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Moisture uptake characteristics of a pultruded fibre reinforced polymer flat sheet subjected to hot/wet aging

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ABSTRACT

This paper studies the moisture uptake characteristics of a pultruded E-glass fibre reinforced (isophthalic polyester) polymer after long-term exposure to hot/wet conditions. Both fully exposed samples of varying aspect ratios and selectively exposed samples were immersed in distilled water at 25 °C, 40 °C, 60 °C and 80 °C for a period of 224 days. For the fully exposed condition, bulk and directional diffusion coefficient values were determined. A three-dimensional approach using Fickian theory was applied to approximate the principal direction diffusions at 60 °C by using mass changes from samples having different aspect ratios. This revealed that the diffusion coefficient in the longitudinal (pultrusion) direction to be an order of magnitude higher than in the transverse and through-thickness principal directions. Diffusion coefficients in the three principal directions have also been determined for the selectively exposed condition at 60 °C through the application of one-dimensional Fickian theory. It was found that the size and shape of the samples influences moisture uptake characteristics, and thereby the values determined for bulk and directional diffusion coefficients. Furthermore, the influence of exposure temperature on moisture uptake and mass loss with time was examined. Investigation of the water medium by means of electrical measurements suggested that decomposition of the polymeric composite initiates very early, even after the very first day of immersion. Comparison between the infrared signatures from the pultruded material and the water's residual substances revealed significant decomposition, and this behaviour is verified by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopic (EDS) analysis as well as the recorded mass loss after 224 days of aging.

1. Introduction

The eagerness for low-cost, high performance and lightweight engineering structures has led to the promotion of Fibre Reinforced Polymer (FRP) composites [1]. In particular, Pultruded FRP (PFRP) shapes and systems are being increasingly used in aerospace, civil and naval engineering applications. They commonly consist of E-glass fibre reinforcement (layers of unidirectional rovings and continuous filament mats) in a thermoset (e.g. polyester or vinylester) resin based matrix. PFRP material has a density about one quarter of steel. Longitudinal tensile strength can be over 200 N/mm^2 and comparable with structural grade steel. The longitudinal modulus of elasticity, at 12–30 kN/mm^2, is up to 17 times lower, whereas the modulus of elasticity perpendicular to the direction of pultrusion is one-quarter to one-third of the longitudinal value. Shear properties are also matrix governed with in-plane strength of 30–80 N/mm^2 and in-plane modulus of 3–5 kN/mm^2. One of the advantages of this construction material over conventional materials is that it is corrosion-resistant in relatively aggressive environments, such as found in aqueous mediums. PFRPs shapes and systems are being extensively considered for primary and secondary structural elements in civil engineering works [2]. The environmental service conditions in any field applications may affect the material's intrinsic structural properties, increasing the probability of failure before the end of the structure's service life. Generally, civil engineering structures are designed for a working

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life of more than 50 years, ideally with minimal maintenance [3]. Long-term property retention is of critical importance to engineers when managing assets and planning for their routine inspection and maintenance. Due to the hydrophilic nature of both the E-glass fibres and the polymer matrix (e.g. due to the ester-end groups), moisture uptake into FRPs is a crucial phenomenon when determining material deterioration and time varying mechanical properties for structural engineering [4]. A thorough investigation into the mechanisms which lead to environmental aging is essential if we are to have reliable and safe designs [5–7].

Understanding how moisture affects the durability, and long-term mechanical property retention, in aggressive environments has to be a prerequisite before any FRP can be qualified as an engineering material [2,8]. At most civil engineering sites the service environment involves, in combination with other actions, the presence of moisture in various forms. Prolonged exposure to moist environments results in both reversible and irreversible internal material changes. Reversible changes are said to be physical, and will recover when the FRP is dried. Physical aging involves changes in the mechanical properties and volume as material swells from the water ingress [9]. Swelling is the resistive reaction to hygrothermal exposure and causes changes in residual stresses. Chemical degradation is irreversible and induces property changes in the polymer matrix, fibre reinforcement, as well as the fibre/matrix interface. Typically, it has been established that the polymer matrix is more prone to damage than the fibre reinforcement [2]. Chain scission, residual cross-linking, hydrolysis, oxidation and plasticization are known major effects of moisture concentration in the polymer [10]. Furthermore, when moisture penetrates throughout the FRP, it may attack the E-glass fibres in the form of stress corrosion, leading to overall deterioration of mechanical properties [11]. The fibre/matrix interface is the crucial component that couples the matrix with the fibres. This constituent is susceptible to chemical degradation in the presence of moisture, which reduces the adhesion [12,13] and enhances interfacial capillary (or wicking) action by exposing the reinforcement surface for the promotion of fibre degradation. It is known that the performance of the interface is always dependent on the chemical, physical and mechanical interaction between fibres and the polymer matrix. Matrix plasticization and interface failures are reported to be the most effective in reducing the bulk mechanical performance [8]. In all situations, it is evident that water ingress has a negative effect on mechanical properties, either by instigating or speeding up the evolution of various forms of internal degradation/damage. Upon moisture uptake, H_2O molecules may either diffuse through the polymeric structure's inherent micro-voids (called 'free volume' or 'free space') and any present porosity or micro-cracks (i.e. from matrix shrinkage after curing), or travel via a capillary phenomenon along the fibre/matrix interfacial regions [7,14]. 'Free volume' or 'free space' refers to the unfilled voiding in a polymer structure that is not occupied by polymer molecules and is the subtraction of the total measured volume of the polymer by the actual volume that is 'filled' with polymer molecules [9].

Long-term exposure in hot/wet conditions has been employed by many researchers [7,15,16] as a means of accelerating aging in order to obtain characterization test results that can forecast the FRP's long-term behaviour. Such an accelerated process speeds up the environmental aging process by taking advantage of the coupling effects formed by temperature and moisture [1,15]. It is the presence of extra thermal energy from an elevated temperature that enhances molecular mobility and accelerates the rate of degradation compared to what would be experienced under field conditions.

This paper reports experimental findings of an extensive investigation regarding the effects of moisture uptake on an 'off-the-shelf' PFRP material (flat-sheet) as part of the EPSRC funded DURACOMP project called 'Providing Confidence in Durable Composites' (EP/K026925/1). Samples were immersed in distilled water at four different constant temperatures of 25 °C, 40 °C, 60 °C and 80 °C for up to 224 days, following the test methodology of Bank et al. [1]. Moisture uptake characteristics were determined by a complementary investigation involving moisture uptake tests on both fully exposed (i.e. all six surfaces unsealed) and selectively exposed (i.e. four surfaces sealed) type of samples. Different sample dimensions were examined and their dimensional effects on the uptake behaviour are discussed. It was found that, different sample sizes and geometries significantly affect the results. Three different approaches involving Fickian theory were used to calculate diffusion coefficients. Fully, and selectively exposed samples were employed to calculate bulk and directional diffusion coefficients, respectively. In addition, electrical measurements and Fourier Transform Infrared Spectroscopy (FTIR) were employed to study the water uptake effects occurring due to hot/wet aging. The infrared spectrums of the un-aged PFRP and the water medium (residual substitutes) were analyzed and discussed. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopic (EDS) analyses assisted in the determination of the source of chemical decomposition found to cause substantial mass loss.

2. Accelerated aging and moisture uptake in FRPs

Long-term assessment of a material's durability in a short and realistic period of time (i.e. one year) could be experimentally feasible by applying accelerated aging. The process requires hygrothermal exposure and relies on the superposition of temperature and moisture to enhance and speed up environmental degradation. In order for accelerated aging to provide a realistic prediction of long-term service behaviour, the maximum exposure temperature according to Bank et al. [1] has to be lower, by i.e. 20 °C, than the polymer's glass transition temperature, T_g. It is recognized that secondary (and unwanted) degradation mechanisms will become activated when the exposure temperature approaches or exceeds T_g, and under this conditioning the accelerated aging fails to simulate the required aging process for field applications [8,15]. The degree of hygrothermal degradation is known to depend on the temperature and its adjacency to the polymer's T_g. Research reported by Surathi et al. [8]. shows that the higher the exposure temperature the higher is the moisture uptake rate and saturation content, as a consequence, the FRP reaches moisture saturation in shorter time periods than it can do so under field conditions.

Several theoretical approaches to modeling the moisture uptake process have been proposed [8,17,18]. From the many, Fick's theory is frequently reported for its suitability in determining moisture

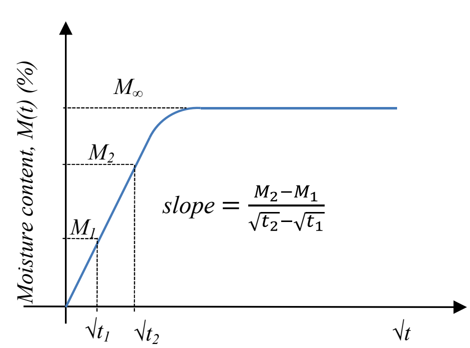

Fig. 1. Representative of a classical Fickian diffusion three-stage curve for $M(t)$ vs. $\sqrt{t}$.