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Accelerated environmental degradation and residual flexural analysis of carbon nanofiber reinforced composites

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ABSTRACT

Hollow particle filled composites known as syntactic foams presently find numerous applications in structures exposed to high moisture and high temperature environments. Carbon nanofiber (CNF) reinforcement is attractive in these composites because of the possibility of increased strength with negligible density variation. In the present study, syntactic foams containing 15–50 vol% glass microballoons (GMB) and 1–5 wt% CNF reinforcement as well as CNF/epoxy composites containing 1–5 wt% CNF were exposed to accelerated weathering by immersion in 90 °C water for two weeks and characterized for their residual flexural properties. In the worst performing composites, a maximum weight gain of 3.5% and 10% was observed for CNF/epoxy and CNF/syntactic foam composites, respectively. The syntactic foams tested were observed to generally decrease in strength after weathering with the exception of the composites containing 5 wt% CNF and 15 vol% GMB, which were observed to increase in strength by 41–51% after weathering. The composite containing 5 wt% CNF was also shown to increase in strength by 27% after weathering. Strength retention is attributed to the presence of CNF, along with competing weathering effects on composite structure and morphology.

1. Introduction

Syntactic foams are hollow particle filled composite materials which, in the present work, consist of glass microballoons (GMBs) dispersed in an epoxy resin matrix. Syntactic foams are used in marine and aerospace applications [1–3], where these materials may be exposed to high moisture content including total immersion for their entire working life at temperature extremes [4,5]. The matrix, matrix–particle interface and hollow particles may interact with water and may have their own degradation mechanisms affecting the properties of syntactic foams over short and long term exposures [6–9]. Therefore, understanding of the moisture absorption characteristics and degradation mechanisms of these composites is critical for existing and potential future applications.

A comprehensive literature review of environmental degradation of syntactic foams is presented in a recent publication [7]. A variety of studies are now available on the effect of moisture and temperature on syntactic foams, which include studies on the tensile and compressive properties after moisture exposure [4,10–15]. Other environmental studies performed on syntactic foams have included analysis of residual flexure properties [6,10,16], thermal/electrical conductivity [2,5,8], permittivity [17–19], and dynamic mechanical properties [9]. Syntactic foams reinforced with an additional phase have been characterized in several existing studies [20]. Most of the available literature has focused on GMB reinforced syntactic foams. It is observed that the commonly used sodalime borosilicate particles may degrade due to dealkalization in contact with water [7]. Sufficient degradation of GMB walls due to dealkalization can open up the porosity enclosed inside them for moisture accumulation. Particles are the major load bearing elements in the material under compression [21,22], therefore, their degradation leads to severe reduction in compressive properties. One of the additional effects of such degradation is that the particle–matrix interface is also severely degraded, such that the strength and modulus of the overall composite are observed to decrease [7]. Moisture effects on plain syntactic foams have been studied at high temperature, where several additional factors are found to contribute to the degradation of syntactic foams [12]. It is observed that the thermal expansion of the matrix at high temperature can also increase the moisture uptake because of reduced resistance to moisture diffusion in the polymer. The

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mismatch in the coefficient of thermal expansion of matrix and particle material can result in high thermal stresses and rapid degradation of the particle–matrix interface.

Reinforcement of syntactic foams with fibers is of great interest to improve their tensile and flexural properties. Extensive work has been performed in the field of polymer matrix nanocomposites [23–25], which can be exploited to improve the properties of syntactic foams. The inclusion of carbon nanofiber (CNF) reinforcement in syntactic foams [26–29] has been recently explored because small quantities of CNFs added to syntactic foams can greatly enhance their mechanical properties [3,30,31]. A rich body of literature is available on the degradation of carbon nanocomposites [32–35] but few have studied nano-reinforced syntactic foams. The moisture degradation of CNF reinforced syntactic foams has been studied at room temperature for long-term water immersion [7]. Evidence of particle degradation was detected in that study and reduction in mechanical properties was also noted. In epoxy and vinyl ester matrix syntactic foams under flexural loading, brittle fracture begins on the tensile side of the specimen. Thus, the flexural properties of syntactic foams show a stronger dependence on the matrix resin properties and are less sensitive to the wall thickness of the particle. Reinforcement of the matrix with fibers can improve the flexural properties of syntactic foams. In the present work, CNF reinforced syntactic foams (referred to as CNF/syntactic foams) are exposed to accelerated weathering through immersion in water at 90 °C for a period of two weeks. The GMBs have been shown to considerably degrade in water within 1 week at such temperatures [7]. Total water uptake and residual flexural properties are measured and analyzed for the exposed syntactic foams.

2. Materials and methods

2.1. Constituent materials

DER 332 epoxy resin (DOW Chemical Co., Midland, MI) cured with triethylene tetramine hardener (Huntsman Co., The Woodlands, TX) is used as the matrix resin. Three compositions of CNF/epoxy composites and fourteen compositions of CNF/syntactic foams are fabricated for this study. GMBs supplied by 3 M (St. Paul, MN), of 220 and 460 kg/m^3 nominal true particle densities, are used in 15, 30 and 50 vol% in different types of syntactic foams. The various compositions fabricated for this study are illustrated in Fig. 1. CNF/epoxy composites are fabricated with 1, 2, and 5 wt% CNFs, procured from Pyrograf Products, Inc., (Cedarville, OH). Vapor grown PR-24 XT-PS CNFs are used in the study (the nomenclature "XT" and "PS" denote that the CNFs have been debulked and have been pyrolytically stripped of aromatic hydrocarbons, respectively). In CNF/syntactic foams, the weight fraction of CNFs is calculated with respect to only the matrix system. The densities of CNFs and the epoxy resin are taken as 1950 and 1160 kg/m^3, respectively, from the manufacturers' datasheets. The composite nomenclature follows the trend where N represents CNF reinforcement, followed by CNF content, GMB density, and GMB volume fraction; for example, N1-460-15 represents a grade of CNF reinforced syntactic foam containing 1 wt% CNF and microballoons of 460 kg/m^3 density at a volume fraction of 15 vol%. The viscosity of the mixture during stirring increases at higher CNF content and makes it difficult to uniformly mix large amounts of GMBs without breaking them. Therefore, fewer compositions, having lower GMB content, are studied at high CNF content.

2.2. Specimen fabrication method

Specimen fabrication is conducted according to the previously optimized procedure described in Ref. [29]. A mechanical mixer with a high shear impeller is used to obtain uniform dispersion of CNFs in the epoxy resin [36]. GMBs and the hardener are then added and slowly mixed by hand using a wooden dowel for 15 min so that the GMBs are uniformly dispersed and then cast in aluminum molds. This mixing method has previously been used to achieve satisfactory dispersion of CNF without clustering as well as uniform dispersion of GMB without breakage. The mixture is cured at room temperature for 24 h and post-cured in a convection oven for 2 h at 90 °C.

2.3. Flexural testing

Flexural properties were measured using an Instron 4469 mechanical test system equipped with a 50 kN load cell and Bluehill 2 software (Instron, Norwood, MA). Specimens had the nominal dimensions of 3 × 11 × 95 mm^3. The flexural testing was conducted under a three-point bend configuration using cylindrical supports of 10 mm diameter and a specimen span length to thickness ratio of

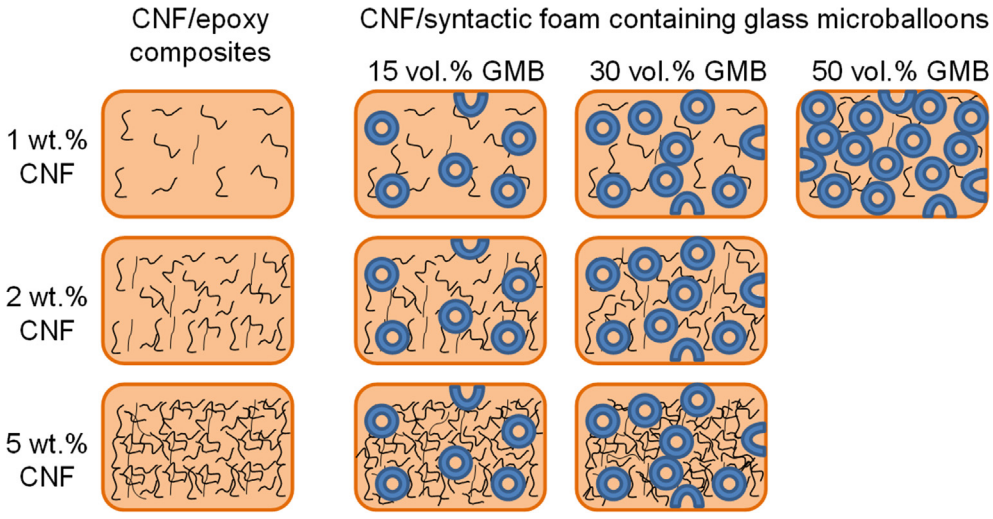

Fig. 1. Compositions of CNF/epoxy composites and CNF/syntactic foams studied. The black lines represent the CNF while the blue open circles represent the GMB. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)