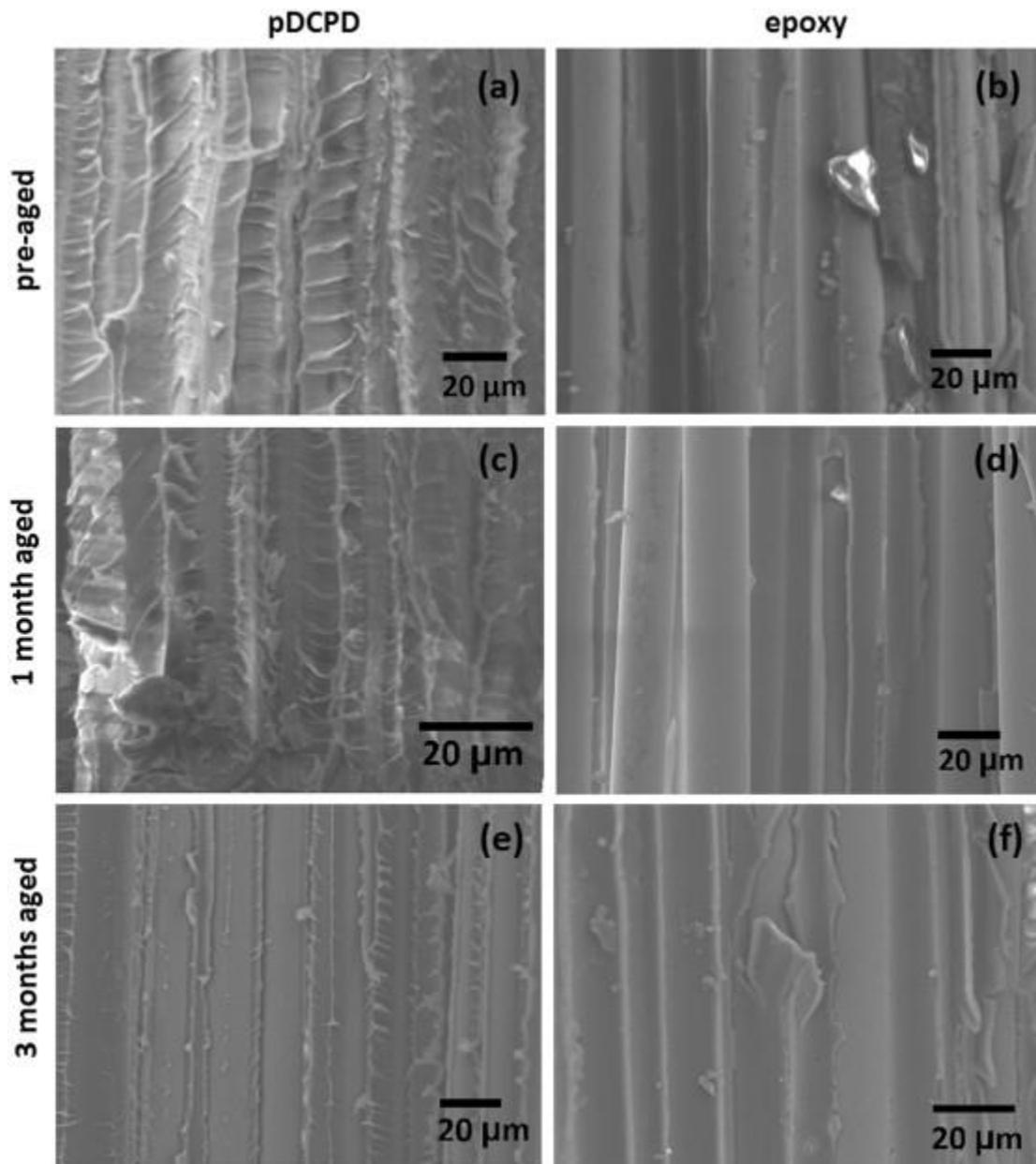


Fig. 3. Fracture surface of  $[90^\circ]_4$  fatigue samples.

In contrast, the fracture surfaces of pDCPD composites (Fig. 3a, c, e) changed with aging time. Pre-aged samples (Fig. 3a) and samples aged one month (Fig. 3c) showed a rough surface with matrix shear ridges and an absence of exposed fiber surface, indicating matrix-dominated failure and thus greater interface strength relative to matrix cohesive strength. After three months of aging (Fig. 3e),



both matrix shear ridges and exposed fiber surface were observed, indicating a mix of interface and matrix failure. Given that the epoxy matrix absorbed more water (leading to greater plasticization and strength decrease), we conclude that the interface strength in pDCPD composites was greater than in epoxy composites throughout the aging period studied.

The superior interface adhesion in pDCPD composites relative to epoxy composites prior to aging arises from multiple factors. The different chemistry of the two resins leads to different fiber compatibility and thus interface bond strengths. Also, the curing cycles of the two resins differ (Section 2.1), and leading to differences in cure shrinkage, coefficient of thermal expansion and local temperature gradient during cooling. Thus, the residual stress in the two composites also differs [29]. Fig. 2 and Fig. 3 indicate the important role of the fiber-matrix interface in the UD composite fatigue performance for both 0° and 90° composites. The interface degradation is affected by the environmental moisture level, which is determined by the amount of water absorption in the matrix. Comparing Fig. 1 and Fig. 2, the amount of water uptake correlated with the fatigue strength decrease, which is consistent with the scenario described above. Thus, matrix hydrophobicity is critical to preserving the fatigue strength of PMCs in humid environment application.

### 3.2. Asynchronous aging of fiber, matrix and interface

Fig. 4 shows the static tensile modulus and the UTS evolution during aging. Note that the four groups of samples were aged and tested at the same time (data points are artificially offset to show the error bars). The effect of aging on modulus is negligible for 0° composites, while in the 90° orientation, the modulus of pDCPD composite increased slightly while the modulus of epoxy composite decreased after three months of aging. The strength in the 0° direction of the two composites are identical (except for epoxy aged in DI water, which is discussed in Section 3.3 below), and showed



significant decrease after aging (40% retention after one year). In the 90° direction, the pDCPD composites showed greater strength retention (70% retention after one year) than epoxy composites (45% retention after one year).

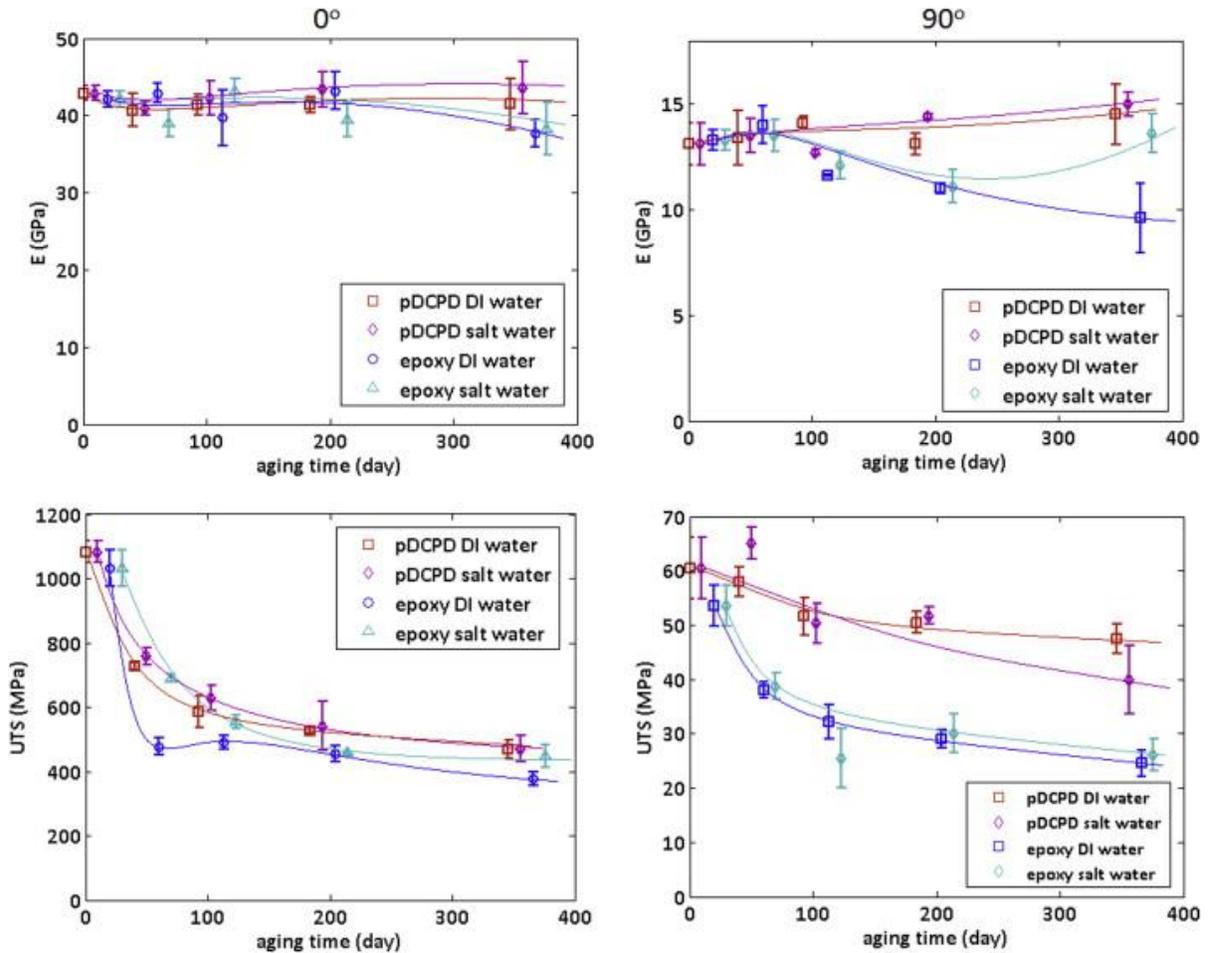


Fig. 4. Static tensile properties evolution after aging.

The relationship for composite modulus and constituents moduli follows a simple rule of mixtures (Eq. (1)).

$$\begin{cases} E_{c,0} = fE_{f,0} + (1 - f)E_m \\ \frac{1}{E_{c,90}} = \frac{f}{E_{f,90}} + \frac{(1 - f)}{E_m} \end{cases} \quad (1)$$

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where  $E_{c,0}$  is the  $0^\circ$  modulus of the composite,  $E_{f,0}$  is the modulus of the fiber in longitudinal direction,  $E_m$  is the modulus of the matrix, and  $f$  is the fiber volume fraction.

Assuming  $E_{f,0} = 82.7$  GPa,  $E_m = 3$  GPa and  $f = 58\%$ , the glass fibers account for more than 97% of the composite modulus. Eq. (1) also applies to strength, and thus the static tensile strength of  $0^\circ$  composites is determined by the glass fiber strength. Thus, from the  $0^\circ$  modulus and strength plots in Fig. 4, hygrothermal exposure severely degraded the glass fiber strength, while the glass fiber modulus was retained. The identical strength values of  $0^\circ$  pDCPD and epoxy composites indicate synchronous degradation of glass fiber in the two composites.

In  $90^\circ$  composites, the modulus is largely influenced by the matrix. Thus, the slight increase in modulus of pDCPD composites was attributed to physical aging of the matrix, and the decrease in modulus of epoxy composites was caused by the plasticization of the matrix. Strength, on the other hand, is determined by the strength of both the matrix and the interface. Thus, the greater strength retention of  $90^\circ$  pDCPD composites is attributed to the greater strength retention of the matrix and interface. Note that the degradation of matrix and interface in the two composites is *asynchronous* during aging.

In  $0^\circ$  composites, the identical static strength degradation of pDCPD and epoxy composites (Fig. 4) is explained by the *synchronous* degradation of glass fiber. On the other hand, the much different fatigue behavior ( Fig. 2a) is explained by the *asynchronous* degradation of the matrix and interface, as fatigue failure is largely influenced by the progressive damage accumulation of the matrix and interface before final rupture. Indeed, the AE signals recorded during fatigue testing support the contention of asynchronous matrix and interface degradation, as described next.



Fig. 5 shows the evolution of sample stiffness and AE signal during fatigue. Sample type and aging time are marked on each figure. All four composites were loaded at  $S = 450$  MPa. In each figure, the curve illustrates the evolution of the secant modulus given by Eq. (2), which provides an indication of sample stiffness:

$$E_s = \frac{S - \sigma_{\min}}{\epsilon_{\max} - \epsilon_{\min}} \quad (2)$$

where  $S$  and  $\sigma_{\min}$  are the maximum and minimum cyclic stress, while  $\epsilon_{\max}$  and  $\epsilon_{\min}$  are the corresponding maximum and minimum cyclic strain.

Strain values are calculated from fixture displacements, although the relative changes are considered significant. Each colored dot represents a damage event in the sample captured by acoustic emission, with different colors indicating different levels of energy released in this event. The right ordinate of each figure displays the location of AE events in the sample gauge length. Thus the bottom sensor sits at  $Position = 0$ , while the top sensor is at  $Position = 100$  mm. High-energy signals reportedly represent fiber breakage, while low-energy signals indicate matrix and interface failure [13], [30] and [31]. There is no distinct boundary between the energy ranges of each damage type, and they overlap appreciably. Here we assume the red dots signify fiber breakage, while the green and blue dots arise from matrix and/or interface failure.

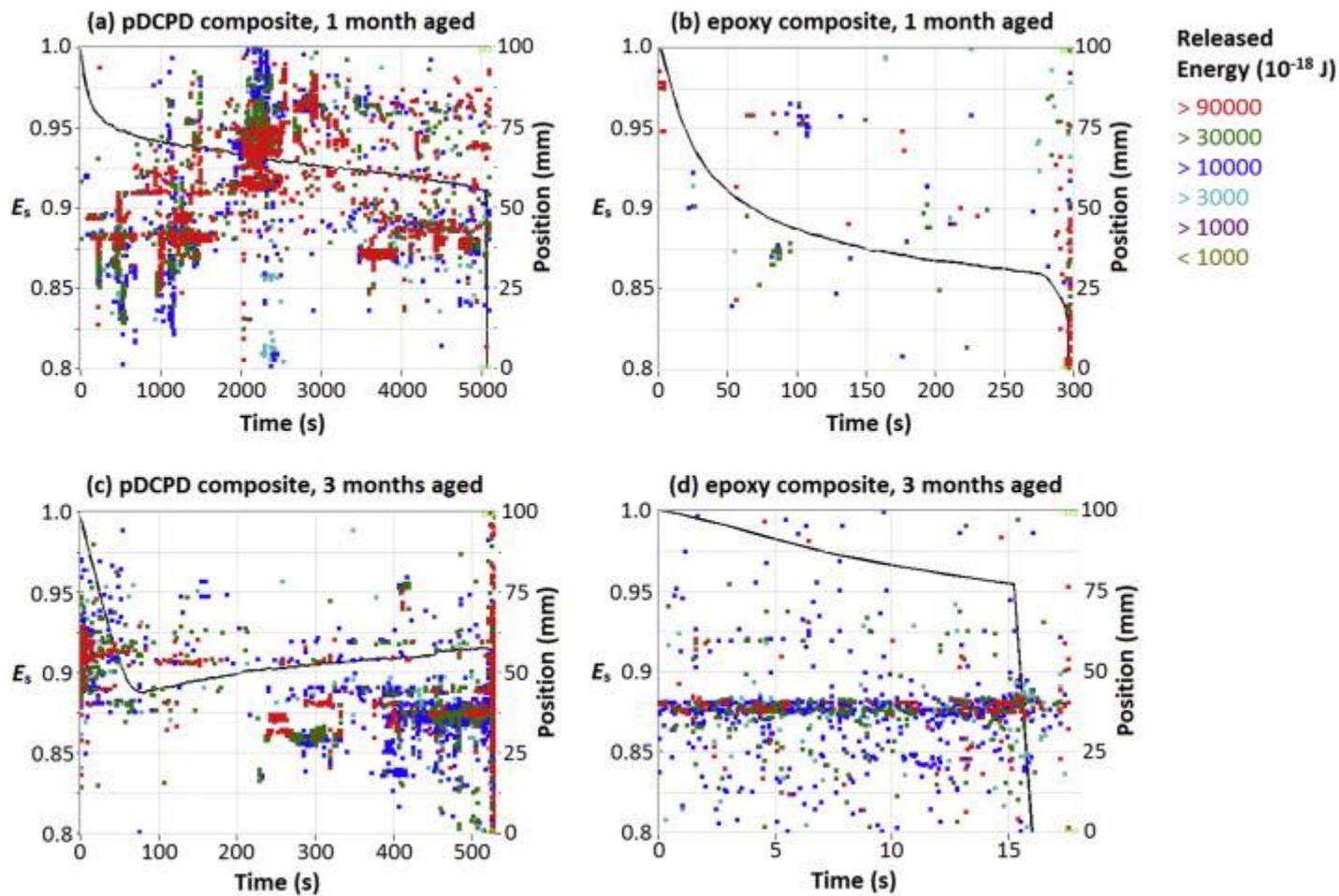


Fig. 5. Damage evolution of  $[0^\circ]_2$  composites.

Comparing the damage evolution process in the two composites as in Fig. 5, less damage accumulation and fewer low-energy events were observed in epoxy composites than in pDCPD composites. Furthermore, the damage in epoxy composites consisted primarily of fiber breakage, while the damage in pDCPD composites included all three types of fiber, matrix and interface failure. The absence of interface failure in aged epoxy samples during fatigue arises because massive interface debonding already occurred prior to fatigue testing. The more extensive interface degradation in epoxy composites is also evidenced by the lower static and fatigue strength values of



90° epoxy composites (Fig. 2 and Fig. 4), and by the fatigue fractography of 90° epoxy composites (Fig. 3).

Summarizing the results and discussion above, the fiber and interface showed coupled but asynchronous degradation, which affected the overall mechanical behavior. The degradation of glass fiber was determined primarily by aging time, while the interface degradation was affected primarily by the moisture level in the matrix. Greater water absorption by matrix accelerated interface debonding, and debonded interfaces became capillary diffusion pathways and accelerated water diffusion into the matrix by increasing the contact area.

### 3.3. DI water vs. salt water aging

The difference in weight change resulting from aging in DI water vs. salt water is shown in Fig. 1. The pDCPD composites showed slightly greater water uptake after salt water immersion compared to DI water immersion. This is atypical for polymers and awaits further investigation. In contrast, epoxy composites showed greater water uptake after DI water immersion than in salt water, a phenomenon that was caused in part by the osmotic effect in salt water and/or by salt crystals obstructing water diffusion [2]. However, the large difference in weight gain (>100%) of epoxy composites in the two environments cannot be fully attributed to these phenomena, but instead is attributed to differences in the extent of interface debonding. Extensive interface debonding occurred during aging in DI water and the debonded interfaces retained significant amounts of water.

A comparison between 0° *S-N* fatigue curves in DI water and salt water aging is shown in Fig. 6. Fig. 6a shows that the fatigue strength of pDCPD composites increased after one month and decreased after three months. The *S-N* curves in DI water and salt water were identical after three months, which is consistent with the similar amount of water uptake in the two environments



( Fig. 1). Fig. 6b shows that for epoxy composites, in salt water aging, the fatigue strength decreased gradually with aging time. In contrast, in DI water aging, the fatigue strength decreased significantly after one month, but increased slightly after three months, which could be attributed to physical aging of the matrix. The slopes of the three lowermost  $S-N$  curves are identical, indicating damage saturation. Thus, for both pDCPD and epoxy composites, the evolution of fatigue strength in the two environments was closely related to the amount of water absorption. Epoxy composites showed significantly greater water absorption in DI water than in salt water, and thus greater decrease in fatigue strength, while pDCPD composites showed similar water absorption in the two environments, and thus similar decreases in fatigue strength. In summary, the salt water environment influenced only the amount of water uptake - no other effects were observed on the studied composites.

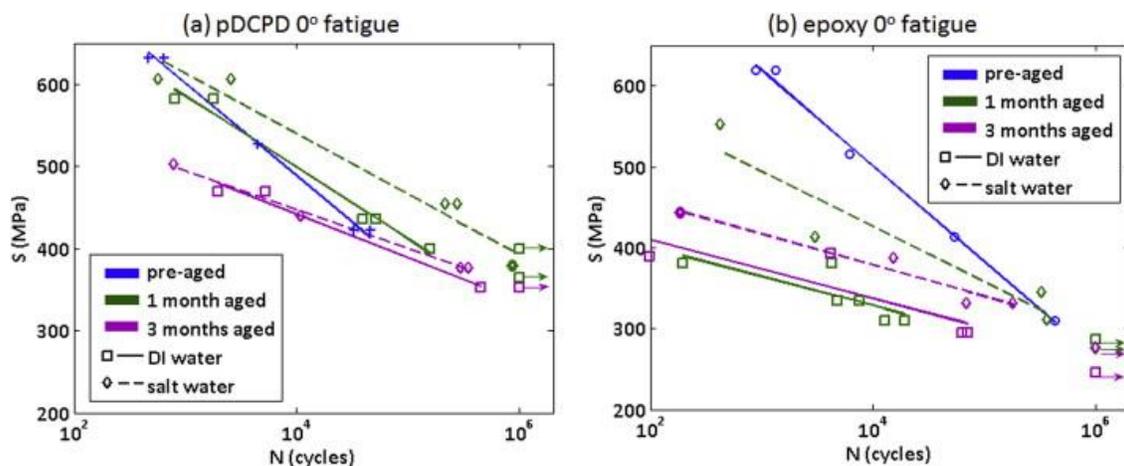


Fig. 6.  $S-N$  curves evolution in DI water and salt water environments.

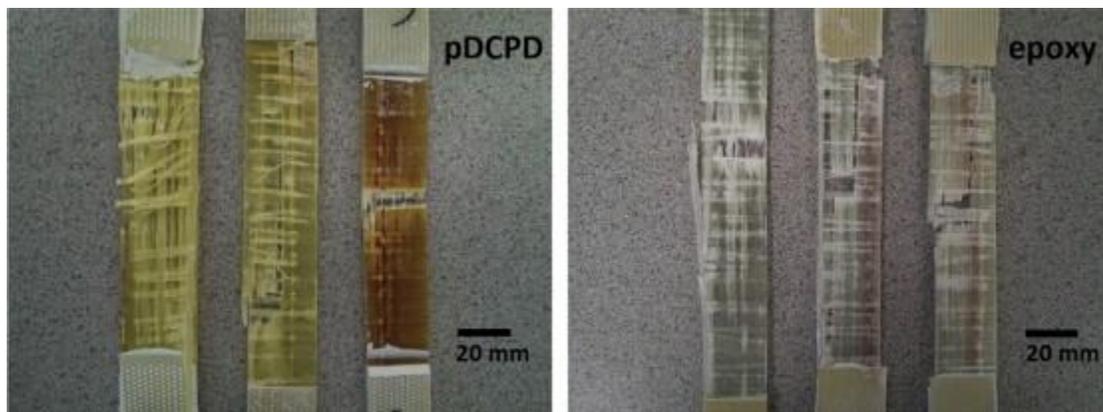
### 3.4. Fatigue damage localization

Damage localization was noticed within the sample gauge length during tension-tension fatigue of aged composites. Comparing the damage evolution between samples aged one month (Fig. 5a and



b) and three months (Fig. 5c and d), damage was dispersed over the entire gauge length for the former, while damage was localized in the latter, where most damage events were clustered at one or two locations. Damage localization is associated with interface degradation and loss of capacity for fiber-matrix load transfer. Once damage initiates at a location, stress cannot be transferred to adjacent areas, and the stress concentration intensifies. Thus, damage accumulates locally, leading to premature failure.

Further evidence of damage localization is shown in sample images after fatigue failure (Fig. 7). Aging conditions for both composites from left to right are: pre-aged, one month aged, and three months aged. Damage localization can be observed as aging time increases, especially for pDCPD composites. The color change of pDCPD samples arises from a surface layer ~100 microns thick caused by oxidation. The oxidized layer is dense and hard, limiting progressive oxidation into the bulk. Epoxy samples changed from semitransparent to internally reflective after aging. However, epoxy neat resin samples did not show such change after aging. Thus, the internal reflection is caused by the reflection of light from the debonded fiber-matrix interfaces.



*Fig. 7. Fatigue failure of  $[0^\circ]_2$  composites.*



## 4. Experimental

The effects of hygrothermal aging on the static tensile and tension–tension fatigue behavior of glass/pDCPD UD composite were investigated using acoustic emission monitoring. A glass/epoxy composite was used as a baseline reference material, and properties of both 0° and 90° composites were measured. The pDCPD composites showed less water uptake than the epoxy composites because of the intrinsic hydrophobicity of pDCPD matrix. The degradation of matrix, fiber and interface (especially the latter two) was significantly affected by moisture uptake level. Thus, pDCPD composites showed superior mechanical performance under dynamic and quasi-static loading in both 0° and 90° directions. Fractography analysis revealed that pDCPD also had greater interface bond strength to glass fibers than the epoxy, contributing to the high strength retention of pDCPD composites.

Hygrothermal aging of PMCs is a major concern for structural durability in humid service environments. The present study demonstrates that pDCPD composites exhibit exceptional resistance to hygrothermal environments and as a result, superior retention of static and dynamic mechanical properties. These characteristics are well-suited to potential applications in wet and corrosive environments, such as wind energy structures, offshore oil platforms, and both land and marine vehicles. The intrinsic hot/wet aging resistance of pDCPD composites indicates potential for high-temperature applications such as the protective shells of offshore oil risers. The current findings highlight the importance of matrix hydrophobicity and interface adhesion to hygrothermal aging resistance. They can be useful to future investigations of aging behavior where mechanical loading, moisture, oxidation and radiation occur simultaneously. However, certain issues warrant further

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investigation, particularly the observation that pDCPD showed greater moisture uptake in salt water, an uncommon phenomenon for polymers. In addition, direct measurements of interface strength as a function of aging could result in more accurate predictions of long-term mechanical behavior, and the insights gained by such measurements could lead to the design of more durable interfaces.

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### **Appendix:**

Both pDCPD and epoxy composites were reinforced with glass fibers with PET sizing. The UD composites were first cut and polished in  $0^\circ$  directions, then examined microscopically. Fig. A1 shows the matrix-rich region between three adjacent fiber tows in a pDCPD composite. Unidentified inclusions (marked with arrow) appear in light contrast in the matrix-rich region. These inclusions showed similar morphology in  $90^\circ$  cross-section (not shown here), and were thus equi-axed.

Further investigation by micro-Raman (Renishaw in Via Raman Microscope) determined that these inclusions originated from the PET fiber sizing and developed during processing. Fig. A2 shows the Raman spectrum of an inclusion. The laser wavelength was 532 nm (green), the laser power was 10% of 0.2 W, the exposure time was 10 s, and the scan range was  $100\text{ cm}^{-1}$  to  $3200\text{ cm}^{-1}$ . Spectra from pDCPD and epoxy composites were identical.

In Fig. A2, the wavenumber and relative amplitude of each peak are identical to the PET reference spectrum [32], confirming the identity of the inclusions. Because PET is relatively insoluble in pDCPD and epoxy resins, these PET inclusions originate from the PET fiber sizing on glass fibers.



Thus, because the sizing disappeared from fibers, the glass fibers and matrix in both composites were in direct contact.

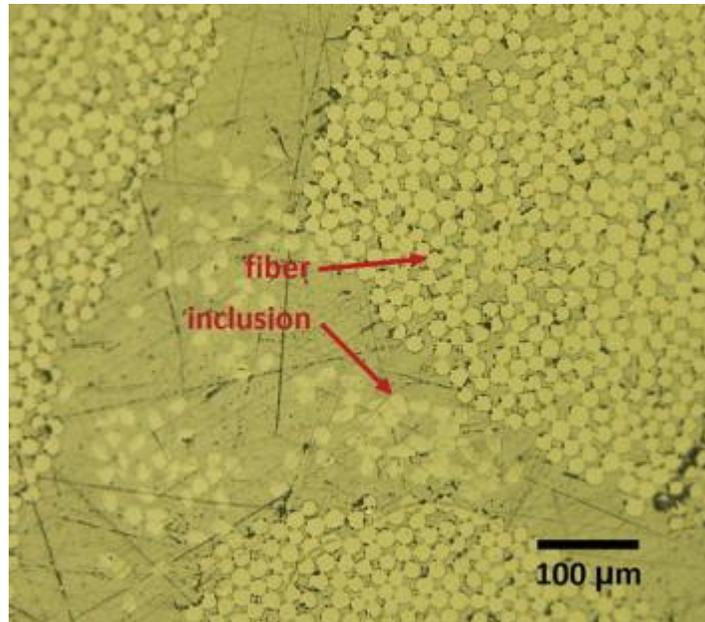


Fig. A1. Optical microscope of 0° polished section.

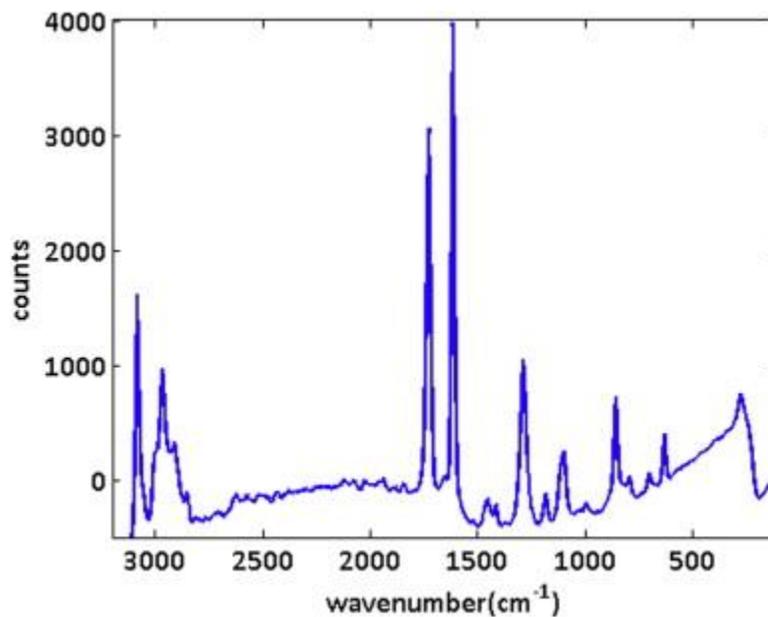


Fig. A2. Raman spectrum of PET inclusion.

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