Effects of environmental aging on physical properties of aromatic thermosetting copolyester matrix neat and nanocomposite foams

Mete Bakir[a], Christine N. Henderson[d,e], Jacob L. Meyer[a,c], Junho Oh[a,g], Nenad Miljkovic[a,f,g], Maciej Kumosa[d], James Economy[b,c], Iwona Jasiuk[a,*]

[a] Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, 1206 West Green Street, Urbana, IL 61801, USA
[b] Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, 1304 West Green Street, Urbana, IL 61801, USA
[c] ATSP Innovations, 60 Hazelwood Drive, Champaign, IL 61820, USA
[d] Department of Mechanical and Materials Engineering, University of Denver, 2390 S. York St., Denver, CO 80208, USA
[e] Bureau of Reclamation, Denver Federal Center, Denver, CO 80225, USA
[f] Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, IL 61801, USA
[g] International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan

A R T I C L E   I N F O

A B S T R A C T

This paper focuses on the effects of cyclic water immersion and salt spray aging tests on the physical properties of aromatic thermosetting copolyester (ATSP) matrix. Neat and graphene nanoplatelet (GNP) incorporated nanocomposite ATSP foam morphologies are employed to have enhanced surface areas exposed to the surrounding aqueous media, via porous configurations, which deliberately aggravate the extent of the aging on the matrix. The ATSP foams are fabricated through a thermal condensation polymerization process. Upon exposures to the periodic aging conditions, ATSP demonstrates an adsorption-regulated mass uptake mechanism. Contact angle measurements reveal GNP-neutral and hydrophobic characteristics for the ATSP matrix. Microstructural imaging exhibits no substantial physical degeneration in the matrix caused by the accelerated aging conditions. Glass transition temperatures of both neat and nanofiller incorporated ATSP forms display only marginal decreases stemmed from small volumes in the matrix occupied through the hygroscopic swelling. Thermal degradation stability of the ATSP morphology is effectively preserved following the aging processes. Compressive mechanical strengths of the foams lie within the regime of their virgin (not exposed to the aging conditions) counterparts yet show slight reductions. The ATSP matrix demonstrates an outstanding aging resistance to the subjected environments which can potentially address high-performance requirements in cutting-edge industrial applications.

1. Introduction

High-performance/high-temperature (HP/HT) polymers demonstrate high physicochemical stability against severe environmental conditions while clearly outperforming conventional engineering and commodity polymers [1]. Well-known examples of the HP/HT polymers include poly ether ether ketone (PEEK), poly phenylene sulfide (PPS), and polyimide (PI) [2]. Particularly, due to their outstanding thermal degradation stability [3], high glass transition temperatures [4], and superior mechanical performance [5], the HP/HT polymers have found uses in a plethora of applications spanning coatings, composite matrices, fibers, foams, and membranes [6–8]. With the recent introduction of polymer nanocomposites, base thermophysical properties of polymers have been demonstrated to be considerably improved

through the addition of miscellaneous nanofiller particles [9–11]. Furthermore, when the polymer morphologies are supplemented with the multifunctional structural properties of nanocomposites, the use of polymers holds a great promise for high-end applications such as energy storage [12], biomaterials [13], recyclable/renewable materials [14], and additive manufacturing [15]. In order to achieve industrial implementation, the polymeric domains need to sustain superb degradation stability through chemical inertness and low moisture absorption in various aqueous solutions while preserving the virgin physical properties and to maintain long service lives.

In a broad sense, polymers have three main degradation mechanisms: (1) physical, (2) chemical, and (3) hydrothermal [16]. First, physical aging involves the combined effects of stress, temperature, and time which result in physical property changes without permanent

---

modifications to chemical chain configurations. Physical aging is also a thermally reversible process so that upon heating above the glass transition temperature, the virgin polymer properties can be recovered [17]. Second, chemical aging takes place at elevated temperatures through exposure to damaging environments which can drastically alter physical properties. In particular, thermal, photochemical, and radiochemical environments can irreversibly decompose chain arrangements at the molecular level [16], [18]. Lastly, hydrothermal aging occurs in the presence of moisture at high temperatures that ultimately triggers a physical aging process. In such conditions, diffusion of water molecules into the matrix degenerates the interaction mechanisms within chain networks (e.g. swelling effect). Hence, increased chain mobility accelerates physical aging which leads to plasticization of the matrix and subsequent formation of microcracks [19]. Considering all these deterioration mechanisms, promising polymer systems to be employed in the industrial applications should demonstrate excellent resistance to aging phenomena when subjected to hostile environments for long durations.

Aromatic thermosetting copolyester (ATSP) was developed in the late 1990s utilizing low cost and easily processable oligomers to design a high-temperature/high-performance polymer system [20–22]. ATSP can be conveniently prepared into various forms including coatings [23], continuous fiber composites [24], thick section/bulk machinable parts [22], adhesives [25], and foams [26]. Compared to other contemporary HP/HT polymers, ATSP demonstrates superior mechanical properties, including unfilled fully dense compressive strengths approaching 300 MPa [22], enhanced thermal degradation performance, and glass transition temperatures up to 310 °C [22]. In addition, ATSP can be used as an ablative material with very high limiting oxygen index (LOI) [27], as a tribological wear coating with a low coefficient of friction, excellent wear and abrasion resistance [23], and as a dielectric material with high dielectric constant and breakdown strength for microelectronics applications [28]. Earlier work on ATSP studied moisture transport characteristics under various temperatures and humidity conditions for its different chemical structures [29]. The study showed that below 100% relative humidity (RH) at room temperature, the moisture uptake proceeded via diffusion, while increased RH and temperature caused the diffusion to progress through an irreversible relaxation mechanism. In this work, we study the effects of water immersion and salt fog spray aging environments on the physical properties of the neat and nanofiller incorporated nanocomposite forms of ATSP. We utilize foam morphology of ATSP to enable increased surface-area-to-volume ratio to accelerate the deterioration mechanisms. We analyze moisture sorption behavior of the structures as well as image the microstructural features after exposure to understand the physicochemical response of the ATSP matrix to the aging environments. We also characterize changes in glass transition temperature, thermal degradation performance, and compressive mechanical properties of the neat and nanocomposite foams.

2. Materials and experimental details

2.1. Fabrication of neat and nanocomposite aromatic thermosetting copolyester foams

The neat and nanocomposite ATSP foams were fabricated via a condensation polymerization reaction between carboxylic acid and acetoxy functional groups in matched oligomer sets. The oligomer groups were initially mixed in solid state at a 1:1 wt ratio. Upon the polymerization process, the oligomer mixture developed a cross-linked aromatic polyester backbone and released acetic acid as a reaction by-product. The acetic acid behaved as a foaming agent during the polymerization process that eventually promoted a porous morphology [26]. The carboxylic acid and acetoxy-capped oligomers were synthesized using biphenol diacetate (BPDA), 4-acetoxybenzoic acid (ABA), isophthalic acid (IPA), and trimesic acid (TMA) (Sigma-Aldrich Co.,

USA) as detailed in prior literature [22] [25], [26]. To fabricate nanocomposite foams, the constituent oligomer groups were additionally incorporated with graphene nanoplatelet (GNP) nanofillers of 3 wt % in solid state at room temperature [30]. The GNP nanofillers (Grade M − 5, XG Sciences, Inc., USA) (flake diameter: ∼5 μm, thickness: 6–8 nm, density: 2200 kg/m^3) were used as received. The neat and nanocomposite foams were obtained by applying a thermal cure cycle to the mixed oligomer and oligomer-nanofiller combinations [26] [30], [31]. The thermal cure cycle comprised of two temperature-dwell stages at 202 °C for 90 min and 270 °C for 150 min, which enabled effective structural relaxation/melting of the constituent oligomers while facilitating blending of the GNP nanoparticles, and nucleation/bubble growth through the release of the acetic acid to form the porous morphology, respectively. Additionally, the thermal cycle had a final cure stage at 330 °C for 90 min. The neat foam and nanocomposite foam refer to neat ATSP and ATSP-GNP loading levels in weight percent, respectively. To characterize the advancing and receding contact angles with water, the ATSP and ATSP-nanofiller powder combinations (2 wt % and 5 wt %) were coated on smooth steel plates using an electrostatic powder coating method and then cured via the applied thermal cycle [23], [32].

2.2. Water immersion and salt fog tests

Accelerated salt spray tests were carried out using a Q-FOG model SSP600 apparatus (Q-Lab Corporation, USA) in accordance with the ASTM D5894 standard during cyclical salt fog conditions. The corrosive electrolyte used during exposure was a dilute Harrison's solution (DHS) including 3.5 wt % ammonium sulfate ($(NH_4)_2SO_4$) and 0.5 wt % sodium chloride (NaCl). Water immersion tests were conducted for extended immersion periods in deionized water in accordance with ASTM D870. The specimens were kept immersed at all times and were only removed for weight measurements once a week.

2.3. Methods of physical characterization

Water immersion and salt spray specimens were patted dry prior to weight measurements. Weight measurements were obtained once a week using a digital scale with a resolution of 0.001 g. Physical characterization measurements were performed on 2-week and 4-week exposed specimens. Scanning Electron Microscopy (SEM) (S-4800, Hitachi, Japan) was operated in high-resolution upper detector mode (10–15 kV voltage, 5–10 μA current) to image microstructures of water immersion and salt fog exposed neat and the nanocomposite foams to analyze local degradation effects. The samples were sputter coated for 20–30 s with Pd-Au (≈10 nm thickness) to minimize charging effects.

The contact angle measurements were carried out by placing ≈100 nL water droplets on the steel coated samples using a microgoniometer (MCA-3, Kyowa Interface Science, Japan). The droplets were deposited on the surface using a piezoelectric injector at a rate of 70 droplets/sec. Both advancing and receding contact angles were characterized on multiple spots of the sample surface. The contact angles were analyzed using a commercial software (FAMAS, interFAce Measurement & Analysis System) with the half-angle method. The results were averaged over 10 measurements.

Glass transition characterization of the nanocomposites was carried out using a Dynamic Mechanical Analyzer (DMA) with a tensile clamp fixture (Q800, TA Instruments, USA). A temperature-ramp cycle was operated with a 3 °C/min heating rate. The specimens were in prismatic geometries in dimensions of 5 × 10 × 25.4 mm^3 (thickness x width x length). The tests were performed in air. The glass transition characteristic curve of the virgin neat ATSP was obtained from a previous study [26].

Thermal degradation stability of the nanocomposite foams was characterized using a thermogravimetric analyzer (TGA) (TGA2950, TA Instruments, USA). A temperature-ramp heating cycle was applied with