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Controlling the Nanostructure of Epoxy Resins: Reaction Selectivity and Stoichiometry

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Abstract: *The internal topology of epoxy resins is, for the first time, shown not to be the determining factor for small molecule transport. Whilst epoxy resins comprise the matrix component of many high performance composites, coatings and adhesives, the nanostructure and transport properties of these materials are not well understood. Here, peakforce AFM imaging, in-situ FTIR cure analysis and nanochemical AFM-IR imaging are used to establish the effects of reaction selectivity and stoichiometry on the nanostructure of epoxy-phenolic resins based on bisphenol-A and diglycidyl ether of bisphenol-A. In the presence of excess epoxy, resins transition from exhibiting homogeneous internal nanostructures to the familiar nodular morphology characteristic of epoxies. This occurs as a result of lower reaction selectivity in the presence of increasing catalyst concentrations. Surprisingly however, chemically similar stoichiometric resins with a heterogeneous nanostructure display improved resistance to corrosion breakdown (ion transport) and lower water uptake than the homogeneous resins.*

Introduction

Reports detailing the complex internal nanostructure of epoxy resins have appeared in literature since the 1950's.[1][2][3][4] Early monographs detailed the observation of nodular internal structures by scanning electron microscopy, and later, AFM studies also consistently showed internal morphologies comprised of highly cross-linked nodules, embedded in a more lightly cross-linked matrix. It has frequently been proposed that these nodules form pre-gelation, as a result of cluster formation followed by predominately intra-nodule cross-linking reactions. Nonetheless, the presence of nodular nanostructures within epoxy resins has historically been disputed. This is because bulk properties (e.g., thermal analysis and scattering studies) rarely support a two-phase structure, and statistical models of network growth predict homogeneous network structures at this length scale.[5][6]

Recently, renewed interest in this area has been generated by the application of advanced high resolution techniques, shedding new light on the presence and formation of nodular structures. For example, recent molecular dynamics simulations provided detailed insights into heterogeneous network formation, demonstrating that cluster growth and aggregation can occur spontaneously pre-gelation.[7] In addition, Izumi et al. recently published new experimental evidence for the development of high and low cross-link density domains during the cure of a phenolic resin using NMR, SAXS/WAXS and SANS/WANS data.[8] This is in keeping with our observations that the nodular features observed in fully cured epoxy-phenolic formulations indeed correspond to chemical heterogeneity associated with an inhomogeneous cure, detected using the AFM-IR technique.[9]

It is important to note that such heterogeneous domains are expected to provide low energy pathways through these widely used resins, giving a structural basis for the relatively low fracture toughness of network polymer materials, and their high permeability.[10][11] However, whilst the presence of these features is now widely accepted, little is understood about how to control their formation and thereby potentially tailor these properties. Previously, Sahagun et al. showed that for epoxy-amines the cure temperature and stoichiometry determine the extent of internal heterogeneity. It was proposed that the relative kinetics of primary (chain extension) and secondary (cross-linking) amine reactions determined the size of nodules. In support of this, we have previously demonstrated that the formation of nodular features in epoxy phenolic resins is dependent on the overall cross-linking density, and can be eliminated using a significant proportion of monofunctional additive.[12] The epoxy-phenolic reaction is more selective than epoxy-

amine, and is therefore well-suited to study the nanostructural control potentially provided by reaction selectivity. In light of this, in the present study we examine a lightly cross-linked epoxy-phenolic system; namely bisphenol-A and diglycidyl ether of bisphenol-A, Scheme 1. This simple 2+2 cure chemistry has previously been used as a model system to examine catalytic selectivity for the epoxy-phenol reaction.[13][14] The effects of catalytic content and stoichiometry on the development of an internal nanostructure is thus investigated, alongside the water uptake and ionic resistivity of bulk resins. Moisture sorption is of particular interest, since it has been linked to service failure of network polymers through cracking, plasticization and swelling. Techniques including positron annihilation lifetime spectroscopy (PALS),[15][16][17] NMR[18][19], FTIR,[20][21][22][23][24] simulation,[25] fluorescence,[26] dielectric spectroscopy[27][28] and gravimetric analysis[29][30][31] have previously been used to correlate the kinetics of water transport, and the eventual equilibrium water content, to the free volume and polarity of epoxy resins.[32][17] Such correlations are however, predicated on the assumption of continuous, homogeneous network structures, and nanostructural effects are generally not considered.

Scheme 1. Reactions between diglycidyl ether of bisphenol-A and bisphenol-A: (a) the epoxy-phenolic reaction, yielding linear polymers under conditions of perfect reaction selectivity, and (b) the epoxy-secondary hydroxyl side reaction, leading to cross-linking and thus gelation.

Experimental

Sample Preparation

Epoxy-phenolic resins were prepared by dissolving bisphenol-A diglycidyl ether (DER332, epoxide equivalent weight $172\text{--}176\text{ g mol}^{-1}$, Sigma-Aldrich), bisphenol-A (> 99 %, Sigma-Aldrich) and tetrabutyl phosphonium bromide (> 98 %, Sigma-Aldrich) catalyst in 3 g acetone (>98 %, Fisher) according to the proportions listed in Table 1. For in situ FTIR experiments the epoxy and phenolic components were dissolved separately and the two mixtures were combined immediately before application onto a preheated KBr window using a paint brush. Otherwise, mixtures were applied onto pre-scored electrolytic chrome-coated steel pieces (25 cm^2) which had been degreased by sonic cleaning in ethanol (Fisher Scientific, > 99 %). Solutions were deposited using an automated bar coater fitted with a $100\text{ }\mu\text{m}$ spiral bar (Model 4340, Elcometer, UK). Samples were then cured by placing in an oven maintained at $150\text{ }^{\circ}\text{C}$ for 1 or 15 hours, and stored at $-4\text{ }^{\circ}\text{C}$ prior to analysis.

Table 1. Formulations used to produce stoichiometric and excess epoxy resins with differing catalytic contents.

Formulation		Bisphenol-A diglycidyl ether	Bisphenol-A	Tetrabutyl phosphonium bromide
Stoichiometric	1 % catalyst	10 mmol	10 mmol	0.2 mmol
	5 % catalyst	10 mmol	10 mmol	1.0 mmol
Excess epoxy	1 % catalyst	15 mmol	10 mmol	0.3 mmol
	5 % catalyst	15 mmol	10 mmol	1.5 mmol
	10 % catalyst	15 mmol	10 mmol	3.0 mmol

For catalytic selectivity reactions, mixtures were prepared by dissolving 4 mmol bisphenol-A diglycidyl ether and tetrabutylphosphonium bromide catalyst (0-10 mol %) in 1 g acetone. For FTIR experiments, 4 mmol 4-benzylphenol (99 % Sigma-Aldrich) was dissolved separately in 1 g acetone, and the two mixtures were combined immediately before application onto a preheated KBR window using a paint brush, Scheme 2.

Scheme 2. Chemical structures of the components used in resin formulations and catalytic selectivity experiments: (a) diglycidyl ether of bisphenol-A; (b) the tetrabutyl phosphonium bromide catalyst; (c) bisphenol-A and (d) 4-benzylphenol

FTIR

Bulk infrared spectra were obtained from 64 co-averages collected in transmission mode using a Fourier transform infrared (FTIR) spectrometer (Nicolet 5700 spectrometer, Thermo Electron Corp.) operating at 4 cm⁻¹ resolution across the 500 – 4000 cm⁻¹ range. For in-situ catalytic selectivity and curing reactions, an open cell heated transmission system was used.

Prior to experiments, the temperature at the surface of the KBr disc was adjusted to 150 °C using a k-type thermocouple and an automatic temperature controller (Graseby Specac).

AFM

In order to expose the internal nanostructure of resins, cured samples coated onto pre-scored steel were fractured under liquid nitrogen immediately before analysis. Atomic force microscopy images (Multimode 8, Bruker, Santa Barbara) were collected in peakforce tapping mode using a Pt-Ir coated probe (nominal spring constant 2 N/m, nominal resonant frequency of 80 kHz, Bruker).

AFM-IR

Nanoscale infrared analysis (AFM-IR) was performed on a NanoIR2 system (Anasys Instruments) operating with top-down illumination. To assess the internal nanostructure, polymer sections of 100 nm nominal thickness were prepared using an ultramicrotome (Leica EM UC6) with a diamond knife. Sections were collected on transmission electron microscopy (TEM) grids, then floated onto a droplet of deionised water placed on a ZnS substrate (Anasys Instruments). Upon evaporation of the droplet, TEM grids were removed, specimen sections remained on the ZnS surface, and these were dried for >16 h in a desiccator prior to examination. During AFM-IR analysis, the microtomed sections were illuminated by a pulsed, tunable infrared source (optical parametric oscillator, 10 ns pulses at a repetition rate of 1 KHz, approximate beam spot size 30 μ m). Sub-diffraction limit resolution was achieved by monitoring the deflection of an AFM probe in contact with the surface. This results from rapid transient thermal expansion of the material in contact with the probe tip in response to infrared absorbance, Scheme 3.[33] The recorded AFM-IR signal is the amplitude of induced AFM probe oscillation, obtained after fast Fourier transform. This has previously been shown to correlate to infrared absorbance measured using conventional macroscopic FTIR.[34] Since the IR pulse (10 ns duration), thermal expansion, and damping down of the induced oscillation occur on a shorter timescale than the feedback electronics of the AFM, simultaneous contact-mode topographical measurement and infrared mapping may also be performed at a given wavelength.[35][36][37] For the present study, AFM-IR images were collected in contact mode at a scan rate of 0.04 Hz using a gold-coated silicon nitride probe (0.07 – 0.4 N/m spring constant, 13 ± 4 kHz resonant frequency, Anasys Instruments). The

amplitudes of infrared induced oscillations were recorded at a given wavelength using 32 co-averages for 600 points per 150 scan lines.

Gravimetric Water Uptake

For gravimetric water sorption experiments, bulk specimens were prepared using reaction solutions identical to those described above, which were then poured into a mould lined with PTFE film and cured. Samples were immersed in deionised water, removed periodically, wiped with lint-free tissue and accurately weighed using a 5 d.p. balance.

Electrochemical Impedance Spectroscopy

Electrochemical impedance measurements were recorded at room temperature using a Gamry Reference 600 potentiostat in the 0.01 Hz - 10 kHz frequency range using a 10 mV AC perturbation with respect to the open circuit potential of the system to ensure linearity. Data acquisition required a three electrode setup, consisting of a saturated calomel reference electrode ($E_{\text{SHE}} = E_{\text{SCE}} - 241 \text{ mV}$ at 21 °C) and Pt ring counter electrode, all enclosed in an earthed Faraday cage. Measurements were obtained periodically during immersion in an aerated 0.1 M NaCl aqueous solution.

Nano-thermal Analysis

Nano-thermal analysis was performed on a NanoIR2 system (Anasys Instruments) using a commercially available thermal probe (AN2-200, spring constant 0.5-3 N/m, resonance frequency of 55-80 KHz, Anasys Instruments) with an in-built doped Si resistor that permits controlled heating of the probe tip. Thermal probe resistance was calibrated using reference materials with well-defined thermal transition points (polycaprolactone, polyethylene terephthalate, and high-density polyethylene). After calibration, the probe tip was heated at a rate of $1 \text{ }^{\circ}\text{C s}^{-1}$ whilst in contact with the epoxy phenolic samples, until a drop in the photodiode output signal of 0.2 V triggered the end of the thermal scan (because this indicates that the tip has penetrated the surface due to material softening), whereupon the probe is automatically retracted away from the surface before re-engaging at the next measurement spot.

Scheme 3. The AFM-IR experiment with top-down illumination. The IR source is pulsed, inducing rapid thermal expansion of the sample, which is detected by deflection of the AFM probe cantilever. The recorded AFM-IR signal corresponds to the amplitude following a fast Fourier transform of the induced deflection signal (inset, left).

Results and Discussion

AFM Morphology

In order to investigate the effects of stoichiometry and catalytic content on resin nanostructure, formulations containing either a stoichiometric ratio of reagents or 50 % excess of epoxy to phenolic groups (1.5:1 epoxy : phenolic groups) were cured in the presence of 1 %, 5 % or 10 % catalyst, Table 1. The internal nanostructure of fully-cured resins was then exposed by cryogenic fracturing, and assessed using peakforce tapping mode AFM, Figure 1.

A well-defined nodular structure (typical of epoxy resins) was consistently detected in the case of stoichiometric resins, where no appreciable difference in morphology was detected between resins cured for 1 hour and 15 hours at 150 °C (Fig. 1 a-c). This is in keeping with our and other author's findings that the internal topology of epoxy resins is established before or at the gel point, and remains unchanged thereafter.[9][11][38] In addition, the catalytic content had no discernible effect on the morphology of stoichiometric specimens. This too was expected on the basis of our previously reported data; the internal morphology of epoxy phenolic resins based on diglycidyl ether of bisphenol-A and a tri-phenolic species cured using the same catalytic accelerator was found to be identical to specimens cured in its absence (at a higher temperature).[9]

Given the unchanged morphology of stoichiometric samples, it is somewhat surprising that for resins prepared using an excess of epoxy, increasingly rough fracture interfaces and the emergence of a nodular morphology was detected as the catalyst concentration increased, Figure 1 (d-f). This indicates that the catalyst content significantly influenced resin formation, since if it behaved only as an accelerant, the same morphology would be expected to emerge regardless. In order to elucidate this effect further, catalytic selectivity was analysed using a series of in-situ FTIR experiments.

Figure 1. 1 μm x 1 μm peakforce tapping mode AFM height images of epoxy phenolic resin fracture interfaces: (a-c) stoichiometric resins, prepared using (a) 1 % catalyst and cured for 1 hour at 150 $^{\circ}\text{C}$; (b) 5 % catalyst and cured for 1 hour at 150 $^{\circ}\text{C}$; (c) using 1 % catalyst and cured for 15 h at 150 $^{\circ}\text{C}$; (d-f) resins cured for 15 hours at 150 $^{\circ}\text{C}$ using a 50 % excess of epoxy in the presence of (d) 1 %; (e) 5 % and (f) 10 % *tert*-butyl phosphonium bromide catalyst. Since it has previously been suggested that nodular features in AFM micrographs correspond to tip artefacts, fresh AFM probes were employed for each specimen.

Catalytic Selectivity

The selectivity of the *tert*-butyl phosphonium bromide catalyst was investigated using a mixture of a model monofunctional phenolic molecule (4-benzylphenol) and diglycidyl ether of bisphenol-A, containing a 50 % excess of epoxy to phenolic functional groups. Since no network is formed, this approach eliminates any possible viscosity/vitrification effects. The mixtures were directly applied to a preheated KBr window, and transmission mode FTIR spectra were gathered continuously for 15 hours at 150 $^{\circ}\text{C}$, Figure 2.

Integration and normalisation of the characteristic epoxy peak at 916 cm^{-1} (asymmetric oxirane ring deformation) showed that in the absence of a catalyst, the reaction rate slowed dramatically as epoxy consumption approached 50 %. An inflection point was anticipated at this stage due to the depletion of primary phenolic groups, after which, in accordance with previous studies, epoxy consumption was expected to slow significantly as a result of the less favourable reaction with secondary hydroxyls.[13][14] In the present case, epoxy consumption then appeared to accelerate at longer reaction times. Since no such effect has been reported for selectivity experiments conducted using titration to monitor excess epoxy consumption,[13][14] this could be attributed to long term epoxy ring opening by bromide ions diffusing from the KBr disc (an ionic acceleration mechanism has previously been suggested, according to which epoxy ring opening is initiated by bulky anions[39][40]). However, in control tests using stoichiometric mixtures of bisphenol-A and

diglycidyl ether of bisphenol-A, gelation was found to occur after sufficiently long curing times in the absence of any catalyst (7-8 hours). This indicates that eventually, reactions through the secondary hydroxyl occur regardless. In the presence of a significant amount of KBr (5 %) gelation occurred earlier (6-7 hours cure time), but note that this compares to 20 minutes in the presence of 5 % tetrabutyl phosphonium bromide catalyst. Thus, any effect of diffusion from the KBr disk on the monitored reaction at short time scales is expected to be negligible. Indeed from FTIR results, it is very clear that under identical conditions, consumption of the excess epoxide progresses much more rapidly in the presence of the *tert*-butylphosphonium bromide catalyst, indicating that reaction through secondary hydroxyl groups is significantly accelerated. As a result, higher catalyst concentrations are expected to increase the relative number of secondary cross-linking reactions within resins.

Figure 2: In-situ FTIR (a) fingerprint region spectra and of 4-benzylphenol in the presence of 50 % excess diglycidyl ether of bisphenol-A and 1 % *tert*-butyl phosphonium bromide catalyst as a function of reaction time at 150 °C, and (b) absorbance of the FTIR epoxy band at 916 cm^{-1} (normalised to the aromatic 1504 cm^{-1} peak) in the presence of 0 %, 1 % or 5 % *tert*-butyl phosphonium bromide catalytic content, as a function of Log_{10} of reaction time at 150 °C.

In-situ Cure Monitoring

To ascertain the effect of catalyst content on reaction selectivity during resin formation, epoxy consumption during reaction between bisphenol-A and diglycidyl ether of bisphenol-A was also monitored using FTIR, and then compared to gel points, Figure 3. Generally, it can be seen that the epoxy consumption profiles display apparently auto-acceleratory kinetics, in keeping with previous kinetic studies examining epoxy-phenolic cures in the presence of triphenylphosphine and phosphonium borate type catalysts.[41][42][43]

Figure 3: Absorbance of the FTIR epoxy band at 916 cm⁻¹ (normalised to the aromatic 1504 cm⁻¹ peak) during the cure reaction of (a) stoichiometric epoxy phenolic formulations and (b) excess epoxy formulations in the presence of 0 %, 1 % or 5 % *tert*-butyl phosphonium bromide catalytic content, displayed as a function of Log₁₀ of reaction time at 150 °C. Dashed lines represent approximate gel points.

In the case of an ideal, perfectly selective reaction between bisphenol-A and diglycidyl ether of bisphenol-A, the absence of any cross-linking through secondary hydroxyl groups would result in soluble, linear polymers, Scheme 1. Since gelation only occurs as a

result of cross-linking side reactions, gel points have been used as a measure of the reaction selectivity.[13] In the present case, gel points were estimated by preparing a series of specimens with increased cure times at 5 minute intervals, until complete dissolution of the specimen no longer occurred (in acetone, after sonic mixing for 20 minutes at 60 °C). For stoichiometric resins cured using 1 % catalyst, complete dissolution was observed for all specimens cured for < 30 minutes, after which time only swelling was observed. FTIR results indicate that at this time just 88 % of the epoxide groups had reacted, confirming that substantial cross-linking occurs through secondary hydroxyl groups. As expected, in the presence of 5 % catalyst, gelation occurs earlier in the reaction (after 20 minutes, at 65 % epoxy consumption), thereby confirming that the catalyst accelerates secondary hydroxyl reactions, resulting in gelation at lower conversions.

For excess epoxy formulations, the gel point would be expected to occur at longer reaction times and higher relative epoxy conversions than for stoichiometric resins. This is because in the presence of excess epoxy, each reaction with a phenolic or secondary hydroxyl group should be statistically less likely to result in a cross-linking event. Indeed, the presence of an inflection point in the reaction profile, and the observation that complete epoxy consumption requires long reaction times (approximately 15 hours), indicate that unreacted groups remain in the reaction mixture for a longer time than in the case of stoichiometric mixtures (where complete conversion of the epoxy groups occurs within 2 hours). Somewhat surprisingly however, the gel point occurs at epoxy conversions comparable to stoichiometric mixtures in the presence of 1 % catalyst (after 35 minutes, 85 % epoxy conversion). An explanation for this can be found in the more homogeneous nanostructure observed for excess epoxy resins, since in the case of heterogeneous resins (stoichiometric specimens), intra-nodule reactions would be expected to contribute to detected epoxy consumption pre-gelation, but not lead to network formation. This explanation is in keeping with results recently reported by Izumi et al., who demonstrated that for phenolic resins, the majority of cross-linking reactions during early stages of the cure did indeed occur *within* agglomerates formed before gelation.[8] Furthermore, for the excess epoxy resins, whilst increasing the catalyst content to 5 % again resulted in gelation at lower epoxy conversion (after 10 minutes, 75 % epoxy consumption), further increasing the catalytic content to 10 % was found to have no measureable effect on the gel point (again occurring after 10 minutes at 75 % epoxy conversion). This can be explained by consideration of the AFM data, which indicates that as catalyst content is raised, an

increased proportion of cross-linking events caused a transition from homogeneous network formation to one involving the formation of observable supramolecular nodules.

AFM-IR Analysis

To confirm that the internal nanostructure of stoichiometric resins correlated to inhomogeneous cure reactions, AFM-IR analysis was performed for the two resins containing 1 % catalyst (i.e., the heterogeneously structured stoichiometric resin and homogeneous sample prepared using excess epoxy). Infrared mapping was performed on microtomed polymer sections (100 nm thickness), by monitoring the induced amplitude signal generated at 1108 cm^{-1} , as has previously been reported.[9][12] This peak corresponds to the out of phase C-C-O stretch for secondary alkyl hydroxyls generated by the cure reaction, Figure 4.

The AFM-IR map of the stoichiometric specimen displayed distinct variations in the local infrared amplitude signal gathered at 1108 cm^{-1} , in keeping with the heterogeneous internal morphology displayed in peakforce tapping mode images of the fractured sample, Figures 1 and 5. In contrast, for resins prepared using an excess of epoxy the signal was found to vary only slightly when imaged under identical conditions. To confirm this corresponds to chemical heterogeneity associated with the cure (rather than e.g., variable tip-sample contact, or sample volume) AFM-IR infrared mapping was additionally performed at 1504 cm^{-1} (corresponding to the aromatic quadrant stretch), and these maps displayed less variation across the scanned region of both specimens.

Figure 4. Transmission mode FTIR spectra of stoichiometric resin formulation containing prepared using 1 % catalyst (a) 0.5 minutes cure at $150\text{ }^{\circ}\text{C}$; (b) 1 minute cure at $150\text{ }^{\circ}\text{C}$; (c) 5 minutes cure at $150\text{ }^{\circ}\text{C}$; (d) 10 min cure at $150\text{ }^{\circ}\text{C}$; (e) 20 minutes cure at $150\text{ }^{\circ}\text{C}$ and (f) 30 minutes cure at $150\text{ }^{\circ}\text{C}$.

Figure 5. 1 μm x 1 μm AFM-IR images of 100 nm thick microtomed sections of epoxy-phenolic resin cured at 150 $^{\circ}\text{C}$ for 15 hours: Contact mode AFM-IR height images of (a) the excess epoxy formulation and (b) stoichiometric resin, alongside AFM-IR IR amplitude images gathered at 1108 cm^{-1} for (c) the excess epoxy formulation and (d) stoichiometric resin; and AFM-IR amplitude images gathered at 1504 cm^{-1} for (e) the excess epoxy formulation and (f) stoichiometric resin.

Water Uptake and EIS Analysis

The presence of such internal physicochemical heterogeneity has been proposed to result in the generation of low energy pathways through networks polymers, permitting rapid small molecule transport.[11][38][44] In order to explore this, water uptake by the fully cured heterogeneous stoichiometric and homogeneous non-stoichiometric resins (cured for 15 h using 1 % catalyst) was compared by gravimetric analysis, and ionic resistance was analysed using electrochemical impedance spectroscopy (EIS).

Gravimetric analysis was performed over a ten day period, throughout which water uptake was found to be more significant for the homogeneously-structured resins prepared using an excess of epoxy, Figure 6. This indicates that these resins are not in fact more resistant to small molecule transport, despite having more homogeneous nanostructures, and further evidence for this was found using EIS. Upon immersion in electrolyte for EIS analysis, the excess epoxy coatings consistently failed, and only three excess epoxy samples (as opposed to six stoichiometric specimens) yielded data for analysis. Over the course of a test, the EIS response of coatings could be classified as either having one-time constant, corresponding to an intact film; or two-time constants, representing a case where an ionic transport pathway is established across the film, creating an electrical connection to the metallic substrate, Figure 7. All of the analysed samples initially exhibited one-time constant behaviour, (i.e., no pre-existing ionic transport pathway) however, with increased immersion time all the excess epoxy samples rapidly reverted to exhibiting two-time constant

behaviour (indicating ions had traversed the film to make an electrical connection). In contrast, the stoichiometric samples survived longer in the one-time constant state, and 66 % did not show any signs of corrosion (two time constant behaviour) within the tested immersion time.

Figure 6. Gravimetric water uptake by bulk stoichiometric and excess epoxy resins prepared using 1 % catalyst as a function of immersion time in de-ionised water.

Examples of the coating resistance and capacitance values obtained from equivalent model fitting of the acquired data are given in Figure 8. All samples exhibited a reduction in coating resistance and an increase in coating capacitance (characteristic of water sorption[45][46]), within 10 hours of immersion. For the stoichiometric specimens shown, a resistance saturation plateau was maintained thereafter, since for these samples no time constant representative of electric charge exchange between the metal and the electrolyte was observed. In contrast, the excess epoxy samples exhibited corrosion initiation, (a two-time constant EIS response) within 6-17 hours of immersion, causing a further resistance drop.

Nano-thermal Analysis

One explanation for the increased water uptake of excess epoxy resins lies in chemical dissimilarity between these and stoichiometric samples. When considering water sorption into chemically dissimilar resins, resin polarity is ordinarily thought to control the overall degree of water sorption.[32][17] This explanation was, however, ruled out by consideration of the expected molecular structures, Scheme 1. In the case of stoichiometric resins, since reaction through secondary hydroxyls results in gelation, it follows that some residual

phenolic groups will be present in the resin. These are significantly more polar than secondary hydroxyl groups. In comparison, for excess epoxy resins, complete consumption of the phenolic groups is expected, in addition to further conversions of the secondary hydroxyl and epoxy ether functionalities into secondary hydroxyl groups and ethers (i.e., conversions lead to functional groups similar in polarity). Thus, despite absorbing more water, excess epoxy resins are considered to be less polar than the stoichiometric specimens.

An alternative explanation for the differences in water uptake and film resistance is an overall lower cross-linking density within resins prepared using an excess of epoxy. Thermal properties of the resins were therefore examined using the nanothermal analysis technique to give an indication of cross-link density. Uniquely, this approach allows local thermal transitions to be measured using the photodiode read-out corresponding to the deflection response of a heated AFM tip in direct contact with the sample surface. As the temperature of the AFM probe is raised, thermal expansion leads to a gradual increase in deflection until, at the transition temperature, the material softens and the AFM probe tip penetrates the sample surface, Figure 9. Thermal transitions can then be assessed by reading off the temperature at which a drop in the photodiode read-out (corresponding to a drop in probe deflection) occurs. For epoxy phenolic resins, this has been shown to correlate well with T_g values measured using conventional bulk thermal techniques.[12] Previously, this approach has been used to show that a heterogeneous nanostructure corresponds to an increased range in thermal transitions.[12] In the present case however, the range of transitions measured (at 100 locations spaced 1 μm apart, Figure 9) was narrow for all specimens. This may be because the heterogeneous structure is significantly finer than that previously investigated, and local differences are in this case beyond the resolution limit of the technique. Mean thermal transition points were measured to be $90.1\text{ }^{\circ}\text{C} \pm 0.9\text{ }^{\circ}\text{C}$ for stoichiometric resins, and $83.4\text{ }^{\circ}\text{C} \pm 0.4\text{ }^{\circ}\text{C}$ for excess epoxy resins prepared using 1 % catalyst. This data supports the notion that stoichiometric resins were more highly cross-linked overall, leading to enhanced resistance to water and ion uptake.

Figure 7. The equivalent circuits used for data fitting for intact and corroding films (top), and the phase (left) and magnitude (right) as a function of frequency measured by EIS for intact (solid line) and corroding (dashed line) excess epoxy films.

Figure 8. Resistance and pseudo-capacitance values calculated from equivalent circuit fitting of the EIS data for two stoichiometric coatings (red markers), and two excess epoxy samples (black markers), as a function of immersion time in 0.1 M NaCl electrolyte.

Figure 9. The nano-thermal analysis experiment: (left) schematic illustrating the technique; an AFM probe is heated whilst held in contact with the substrate, inducing thermal expansion followed by softening; (right) corresponding deflection signal of the AFM probe as a function of temperature for an excess epoxy resins cured using 1 % catalyst. Probe positions on the specimen are shown by markers in the inset.

Conclusions

The present study demonstrates that an internal nodular morphology develops in even very lightly cross-linked epoxy-phenolic networks, indicating that this nanoscale structure is likely to be an intrinsic feature of network systems. Whilst nodular dimensions have previously been linked to the relative kinetics of primary and secondary amine reactions for highly cross-linked epoxy amine systems[11], the very presence of this morphology is here found to be dependent on the selectivity of epoxy-phenolic reaction pre-gelation. Importantly, this finding allowed chemically similar resins to be produced with differing internal nanostructures, in order to study the effects on small molecule transport. It has long been postulated that heterogeneously cross-linked nanodomains provide low-energy transport pathways, but, due to the difficulty in producing homogeneous resins, this hypothesis has never been tested. Here, heterogeneous stoichiometric resins were found to retard water uptake and display enhanced corrosion resistance when compared to less polar homogeneously structured resins. This is attributed to a higher cross-linking density within stoichiometric specimens, whilst nanostructure does not seem to be a controlling factor. Further investigations controlling for the overall cross-linking density are however needed to fully ascertain the effects of internal topology on transport properties.

Conflicts of Interest

There are no conflicts of interest to declare.

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