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In situ monitoring of organic coating swelling by dynamic mechanical analysis and scanning electrochemical microscopy

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ABSTRACT

During hygrothermal ageing of organic coatings, the water uptake leads to a modification of barrier properties and to a possible swelling which is difficult to estimate. In this work, a DGEBA/DAMP polyepoxide resin with a thickness about 100 μm, completely cross-linked, was allowed to swell under two conditions: as free films and as coatings applied onto a metallic substrate. The swelling kinetics of the free films are in situ monitored using immersed dynamic mechanical analysis (DMA) tests, while the swelling kinetics of the coatings are estimated in situ by using the scanning electrochemical microscopy (SECM).

It is shown that the maximum dimensional changes of the DGEBA/DAMP resin during the water absorption are about 5% for the coatings while they are only about 2% for the free films. This difference can be explained by the fact that, in the case of the coating, the metal substrate can constrain the polymer in the plane which affects the swelling upon water absorption by the relaxation of internal stresses developed during the curing process. We also mention the technical aspects when using SECM and DMA as convenient methods to evaluate the swelling.

1. Introduction

The swelling is a phenomenon that appears when a solvent (e.g., water) enters a polymer. The volume of the solvent tends to be additive in the polymer network, causing the dimensional growth of the system. The swelling is also a kinetic process generally associated with the disruption by water molecules of the intermolecular hydrogen bonds within macromolecular chains [1]. Two types of water interact with the polymer matrix: free water and bound water [2]. The free water can reside in the free volume of the polymer network and may lead to the formation of free water clusters [3–5]. The bound water is connected to the polar groups of the polymer chains by intermediate hydrogen bonding, which is proposed to be responsible for swelling [2].

Many studies were performed to investigate the water absorption processes in polymers and/or coatings [4–13]. The water uptake is often estimated by gravimetry but this method is only applicable to free films. For coated substrates, electrochemical impedance spectroscopy (EIS) can be performed to measure the water uptake using the empirical relationship proposed by Brasher and Kingsbury [14]. It is important to note that this relationship considers a homogeneous diffusion of water in the polymer, the absence of interactions between the solvent and the polymer and the absence of swelling of the coating. Both methods allow obtaining water sorption curves and then, the water content and the water diffusion coefficient into polymer films using the Fick's law. In the case of experimental non-fickian sorption curves, some authors modified the Fick's law by the inclusion of a swelling coefficient to better model the water uptake process [12,15]. However, this empirical factor is not linked to the physical properties of the polymer matrix. Several research groups had worked onto the theory of swelling kinetics. Tanaka and Fillmore [16] proposed a linear diffusion equation by treating the swollen polymer as a mixture of solid polymer network and solvent with a friction coefficient for the interaction. Bouklas and Huang [17] compared the linear and nonlinear theories for the swelling kinetics of a polymer gel. However, few works have been done to measure experimentally the swelling kinetics of both free films and coated substrates. Hayward's group investigated the swelling kinetics of thin gel layers with thicknesses ranging from 76 to 504 μm by using the fluorescence microscopy [18]. The authors proved that the experimental swelling (up to 80%) for free films and coatings are not the same using the linear poroelasticity theory. Different techniques can be applied or adapted to measure the swelling of free films and/or coatings [19]: the buoyancy force (Archimedes principle) is not applicable for thin free films, the optical microscopy is difficult

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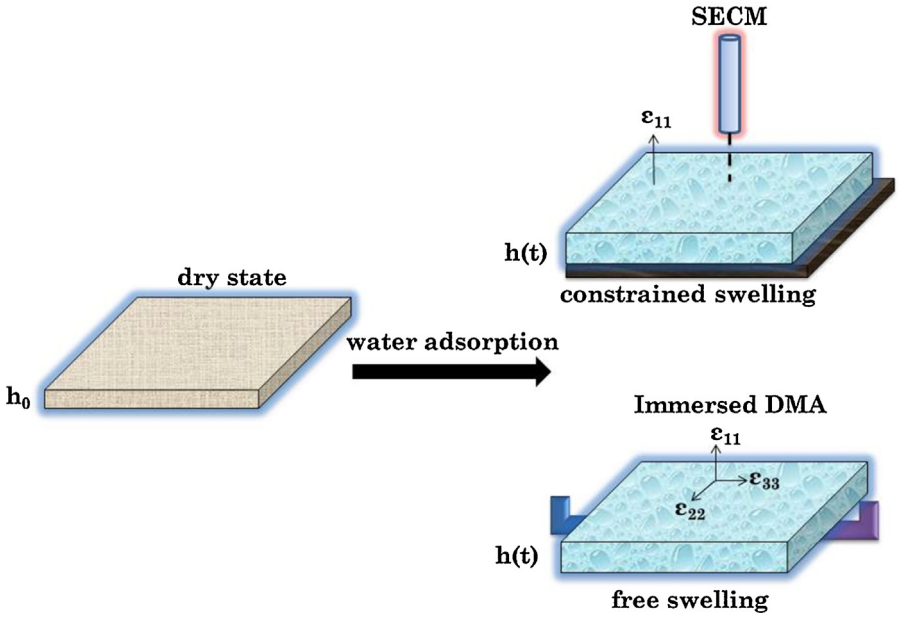

Fig. 1. Schematic illustration of a free film subjected to free swelling and the coated substrate under constrained swelling. The thickness h_0 is about 100 μm. The free film is assumed to be isotropically swollen in three directions.

to apply to transparent polymers, ellipsometry needs to prior know the refractive index, and the quartz crystal microbalance was also employed but it considers that the mass gain is correlated to the swelling at a constant density. The scanning electrochemical microscopy (SECM) was used to observe the swelling of coil-coated sheet but the dimensional changes were not quantified [20].

In the current work, we present two convenient methods to in situ monitor the swelling of an epoxy resin under two conditions shown in Fig. 1, namely, free swelling and constrained swelling. A thin free film undergoes swelling freely in the three directions with three deformations ε_{11}, ε_{22} and ε_{33}. The coating attached to a rigid substrate can swell only in one dimension due to the stress imposed by the adhesion to the substrate. It can then be supposed that the boundary conditions for the coating are $\varepsilon_{22} = \varepsilon_{33} = 0$.

The dimensional changes due to swelling for the free films and the coated substrate are in situ monitored by using immersed dynamic mechanical analysis (DMA) tests and scanning electrochemical microscopy (SECM), respectively. In order to avoid the influence of pigments, adjuvants and other fillers that exists in commercial coating formulations, the epoxy system DGEBA/DAMP, completely cross-linked, was chosen as a model system.

2. Materials and methods

2.1. Preparation of free films and coatings

The epoxy resins investigated were prepared from Diglycidyl Ether of Bisphenol A (DGEBA) cured with methylpentanediamine (DAMP). All materials are used as received without further purification. A stoichiometric amount of DGEBA was added to the amine hardener, mixed at room temperature and degassed under vacuum. In order to create free films, the mixture was transferred to a mould, which consisted of two Teflon sheets which are separated by a spacer of about 120 μm thick. For coated steel panels, the mixture was deposited onto steel Q-Panels and inserted in the mould used for free films.

A controlled curing protocol was used to create a homogeneous fully cured network: 7 h at 30 °C, followed by 3 h at 60 °C, followed by 3 h at 80 °C, followed by 3 h at 100 °C, followed by 3 h at 120 °C, and a postcure period for 1 h at 130 °C. The systems were cooled to room temperature with a rate of 10 °C min^{-1} to avoid physical ageing. The cured specimens were stored in a desiccator containing silica gel desiccant to prevent moisture absorption before immersion. The dry thickness h_0 is about 100 ± 6 μm for free films and coatings (measured by an Elcometer 311 Gauge Thickness). Each measure is repeated at least two times to verify the repeatability and the accuracy of the method.

2.2. Measurement of swelling kinetics of free films by gravimetry

For the free films, the water uptake $\chi_m(t)$ was measured by gravimetry using a balance PRECISIA with precision 10^{-5} g. The initial mass of the sample is recorded. The sample was fast dried by using absorbing paper and then weighted at different time interval. For each measure, three samples are used. The swelling kinetic monitored is presented as

$$\chi_m(t) = \frac{m(t) - m_0}{m_0} \times 100 = \frac{m_{H_2O}}{m_{polymer}} \times 100 \quad (1)$$

where $m(t)$ is the mass of the wet specimen at time t, m_0 is the mass of the dry specimen. The relative swelling of free films is calculated from Eq. (2), assuming there is no lixiviation/hydrolysis process.

2.3. Measurement of swelling kinetics of free films by immersed DMA tests

The free films were immersed in deionized water and swelling kinetics were monitored during two weeks using dynamic mechanical analysis (DMA of TA instrument Q-800) with submersible clamps at 30 °C. The free film was placed between the two clamps (one fixed and one movable), located in a stainless steel isothermal tank as shown in Fig. 2. A zero constant stress was kept at the free film to avoid having a constrained film. The tank was then filled with water so that the film was completely immersed and the water level was kept constant during the measurements to avoid partial desorption of the free film. The free films absorb water, and the swelling occurs, creating an elongation in the three directions of space. The three deformations of the film due to the swelling are time-dependent and defined as relative displacements in space as shown in Fig. 1: ε_{11}, ε_{22}, and ε_{33}.

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