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Influence of hygrothermal aging on carbon nanofiber enhanced polyester material systems

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ABSTRACT

Four polyester composites (neat polyester, polyester reinforced with glass fibers, polyester reinforced with carbon nanofibers, and polyester reinforced with both glass fibers and carbon nanofibers) were prepared with the Vacuum Assisted Resin Transfer Molding (VARTM) process. These material systems were exposed to 60 °C/60% RH for 3600 h. Diffusivity was determined using moisture uptake curves. And, it was discovered that the addition of glass fibers (GFs) increased diffusivity, while the addition of carbon nanofibers (CNF) decreased diffusivity. Optical analysis was performed on the manually delaminated glass fiber reinforced polymer (GFRP) and nano-enhanced GFRP. This analysis indicated that the addition of CNF retarded the degradation of the matrix after exposure to elevated heat and humidity. Thermomechanical analysis was performed across material systems during various stages of the environmental preconditioning to determine alterations in properties such as storage modulus (SM) and glass transition temperature (T_g). The addition of GF to the system initially increased the maximum storage modulus, it also increased degradation from elevated heat and humidity exposure In contrast with GF, the addition of CNF retarded SM degradation and increased thermal stability. Upon re-drying, the nano-enhanced material systems recouped more than 90% of the maximum SM and maintained a T_g between the baseline and saturated hygrothermal treatments. This indicated both a reversible plasticization and an irreversible retarded degradation which could be potentially attributed to the addition of CNF.

1. Introduction

Mechanical performance degradation is a significant problem found in fiber reinforced plastics (FRP) exposed to moisture. This problem is amplified when FRP are exposed to high temperature-high moisture environments (hygrothermal aging) [1–4]. Matrix degradation and fiber-matrix interface damage are two major problems caused by hygrothermal exposure. A remedy to address these issues would significantly improve FRP's environmental durability and provide cost savings to companies whose products experience extreme conditions.

FRP has already been extensively used in the boating industry for decades, but there is still room for expansion. Improvements in FRP would allow even large container ship hulls to be made of FRP, the current limitation being long term durability of such a hull [5]. Wind energy, however, is a newer industry in need of FRP durability enhancement. Energy companies are installing larger turbines and expanding into more remote locations to keep up with a growing global demand for renewable energy. Increased durability and strength in turbine blades, primarily made of FRP, may determine if further expansion in wind energy is economically viable [5,6]. As the durability of FRP increases it will have a very broad impact on all industries that are involved with high moisture environments.

Research conducted on ambient and thermally preconditioned FRPs show an improvement in matrix and interface dominated properties, such as fatigue and fracture failures, when nano-reinforcements are added to the composite [7–9]. As a reasonable hypothesis, adding carbon nanofibers (CNFs) into FRP could also significantly reduce the severity of the hygrothermal aging problem. Furthermore, since hygrothermally aged matrices are weaker than both dried and as received matrices; the relative improvement when nanoreinforcements are added to FRP is anticipated to be more significant in hygrothermally aged cases [7–9]. It is the intent of this text to discuss the influence of through thickness hygrothermal preconditioning on the physical and mechanical properties of CNF enhanced polyester material systems.

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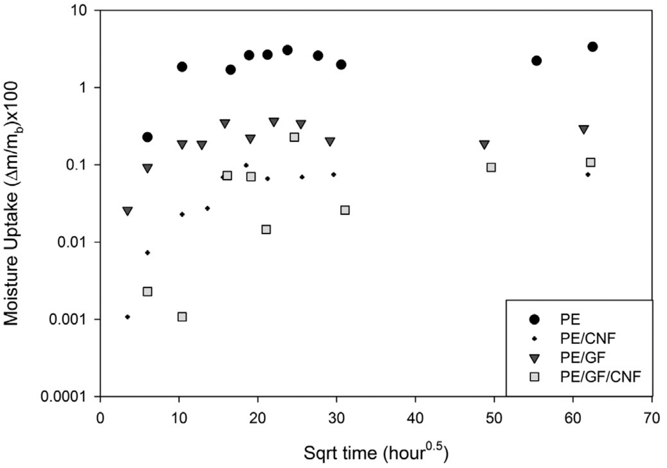

Fig. 1. Water absorption curves for neat polyester (PE), nano-enhanced polyester (PE/CNF), glass fiber reinforced polyester (PE/GF) and nano-enhanced glass fiber reinforced polyester (PE/GF/CNF) material systems.

2. Methodology

2.1. Specimen preparation/processing

Four distinct panels (nominally 254 mm × 254 mm × 3 mm) were manufactured: neat polyester (PE), nano-enhanced polyester (PE/CNF), glass fiber reinforced polyester (PE/GF) and nano-enhanced, glass fiber reinforced polyester (PE/GF/CNF). For each material system, the unsaturated polyester resin (Cook Composites & Polymers, C1-1001-25) was sonicated then degassed for a total of 30 min to remove trapped micro-bubbles.

For PE and PE/GF systems, 0.95 wt% of Methyl Ethel Ketone Peroxide (MEKP) curing agent was added to the resin after degassing then stirred for 5 min. The solution was then poured into a mold to obtain the neat panel; and was injected into a mold of 8 ply E-glass random chopped strand glass fiber mats (Saint-Gobain Vetrotex America INC, random chopped strand mat) via the Vacuum Assisted Resin Transfer Molding method (VARTM) [7] to obtain the glass fiber reinforced PE (GFRP) panel.

For the PE/CNF and the PE/GF/CNF material systems, the nano-enhanced resin was prepared by mixing 1 wt% carbon nanofibers (Pyrograf, PR-24 LHT) with the resin. This nano-enhanced resin was stirred, sonicated, and then degassed for 30 min. MEKP curing agent was added to the nano-enhanced resin and the solution was mixed for 5 min. This solution was then poured into a mold to obtain the nano-enhanced polyester panels; and was injected into a mold of 8 ply E-glass random chopped strand glass fiber via the VARTM method to obtain the nano-enhanced GFRP panels.

After each distinct material system was manufactured, at least 100 coupons (nominally 30 mm × 7 mm × 3 mm) were sectioned from each panel. The panel location of each coupon was noted. Furthermore, the coupons were placed in randomized predetermined locations in a furnace held at 40 °C for 36 h prior to baseline mass measurements.

2.2. Hygrothermal aging

After pre-drying, at least 3 baseline mass measurements of each specimen were taken using a precision balance (A&D Weighing, FX 300), averaged then denoted as the specimen's baseline mass, m_B. At this time 5 coupons from each system were removed for corresponding baseline optical and thermo-mechanical analysis. During environmental preconditioning, 95 coupons of each material system were aged in a 60 °C/60%RH temperature/humidity chamber. Mass measurements of a pre-selected subset of specimens from each system were taken at predetermined intervals. Moisture uptake, M(t), was determined from the average specimen's mass at time t, m(t), in relation to its pre-dried baseline mass [10,11].

$$M(t) = \frac{m(t) - m_B}{m_B} \times 100$$

When a group of specimens were removed from the temperature humidity chamber for both mass measurements and thermo-mechanical analysis, then 5 additional samples were simultaneously removed and placed in a desiccator for 2 months prior to characterization.

2.3. Characterization

2.3.1. Optical

Optical microscopy (OM) was used to analyze morphology using high resolution composite images with a Nikon Eclipse LV150 industrial microscope. Each viewing surface was generated by manually peeling between three and five plies of each specimen, exposing the central layers of that specimen. At least fifty two-dimensional (2D) images (optical slices with 1124 pixels × 843 pixels) were taken of the delamination surfaces in 5.5 nm z-steps with a recorded visual magnification of 1000×. RGB components in the acquisition color settings were adjusted to allow the CNFs to be readily distinguishable. For each material system and condition the 2D z-projection image was constructed from the associated 2D slices. All post processing was performed using NIS Elements version 3.22.14.

2.3.2. Thermo-mechanical

Dynamic Mechanical Analysis (DMA) was employed to determine the thermo-mechanical response for each material system after environmental exposure. All experiments were performed using a 3-point bend clamp with a 20 mm span length (TA Instruments, Q800) in multi-frequency strain mode. Experiments used a 1 Hz frequency and 15 μm amplitude while heating specimens from room temperature to 115 °C at a rate 2 °C/min to determine potential transitions. Glass transition temperature (T_g) was determined both by the onset temperature of the Storage Modulus (SM) – temperature curve as well as the peak in the tan δ – temperature curve [12].

Table 1
Effect of filler type on diffusion for neat, GFRP and nano-enhanced material systems.

Material system	Effective saturation, M_{eff} (g/g)	Initial slope of moisture uptake plot ($s^{-0.5}$)	Diffusion coefficient, D_{eff} (mm^2/s)
PE	2.87	3.21E-03	2.20E-06
PE/CNF	0.11	5.23E-05	3.79E-07
PE/GF	0.29	3.89E-04	4.84E-06
PE/GF/CNF	0.086	2.58E-06	2.14E-09