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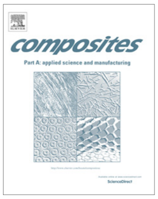

Impedance spectroscopy as a tool for moisture uptake monitoring in construction composites during service

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ABSTRACT

This is a first study comparing dielectric spectroscopy and gravimetric measurements of moisture uptake in pultruded glass fibre reinforced polymers (FRPs). Specimens were subjected to sub-Tg hygrothermal aging for 224 days. Impedance spectra in the frequency range 0.1 Hz to 10 MHz were captured during exposure and compared with gravimetric measurements. Moisture concentration was found to increase the FRP's dielectric permittivity monotonically and decrease bulk resistance. High quality dielectric data was obtained as moisture uptake is independent of inherent changes suggested by mass loss which compromise gravimetry. Dielectric measurements remained sensitive to moisture despite significant mass loss, which typically distorts the weight gain process complicating the commonly adopted gravimetric methodology. Real-time dielectric measurements were obtained from FRP specimens continuously immersed in water and without making use of any additional sensing elements. The novel approach adopted is of high commercial impact as moisture uptake control is recognized as a significant problem by industry.

1. Introduction

Pultruded FRPs are commonly used materials in the civil engineering sector. They are usually employed as primary and secondary structural elements providing high resistance to extreme environmental conditions [1,2]. Compared to conventional engineering materials such as steel, FRPs possess high strength and stiffness-to-weight ratios as well as flexibility in the design of complex shapes [3–9]. In addition to bridge engineering, civil FRPs [10] are used in a variety of other engineering applications including facades, off-shore and on-shore platforms, wind turbine blades, ladders and composite utility poles [6,11,12], as well as reinforcement of concrete [13] and steel [14] structures.

It took many years for FRPs to enter the civil engineering market due to the increased manufacturing costs and lack of long-term service experience. The latter combined with the high retrofitting costs and the extensive maintenance regime has increased the need for efficient structural health monitoring in-service, which is crucial to the widespread adoption and safe design of FRP structures [15].

The primary cause of FRP structural degradation during service is environmental aging [15]. It has long been known that moisture absorbed during service has deleterious effects on FRPs' structural performance [1,15–17]. Absorbed moisture influences the electrical [18], physical, chemical and mechanical properties inducing both reversible and irreversible changes [19]. Reversible changes are physical, involving dimensional and mechanical property modifications [20]. Irreversible changes are attributed to chemical reactions resulting in permanent property changes. Matrix cracking, chain scission, residual cross-linking, hydrolysis, oxidation, softening and plasticization are the major effects of such moisture absorption [21,22]. In FRPs, moisture penetrates the surface and then diffuses and/or 'wicks' in the interior of the composite structure. Fibre/matrix interfacial loss reduces the adhesion between the fibre reinforcement and the matrix [23,24] enhancing interfacial capillary action by uncovering the reinforcement and therefore promoting fibre degradation. It has also been reported that moisture also attacks the fibre reinforcement itself, leading to significant mechanical property loss [25]. Capillary action or 'wicking' along the fibre reinforcement/matrix interface has been shown to be more pronounced than moisture diffusion within the composite matrix [26] which is verified by the higher amount of absorbed

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moisture uptake in reinforced composites vs. plain resin polymers [27,28].

Water in composites can exist in different forms; free water molecules (unbound) which have diffused into the 'free-volume' from the outer surface of the composite, and water bound with the polymer matrix chain network [29]. Bound water is reported to induce the chemical interactions with the matrix compounds and is extremely difficult to be removed after drying [30–32]. Moisture concentration increases with time and reaches a saturation point after an extended period of time which is always dependent on the exposure temperature, the type and thickness of the material. Generally, moisture absorption in polymer composites follows a Fickian diffusion trend [15]. However, Fickian theory is unable to describe the moisture diffusion process when significant mass loss due to chemical decomposition occurs simultaneously with moisture absorption [33]. Other models have also been documented to describe the moisture diffusion kinetics, such as the Langmuir model [34]. Fig. 1 depicts 3 moisture uptake vs. time curves that are representative of (a) a classical Fickian diffusion three-stage curve with no mass loss, (b) a diffusion curve affected by mass loss taking place, and, (c) a 'true' diffusion curve when mass loss takes place without affecting the moisture uptake measurements.

For the assessment of moisture absorption characteristics, the gravimetric methodology has been largely employed by many researchers in both fully immersed and humidity-exposed conditions [3,15,20,33,35,36]. However, interpretation of gravimetric data becomes challenging when swelling, polymer relaxation and chemical decomposition processes take place at the same time as moisture absorption [37]. Dimensional changes due to swelling differentiate the 'free-volume' [20]. Chemical decomposition results in significant mass loss. This mass loss, which stems from the initial dry mass of the material, masks the mass gain due to moisture absorption [33]. Here an innovative method of probing moisture absorption in polymer composites via Electrical Impedance Spectroscopy (EIS) [38,39] is presented. Impedance spectroscopy is efficiently employed to capture moisture ingress independently of mass loss. Preliminary experiments of the present work were published in [40]. Conventional EIS has been extensively used to study corrosion of metallic materials [41] and metal coatings [42]. Dielectric property measurements have been applied to monitor curing of polymer matrix composites [43,44], environmental degradation [45], damage [46–48] as well as the dispersion of nano-particles in polymer matrices [49,50]. Impedance spectroscopy measurements have been used to study moisture movement in mortar based construction materials [51,52] in addition to the more recent use in medical applications for moisture monitoring of wound dressings [53].

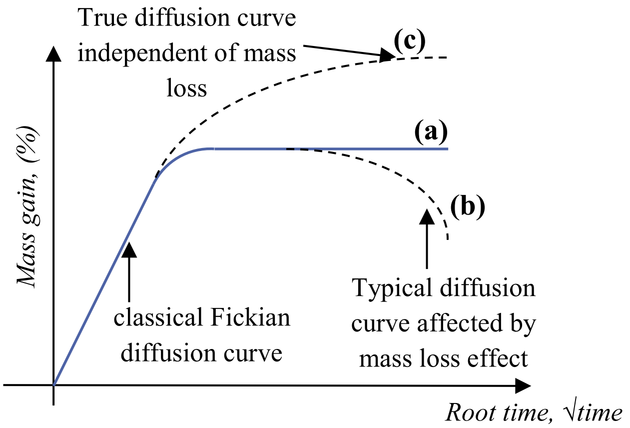

Fig. 1. Representative plot of (a) a classical Fickian diffusion three-stage curve with no mass loss, (b) a diffusion curve affected by mass loss and (c) a 'true' diffusion curve when mass loss takes place without affecting moisture uptake measurements for *Mass gain* (%) vs. $\sqrt{t}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

EIS is very sensitive to the presence of water due to the charge associated with the dipoles of water molecules [39,54]. Impedance measurements are expressed by the dielectric properties of the interrogated polymer composite coupled with the dielectric properties of the absorbed moisture [55]. The amount of moisture absorbed can be correlated directly with changes in the dielectric properties of the system. Impedance measurements involve the imposition of an AC potential field in a capacitor-like form. This field polarizes both the polymer and the water molecules (dipole polarization of the polar groups) inducing a frequency dependent displacement.

Maffezzoli et al. have used dielectric measurements to monitor water uptake characteristics in epoxy resin materials exposed to hygrothermal environments. Permittivity changes were used to determine moisture diffusion coefficient values and were evaluated against conventional gravimetric measurements. However, quantitative measurements of water uptake were not feasible. In the same work, an embedded dielectric sensor was adopted to record permittivity changes of samples that had to be removed from the aging medium for measurement [56]. Fraga et al. studied moisture uptake in polyester matrix glass [57] and jute [58] reinforced composites via the dielectric response and gravimetric measurements. Again, the interrogated samples were removed from the aging baths for the mass and dielectric measurements to be recorded. An increase in dielectric constant with moisture absorption was observed. Estimation of diffusion coefficient was also performed. However, quantitative measurements of moisture content were not made. Maxwell et al. studied the dielectric response of epoxy resin absorbing moisture over extremes of temperature (−60 °C to 70 °C) and distinguished the effect between 'unbound' and 'bound' water [59]. It was found that the behavior of dielectric conductivity is correlated with the water's molecular mobility. Chauffaille et al. applied electrical impedance spectroscopy to measure moisture uptake characteristics in thin polymeric adhesive films [39]. Moisture diffusion coefficient and moisture content were measured by bonding thin aluminum sheets to the polymeric film to act as measuring electrodes. In this work a methodology for permittivity suggested by Brasher and Kingsbury in 1954 was adopted [60]. Davis et al. demonstrated similar studies in adhesively bonded joints [55] as well as CFRP-reinforced concrete structures. Moisture ingress increases the amount of polar molecular fragments (contribution of both the large dipolar character and high mobility of polymer molecules) and therefore increases further the permittivity and phase delay [61,62]. As a consequence of the presence of mobile water dipoles, the overall conductivity of the exposed material is expected to increase at higher values of moisture ingress [63].

Although, it has been evident that impedance spectroscopy is sensitive to the presence of moisture or changes in moisture content, it is challenging to ascribe changes in impedance measurements to changes in moisture content alone. The dielectric properties of a polymer-water system are influenced by the nature of interaction between the water molecules (bound or unbound), the interrogated material, the polarization of the tested material and the surrounding system, the measuring electrodes as well as the electrical properties of the interrogated system as a whole. These parameters play a significant role in the dielectric measurements. Since dielectric changes are strongly associated with changes in moisture content, they carry important information that may be utilized as an efficient indicator of characteristics