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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 (pDCPD) composites. Samples were immersed in deionized (DI) water and salt water, and glass/epoxy composites were used as a benchmark for comparison. Composites of pDCPD showed less water uptake and superior fatigue performance compared to similarly aged epoxy composites, a distinction attributed to the intrinsic hydrophobicity of the pDCPD resin. Superior fiber-matrix interface adhesion in pDCPD 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.

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 [1–17]. 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 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 [13,15]. 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],

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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 [10–17]. 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 [22–25]. Although the fatigue behavior of pre-aged pDCPD composites has been reported [26,27], 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. Sample 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 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.

The laminates were prepared using non-crimp fabric (E-LT 3500, Vectorply, Corp.) comprised of E-glass (94 wt% PPG Hybon® 2026 in the warp direction and 6 wt% PPG Hybon® 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 $[0^\circ]_2$, while 4-ply laminates were used for 90° testing and denoted as $[90^\circ]_4$. The thickness of $[0^\circ]_2$ laminates was 1.6 mm, while the $[90^\circ]_4$ laminate thickness was 3.2 mm. The fiber volume fraction for both laminates was ~58% (determined by burn-out method).

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

	T_g (°C)	Density (g/cm^3)	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%

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.

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° and for 90° fatigue test, respectively. (The load level in 0° 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.