Water transport in an epoxy–phenolic coating

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ARTICLE INFO

ABSTRACT

Thermoset coatings commonly rely on high cross-linking density to provide enhanced barrier properties. Hence it is surprising that for the industrial epoxy–phenolic network investigated, equilibrium moisture uptake is found to increase with respect to cure time, i.e., with greater cross-linking. Molecular interactions between absorbed water and the resin are characterised using infrared spectroscopy, and water uptake is correlated to network polymer features such as polarity and free volume.

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1. Introduction

Epoxy resins are widely used in the fields of aerospace engineering [1–3], marine coatings [4], microelectronics [5,6], and packaging [7] in the form of paints [8], adhesives [9] and composites [10,11]. Such resins are known to confer excellent mechanical properties [12,13], chemical resistance [14], anti-corrosive properties [15–17] and thermal stability [18,19] due to their highly cross-linked nature. Nonetheless, for every application reliant on the mechanical or barrier properties of an epoxy resin, moisture absorption is a key consideration in the evaluation of long-term performance. Significant water uptake is characteristic of epoxy coatings, and has been demonstrated to induce swelling [20,21], hydrolysis [22,23], crazing [24], cracking [25], plasticisation [26] and lowering of the T_g [27,28]. Yet, to date, a comprehensive mechanistic understanding of the water sorption process remains elusive.

Moisture uptake by epoxy resins has previously been investigated using techniques such as positron annihilation lifetime spectroscopy (PALS), NMR, FTIR, fluorescence, dielectric spectroscopy and gravimetric analysis. The development of PALS has been instrumental in defining the role of free volume contained within epoxy resins. Despite some apparently contradictory results, a picture has emerged where resins containing a greater proportion of free volume absorb more water when polarity is controlled [29–33]. However, equilibrium water uptake is primarily determined by the hydrogen bonding capability of the network (polarity) [34–38]. Meanwhile, water in epoxy resins has long been established by FTIR techniques to exist in both a free form (not interacting with the resin), and also in a bound state, hydrogen bonded to polymeric sites [39–43]. This dual nature for sorbed water is supported by an abundance of evidence from simulation [44], dielectric measurements [45–47], and fluorescence [48]. NMR studies have further found that water in resins may be sub-categorized according to mobility [49,50]. Soles et al. [32] have suggested a model encompassing these results, where water transport in epoxies occurs via the free volume, allowing access to neighbouring polymeric hydrogen bonding sites.

The majority of the aforementioned studies have focussed on model epoxy–amine resins. Little attention has been given to industrial systems, which typically comprise a complex mixture of resin and cross-linker, solvents, and numerous additives to promote wetting of the substrate, drying and curing. Typical additives have been shown to be hygroscopic, so that water uptake may be dependent on their concentration and distribution rather than bulk polymeric properties [51,52]. Furthermore, relatively few studies have reported on water uptake for epoxy–phenolic systems, despite their prevalence in food contact and beverage can-coating applications, i.e., where the applied film is submerged throughout its lifetime [53,54]. Suzuki et al. [55,56] measured free volume for a range of epoxy–phenolic resins using the PALS technique, and found a direct correlation between free volume and water uptake, however the effect of resin polarity was neglected. Conversely, Zhang et al. [15] examined two epoxy–phenolic systems and reported greater water sorption for the resin containing less free volume, so concluded that water uptake was dependent only on polarity. Numerous 2D ATR-FTIR investigations have also

confirmed the presence of free and bound water for epoxy–phenolic formulations [37,57–59].

In the present study, the effect of free volume on moisture uptake is evaluated using time-resolved FTIR for an industrial epoxy–phenolic coating. In order to control polarity and isolate the effect of cross-linking density (closely related to free volume), variable cure times are used, since alternative strategies such as varying the cross-linker to epoxy ratio, or else the chemical structure of the cross-linker, frequently constitute a variation in resin polarity.

2. Experimental

2.1. Sample preparation

Electrolytic chrome-coated steel pieces ($4\,cm^2$) were degreased by rinsing in ethanol (Fisher Scientific, >99%). Thin films of epoxy–phenolic Vitalure 345 Lacquer (AkzoNobel Packaging Coatings, Elbeuf, France) were then spin cast onto the steel pieces at 2000 rpm for 30 s (Headway Research Inc., 1–10,000 rpm). Samples were cured by placing in an oven maintained at 200 °C for a prescribed time interval (5–30 min).

2.2. Film characterisation

In order to assess film thickness, samples were sputter coated with gold (Polaron E5100), mounted at 90° in araldite resin (10:1 Araldite AY 103-1:Aradur HY 951, Huntsman) and polished to expose cross-sections. These were then carbon coated (Edwards E306) and measurements were taken using a scanning electron microscope (Zeiss Evo 50).

Sessile contact angle analysis was performed at 20 °C using video capture apparatus (FTA188 Tensiometer, FTA Europe) and 5 μL of high purity water.

For modulated DSC, epoxy–phenolic coatings were mechanically removed from the substrate, and 1–3 mg placed in aluminium pans. DSC curves 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).

Infrared spectra are the result of 16 accumulations collected in reflectance mode using an FTIR spectrometer (Spectrum 2000, Perkin Elmer), operating at 4 cm^{-1} resolution across the 700–7000 cm^{-1} range. In order to assess water uptake, saturated NaCl solution was warmed to 50 °C and 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 5 min of salt solution insertion, humidity within the sample chamber was measured to be 80 ± 1% RH, and remained stable throughout the experiment. FTIR spectra were gathered continuously for 60 min following insertion of the coated sample. For peak-fitting of the acquired spectra Gaussian functions were fitted using a least squares fitting technique based on a Levenberg–Marquardt algorithm (Fitky 0.9.8 Software v.2 [60]).

Gravimetric uptake was performed using free-standing films acquired by cathodic delamination. Cured, spin cast coatings were removed from tin-plated steel by application of +3 V (vs. Ag/AgCl reference electrode) for 5 h. After removal from the substrate, the films were soaked in deionised water and dried in a desiccator for 2 weeks. The thus-obtained free standing films yielded unchanged ATR-IR spectra and contact angles on both sides, indicating that the polymer film was unaffected by the delamination procedure. For gravimetric uptake, films were accurately weighed, placed in the FTIR chamber under raised humidity for 60 min (i.e., under
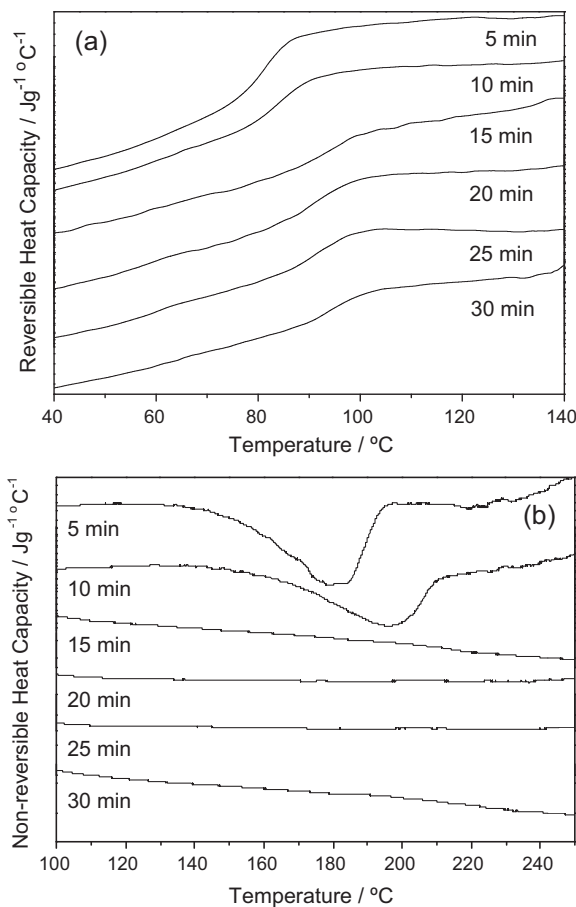

Fig. 1. Modulated DSC (a) reversible and (b) non-reversible heat capacity traces for epoxy–phenolic thin films cured for 5–30 min at 200 °C.

conditions identical to those described for time-resolved FTIR analysis) and then re-weighed.

Atomic force microscopy images were obtained using a Multimode 8 (Bruker, Santa Barbara) operating in Peakforce Nanomechanical Mode using a Tap525 probe (Bruker, nominal spring constant 200 N/m, nominal resonance frequency of 525 kHz). Deflection sensitivity was calibrated against a sapphire reference, and a relative calibration technique was performed using polystyrene to ascertain tip radius and spring constant. Measurements were made using a custom made humidity chamber. Air was bubbled through saturated salt solution into the chamber to achieve 70% RH. The DMT modulus and topography signals were then continuously recorded for 2 h. All images were gathered using the same probe, operating at a 0.5 Hz scan rate. Mean values quoted are for 512 sample points per 512 scan lines over 100 μm^2.

3. Results

3.1. Coating characterisation

DSC analysis of the epoxy–phenolic films yielded increasing T_g values and broadening transitions as a function of cure time, indicating enhanced cross-linking, Fig. 1 and Table 1. In addition, the excess cure detected in the irreversible trace (from residual reactants, at 180–200 °C) was attenuated with respect to cure time, until no signal was detected for cure times exceeding 10 min, Fig. 1. Further evidence for the cross-linking reaction was gathered by SEM analysis, which revealed initial shrinkage with curing, followed by gradual increase in coating thickness when the reaction is close to