Mapping water uptake in an epoxy-phenolic coating

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ARTICLE INFO

ABSTRACT

Water sorption in epoxy networks is associated with deleterious physical effects such as swelling, hydrolysis, lowering of the T_g, cracking and crazing. Nonetheless, water uptake in epoxy coatings is poorly understood in relation to macromolecular structure. In this contribution, we study the effect of cure time (closely related to cross-linking density and free volume) on water uptake for a model epoxy-phenolic coating. Localised water uptake is then mapped with nanoscale lateral resolution using AFM-IR, and correlated to cross-linking density.

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1. Introduction

Epoxy resins are commonly used as binding agents in complex formulations comprising marine [1], aerospace [2,3] and coil coatings [4,5]. These resins are known to confer excellent mechanical properties [6,7], chemical resistance [8], anti-corrosive properties [9–11] and thermal stability [12,13] due to their highly cross-linked nature. However, some degree of water uptake is characteristic of epoxy resins, and has been demonstrated to induce swelling [14,15], hydrolysis [16,17], crazing [18], cracking [19], plasticisation [20] and lowering of the T_g [21,22]. It follows that localised water uptake by epoxy components may represent failure points in the mechanical integrity of a coating. A comprehensive understanding of the macromolecular structure underpinning water sorption is therefore a key step towards the development of coatings with improved long term properties.

In the case of epoxy networks, structure–property relationships have previously been evaluated by correlating bulk resin properties to overall water uptake, which is commonly measured using techniques such as NMR [23,24], FTIR [25,26,27,28,29] or gravimetric analysis [30,31]. For example, positron annihilation lifetime spectroscopy (PALS) has been instrumental in defining the role of free volume contained within epoxy resins. A number of reports have concluded that resins containing a greater proportion of free volume absorb more water when polarity is controlled [32–36]. Equilibrium water uptake is, however, primarily determined by the hydrogen-bonding capability of the network (polarity) [37–40]. In such studies, the polarity and/or free volume of resins is ordinarily controlled using the cross-linker to epoxy ratio [41,42] or else the chemical structure of the cross-linker [32,43,44]. However, when considering localised water uptake, a major source of heterogeneity lies in the distribution of cross-linking density, which is typically large for epoxy resins (characterised by high molecular weight distributions prior to gelation, yielding broad T_g transitions by DSC analysis [45,46]). Therefore, defining the relationship between the degree of cure and network polarity/free volume should provide an indication of how water uptake is expected to vary across an epoxy resin. To this end, in the present study we assess water sorption under humid conditions for a series of model thermoset epoxy-phenolic coatings produced using different cure schedules. Furthermore, the correlation between local cross-linking and water sorption is then investigated by directly mapping cross-linking density and water uptake.

Few reports exist on localised water uptake in epoxy resins, due to a dearth of techniques capable of mapping chemical functionality under ambient/humid conditions. Acoustic microscopy has been used to identify solutions in blisters after corrosion onset, but the small volume of water absorbed by epoxy resins prior to coating failure (typically < 5 wt%) has not been detected [47–49]. Alternatively, FTIR micro-spectroscopy techniques are capable of highly sensitive mapping of chemical functionality. However, this approach conventionally suffers diffraction-limited resolution associated with the wavelength of light in the mid-IR spectral range, typically several microns per pixel. AFM-IR has been shown to circumvent this limitation, by using photothermally induced resonance (PTIR) of an AFM probe in contact with the sample
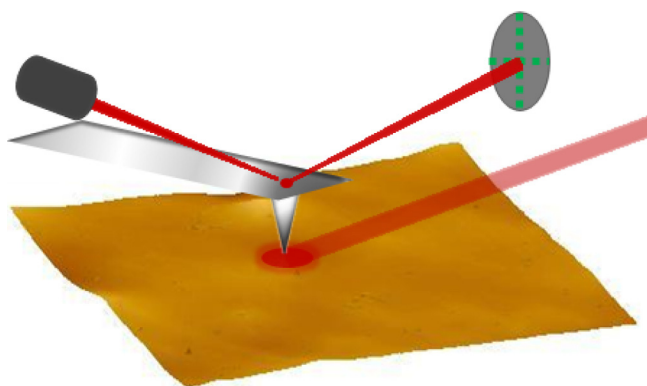
Scheme 1. Experimental set-up of AFM-IR with top-down illumination.
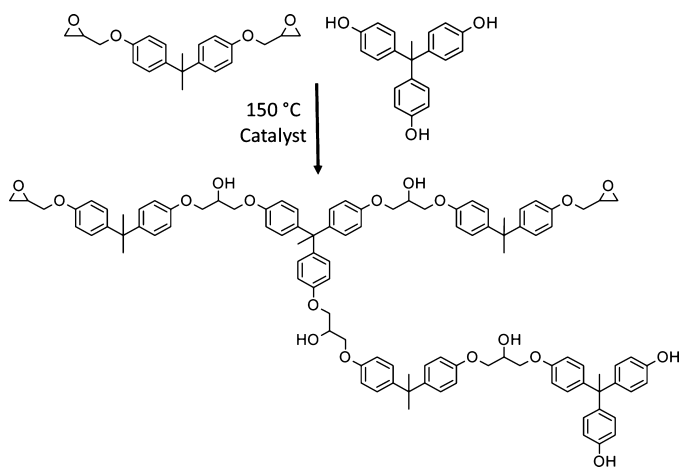
Scheme 2. The cross-linking reaction between bisphenol-A diglycidyl ether and 1,1,1-tris(4-hydroxyphenyl)ethane catalysed by tetrabutylphosphonium bromide.

surface to detect highly localised IR absorbance [50,51]. During AFM-IR, the sample is illuminated by a tunable infrared source, which is pulsed rapidly. On absorbance, abrupt transient thermal expansion of the sample excites the AFM probe in contact with the surface to oscillate at its resonant frequency modes, Scheme 1. It has been shown that the amplitude of this oscillation is proportional to IR absorbance, so that plotting the amplitude as a function of IR wavelength yields spectra closely matched to those obtained by macroscopic transmission-mode FTIR [52]. Furthermore, the infrared pulse (~10 ns duration), thermal expansion and damping down of the induced resonance occur on a faster timescale than the feedback electronics of the AFM, enabling simultaneous contact-mode topographical measurement and localised IR absorbance mapping at a given wavelength [51]. AFM-IR imaging in this manner has previously been applied to detect nanoscale structures for a variety of materials including polymer blends [53–55], biological samples [56–61] and composites [62]. Moreover, AFM-IR has also been used to identify water transport channels in Nafion networks with dimensions of approximately 20 nm [63].

Since a distribution of cross-linking densities is expected in epoxy coatings, the aim of the present study was to investigate how this affects water diffusion into an epoxy coating. Bulk effects are first examined by evaluating moisture uptake under humid conditions for a simple model epoxy-phenolic consisting of bisphenol-A diglycidyl ether cross-linked with 1,1,1-tris(4-hydroxyphenyl)ethane, Scheme 2. AFM-IR analysis is then performed to verify that the relationship obtained between cure degree and water uptake for bulk specimens corresponds to local water diffusion.

2. Experimental

2.1. Sample preparation

3.06 g (10 mmol) 1,1,1-tris(4-hydroxyphenyl)ethane (99%, Sigma–Aldrich) and 0.10 g (0.3 mmol) tetrabutylphosphonium bromide (+98%, Sigma–Aldrich) were dissolved in 6.0 g acetone (>98%, Fisher). 5.16 g (15 mmol) bisphenol-A diglycidyl ether (DER332, epoxide equivalent weight 172–176 g mol^{-1}, Sigma–Aldrich) was then added and stirred until a homogeneous mixture was obtained. This solution was cast onto electrolytic chrome-coated steel pieces (4 cm^2) which had been degreased by sonic cleaning in ethanol (Fisher Scientific, >99%). Spin coating was performed at 2000 rpm for 30 s (Headway Research Inc., 1–10,000 rpm). Samples were then cured by placing in an oven maintained at 150 °C, corresponding to the peak cure temperature determined by DSC analysis, and stored in a desiccator until use.

2.2. Film characterisation

Infrared spectra were obtained from 64 co-averages collected in ATR mode using an FTIR spectrometer (Nicolet 5700 spectrometer, Thermo Electron Corp.) operating at 4 cm^{-1} resolution across the 500–4000 cm^{-1} range.

For modulated DSC, epoxy-phenolic coatings were mechanically removed from the substrate and 1–3 mg placed in closed aluminium pans. DSC thermograms were obtained over a temperature range of −90 °C to 300 °C under nitrogen, using a heating/cooling rate of 3 °C min^{-1} with a modulation period of ±1 °C min^{-1} (Q100 modulated DSC, TA Instruments).

Sessile contact angles were obtained using 5 µL droplets of high purity water at 20 °C, and analysed with video capture apparatus (FTA188 Tensiometer, FTA Europe).

Film thickness was assessed using a scanning electron microscope (Zeiss Evo 50). Spin-coated samples were sputtered with gold (Polaron, E5100) and mounted at 90° in araldite resin (10:1 Araldite AY 103-1:Aradur HY 951, Huntsman). Once set (>48 h under ambient conditions), cross-sections were polished and carbon coated (Edwards E306) prior to analysis.

2.3. Water uptake

In situ FTIR analysis was initially used to monitor water vapour diffusion into the epoxy phenolic coatings. This was achieved using an FTIR spectrometer (Spectrum 2000, Perkin Elmer), operating at 4 cm^{-1} resolution across the 700–4000 cm^{-1} range. Saturated NaCl solution was placed in recrystallizing dishes at the bottom of the sample chamber, which was fitted with a portable temperature and humidity data logger (Lascar Electronics). Humidity was allowed to equilibrate for 20 min prior to collection of the background spectrum (electrolytic chrome-coated steel substrate). Within 10 min of salt solution insertion, humidity within the sample chamber was measured to be 64 ± 1% RH at 20 °C, and remained stable throughout the experiment. FTIR spectra were gathered continuously for 30 min following transfer of the coated sample into the FTIR chamber.

Gravimetric water uptake was analysed for free-standing films acquired by delamination from PTFE (Polyflon). In order to replicate cure conditions, PTFE films were first attached to steel substrates, then coated and cured under identical conditions to coatings on steel. For gravimetric uptake, free-standing films were accurately weighed, placed in a chamber under 80% RH for 2 h and then re-weighed. These exposure conditions were selected because a high humidity was required in order to detect water sorption gravimetrically, whereas the exposure time was chosen on the basis of in situ FTIR analysis which showed rapid water sorption into