Continuously responsive epoxy-amine cross-linked silicon sol–gel materials

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Abstract Advanced materials capable of responding to their chemical environment have been synthesized from the highly tailorable combination of sol–gel chemistry and epoxy-amine cross-linking reactions. Several materials were prepared from tetramethoxysilane (TMOS), and 3-glycidoxypropyltrimethoxysilane (GPTMS), and polyamine cross-linking agents. These cross-linking agents included diethylenetriamine (DETA), N-(2-aminoethyl)-piperazine (AEP$_Z$), 1-(2-aminoethyl)-piperidine (AEP$_D$), and ethylenediamine (EDA). Selective release of the indicator 4-methylaminoazobezene-4′-sufonic acid from these materials was monitored using UV–visible spectroscopy. Studies of the release demonstrate that it is continuously pH responsive with the greatest release at extreme pHs. Release is triggered by changes in the electrostatic interactions between the molecular additive and the matrix. These interactions can be readily tuned by altering the cross-linking agent.

Introduction

Responsive materials are of significant interest to materials chemists because of the range of potential applications including controlled drug-release [1], triggered-release of antimicrobial agents, biosensors [2, 3] and active corrosion inhibition [4]. There are a number of routes to the formulation and preparation of these types of materials including the use of organic polymer, block copolymers, dendrimers, biomaterials and sol–gel derived materials. A recent paper by the Barrett group [5] describes the release of dye molecules from multilayer films prepared from two polyelectrolytes. In that work release was controlled via pH and was a function of the electrostatic interaction between the dye molecule and the swelling of the material. In another example of controlled release [6] functionalized block copolymers have been used to control the release of hydrophobic drugs via hydrogen bonding. The interaction occurs between a functional group added to the block copolymer, and the functionalities present on the additive as a function of pH. These examples revolve around the use of organic polymers. Another approach to the formulation of controlled or triggered release is the use of sol–gel chemistry. These materials are typically inorganic or organic–inorganic hybrid in composition and are often more robust in extreme environments than purely organic polymer analogues. Additionally, their synthesis and encapsulation typically involves mild, aqueous conditions, which can represent a substantial advantage when incorporating chemically susceptible additives such as drugs.

Research groups have demonstrated the encapsulation of small molecules in silane sol–gel prepared materials. Avnir demonstrated the encapsulation of dye molecules such as methyl red and Reichardt's dye into gels prepared using the alkoxysilane tetramethoxysilane (TMOS) and alkylalkoxysilanes such as methyltrimethoxysilane (MTMOS) and vinyltrimethoxysilane (VTMOS) [7, 8]. Avnir found that by adding hydrophobic alkylalkoxysilane to the sol–gel matrix, leaching

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of the dopant could be slowed or prevented due to a decrease in the ingress of water into the material. In that case, the inclusion of alkylsilanes such as MTMOS and VTMOS were used to modify the hydrophobicity of the material without utilizing the organic functionality of the silane for subsequent reactions.

Using the same principles, the release of molecular additives from silane sol–gel materials can also be controlled. In previous work, we have demonstrated that the appropriate amount of MTMOS added to a cross-linkable matrix could lead to improved wet adhesion while maintaining the triggered-release character of the material [9]. Bottcher [10] has demonstrated the controlled release of biocides from sol–gel prepared xerogels of tetraethoxysilane (TEOS). Release in this case is controlled by the ratio of silica to biocide and by the addition of hydroxypropylcellulose. In that case and in similar research, sol–gel materials have been prepared from alkoxysilane precursors creating an inorganic matrix where release is mediated through control of pore size, the dissolution of a sacrificial organic polymer or the modification of surface polarity via the addition of an alkylalkoxysilane [11]. This approach is effective for many applications however; it is limited by the fact that after initiation the materials are not sensitive to their immediate chemical environment. This work describes the triggered-release behavior of a series of cross-linked sol–gel materials in which release is continuously responsive to the chemical surroundings.

Sol–gel materials were prepared through the acid-catalyzed hydrolysis and subsequent condensation of 3-glycidoxytrimethoxy silane (GPTMS) and TMOS. Because of the large H_2O:Si ratio used in this formulation, gelation does not occur. This allows for the utilization of epoxy-amine cross-linking for solidification of the material and incorporation of the amine moieties into the solid.

There are a number of known methods for cross-linking epoxy functionalities including the use of strong acids such as HCl, thermally curing the material and photo polymerization. We have chosen to use room temperature epoxy-amine chemical cross-linking. This method is desirable because it is fast and efficient, adds an additional functionality to the coating and allows for the use of different types of polyamines in the cross-linking step. Here, we describe the critical role that amines play in the triggered-release of molecular additives. These cross-linked materials demonstrate pH-dependent triggered-release, which is a function of electrostatic interactions between the molecular additive and the matrix. These interactions are dominated by the amine moieties resulting form the epoxy amine cross-linking process. The crucial role of the

amine cross-linker has been confirmed by studying the changes in the triggered-release profiles when different polyamines are used and by comparing these systems with the release profile of uncross-linked TMOS and GPTMS:TMOS materials. pH exposure cycling experiments demonstrate the ongoing responsive nature of these materials to their chemical environment.

Three organic cross-linkers, ethylenediamine (EDA), N-(2-aminoethyl) piperazine (AEP_Z) and 1-(2-aminoethyl)-piperidine (AEP_d), were considered in this study (Fig. 1). Triggered-release of an additive from DETA cross-linked materials has previously been studied and was used as a benchmark in this study [9].

The additional cross-linkers were selected for their structural differences or similarities to DETA. EDA is essentially a truncated version of DETA. AEP_Z was chosen as a cross-linker because of its cyclic structure in contrast to the linear structures of EDA and DETA. AEP_z was expected to lead to a more rigidly cross-linked material because of its cyclic structure. A fourth amine-containing molecule was added to this study, AEP_d, to aid in elucidating the behaviour observed for AEP_z materials. AEP_d and AEP_z differ from each other by one secondary amine in AEP_z. Additionally both AEP_z and AEP_d are of interest for applications of these materials as active corrosion suppression coatings.

The molecular additive chosen for this work was the pH indicator methyl orange. This additive was selected for its easily quantifiable release using UV–visible spectroscopy and the fact that it contains several functional groups often present in molecules of practical interest for triggered- or controlled-release. While the triggered-release profile characterized in this work is specific to methyl orange, we believe that an understanding of what drives release, in particular the electrostatic interactions occurring between the matrix and functional groups of the additive, will allow for the prediction of the triggered-release profiles of different additives from this type of material.
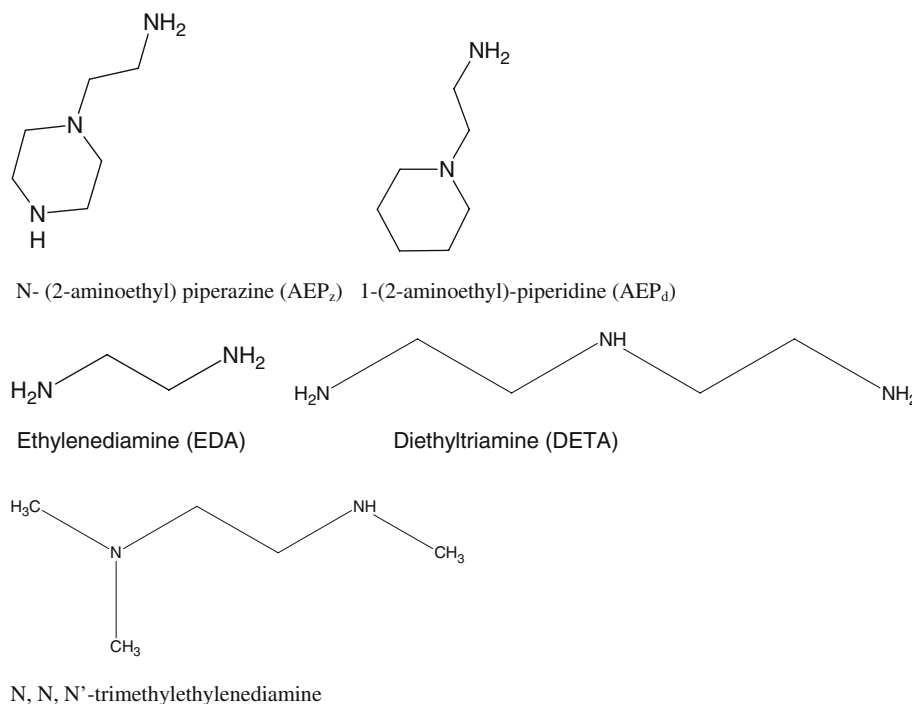
The cross-linked materials were characterized through solid-state NMR measurements, Raman and IR spectroscopy, pK_a computation, triggered-release experiments, pH cycling experiments, and zeta potential measurements.

Experimental

1:3 Tetramethoxysilane: 3-glycidoxypropyltrimethoxysilane

The 1:3 TMOS: GPTMS (Sigma-Aldrich) coating was prepared by drop-wise addition of a mixture of 0.02 mol

Fig. 1 Amine cross-linkers used for triggered release materials described here

N- (2-aminoethyl) piperazine (AEP$_z$)　　1-(2-aminoethyl)-piperidine (AEP$_d$)

Ethylenediamine (EDA)　　　　　　Diethyltriamine (DETA)

N, N, N'-trimethylethylenediamine

of TMOS and 0.06 mol of GPTMS to 21.60×10^{-6} m^3 of acidified deionized H$_2$O (0.05 M acetic acid). Once the addition was completed, the solution was allowed to age closed for 72 h with continuous stirring. Following aging, 19.38×10^{-6} m^3 of a surfactant solution (0.1% w/w solution in deionized H$_2$O of 3M Flourad) was added. The solution was gently stirred and filtered using a 0.8 μm cellulose acetate filter (Cole-Parmer). The cross-linker DETA, EDA, AEP$_z$ or AEP$_d$ (Sigma-Aldrich) was added to the sol in a 1:1 ratio of epoxide to amine proton with an equivalent volume of H$_2$O. Into the resulting solution clean, glass substrates were dipped. Each slide received three consecutive dips into the solution before being allowed to air dry at room temperature for 24 h. The edges of the slides were taped to create a well-defined surface area with minimal perturbation from edge effects for leaching purposes. The pH indicator methyl orange (4-methylaminoazobenzene-4'-sulfonic acid) was incorporated into the coatings following the addition of the silane to the acidified H$_2$O. It was determined in previous research that a 0.5% w/w mass of molecular additive is an appropriate amount in order to observe significant leaching from the coatings without disturbing the mechanical or chemical properties of the matrix [9].

TMOS coating

To identify the factors affecting the triggered-release process, a tetramethoxysilane only film was also

prepared. About 0.05 mol of TMOS (Sigma Aldrich) was added drop-wise to 21.6×10^{-6} m^3 acidified H$_2$O. The solution was allowed to for age 2 h with continuous stirring. Following aging, the solution was removed from the stir plate; 19.38×10^{-6} m^3 of a surfactant solution (0.1% w/w solution in deionized H$_2$O of 3M Flourad) was added. The solution was stirred manually and then filtered using a 0.8 μm cellulose acetate filter (Cole-Parmer). Coatings were prepared as described above.

Zeta potential measurements

The 1:3 coating was prepared as described above however, instead of the addition of a cross-linking agent, an amine epoxide terminating species was used. Two different terminating groups were chosen: diethylamine (DEA, Sigma Aldrich), 6.65×10^{-6} m^3 (0.06 mol) or N,N,N'-trimethylethylenediamine (MEDA, Sigma Aldrich), 2.03×10^{-6} m^3 (0.06 mol) was added to the solution following the filtration step. About 0.05 g of Snowtex-ZL silica particles (Nissan Chemical Industries) were added to 3×10^{-6} m^3 of the terminated sol–gel, the mixture was sonicated for 2 min and then placed in a centrifuge for 3 min. The sol–gel solution was then decanted off the coated silica particles. The above procedure was performed three times, after the final repetition; the particles were suspended in 5×10^{-6} m^3 of distilled water. This protocol results in nanoparticle substrates coated with amine terminated

sol–gel material suitable for zeta potential analysis. A very similar process has been described elsewhere and has been used in zeta potential analysis of polymeric coatings and sol–gel derived materials [9, 12].

The zeta potential measurements were performed using a Brookhaven ZetaPlus: Zeta Potential Analyzer. The sol–gel coated colloidal silica was studied using microelectrophoresis over a pH range of 2.0–12.5. The studies were carried out in a solution of deionized water. Twenty zeta potential measurements were taken for each of the pHs at a fixed temperature of 25 °C.

Substrate preparation

The substrates used were plain glass microscope slides (Corning 2947), cleaned as follows: 3 min sonication in methanol, followed by a 3 min immersion in concentrated KOH/ethanol, followed by 3 min of sonication in distilled water. The slides were rinsed between steps with distilled water to avoid contamination of the different baths. After completely drying in air, a surface treatment was applied to the slides. The surface treatment was a solution of GPTMS ($4.42 \times 10^{-6}\,\mathrm{m}^3$) combined with acidified H_2O ($36.0 \times 10^{-6}\,\mathrm{m}^3$) in a drop-wise manner. The solution was stirred for 30 min. Clean substrates were immersed in the resulting solution for 20 min and allowed to dry for 12 h.

Triggered-release protocol

The triggered-release studies were performed in seven different buffered solutions with one slide per solution. The buffered solutions spanned the pH range from 2.5 to 11.0. The buffers for the range between 2.5 and 5.0 were prepared from a 0.1 M solution of sodium acetate, the 6.0–8.0 range was prepared from a solution of NaH_2PO_4 with a concentration of 0.1 M, and the range form 9.0–11.0 was prepared from a solution of concentration 0.1 M of Na_2HPO_4. The pH of all of the buffered solutions was adjusted using either concentrated HCl or NaOH. The coatings were leached over a period of 1440 min into $50 \times 10^{-6}\,\mathrm{m}^3$ of buffered solution. The first sample was removed after 20 min of exposure to the buffered solution (approximately $3 \times 10^{-6}\,\mathrm{m}^3$) two additional samples were taken after 60 and 90 min had passed. A fourth sample was taken at the 120-min point and every 60 min after that for a total of 360 min. A final sample was taken after a total of 1440 min. Once all the samples were collected, the pH of each sample was adjusted to 2.5 using concentrated HCl. This pH corresponds to the highest molar absorptivity for methyl orange. The UV–visible spectra of the leachate were measured using an Ocean Optics Inc. USB 2000 USB-ISS-UV/VIS spectrometer between 400 and 600 nm.

Raman spectroscopy

Raman spectra were obtained on a Reinshaw inVia Raman microprobe with an excitation wavelength of 633 nm, from a helium neon laser at a maximum power of 20 mW. Samples were dip-coated onto aluminum substrate and the spectrum was acquired with a typical exposure time of 3 min.

Infrared spectroscopy

Grazing angle IR spectra of the coatings on aluminum alloy substrates were obtained on a Bruker Equinox 55 Spectrometer with liquid nitrogen cooled MCT detector. Typically, 100 co-added sample scans were ratioed against scans from a gold mirror background to generate the log reflection spectra presented here.

NMR spectroscopy

All solid-state ^{29}Si and ^{13}C NMR spectra were obtained at a frequency of 515 Hz on a Bruker ASX-200 NMR spectrometer using a 5 mm solid-state probe. Spectra were obtained at 294 K. Spectra were acquired for 3 h to achieve the desired signal to noise.

Results

Adhesion test

It is important that these materials demonstrate good wet adhesion for a number of reasons; in particular, good wet adhesion insures long lifetimes for the coating as many of the proposed applications involve the exposure of these materials to wet environments. It also insures that the primary release mechanism is something other than simple coating delamination. As well, all release studies are performed while coatings are submerged into aqueous solutions for several hours to several days. Good wet adhesion under such circumstances is necessary for these measurements to be made. Good adhesion was judged to be the absence of visible blistering or flaking of the coating during the adhesion tests.

The coatings' wet adhesion performance varied as a function of the amine cross-linker. EDA cross-linked materials demonstrated the best performance with excellent adhesion in dilute Harrison solution (3.5% ammonium sulphate and 0.5% NaCl) for over

12 months. By contrast, AEP$_z$ had the poorest adhesion with delamination occurring after only 2 h in solutions of all pHs and ionic strengths.

Triggered-release

The triggered-release profiles of the coatings were studied over a period of 24 h. All coatings containing the molecular additive were orange in colour initially and remained unchanged throughout the triggered-release period indicating that not all of the molecular additive was removed from the matrix over the release study. The triggered-release profiles for all of the coatings are shown in Fig. 2. They are subtly different from one another with EDA and AEP$_d$ having release minima at pH 6.0; DETA and AEPz at pH 5.0. Triggered-release experiments performed with TMOS and uncross-linked TMOS:GPTMS coatings had very different results from those of the cross-linked materials. A comparison of triggered-release from TMOS and from a DETA cross-linked material is shown in Fig. 3.

pH cycling

pH cycling experiments were carried out for all of the coatings. The samples were alternated between extreme pH (2.5 or 11.0) and moderate pH (6.0). Typical results are presented in Fig. 4. The materials demonstrated an instantaneous response to their pH environment [9].
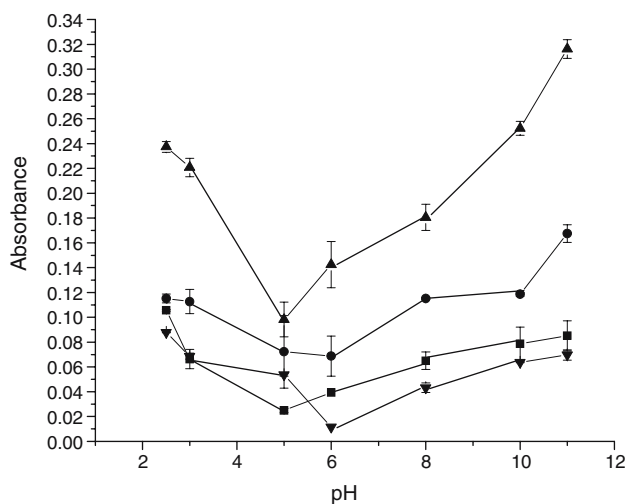
Zeta potential measurements

Zeta potential measurements allow for the isoelectric point of the coating to be estimated by studying the behaviour of coated nanometer diameter silica particles under the influence of an electric field in solution as a function of pH. The charge on the coated particle is determined to be zero at the pH where it demonstrates no mobility in an electric field. Given that the charge behaviour of a non-conducting coating and particle will be dominated by the composition of the coating, this procedure effectively measures the zeta potential of the sol–gel coatings described here. This
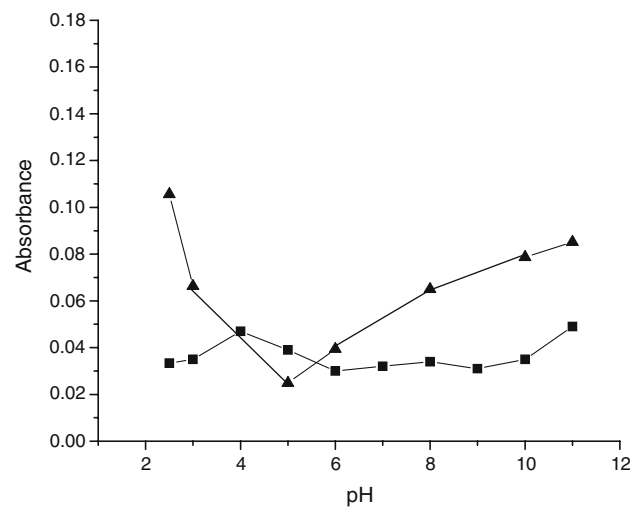

Fig. 3 Triggered release of methyl orange from (■) TMOS matrix and (▲) DETA cross-linked matrix

Fig. 2 A comparison of the triggered release of methyl orange from each of the coatings; (■) DETA cross-linked, (●) EDA cross-linked, (▲) AEP$_Z$ cross-linked and (▼) APE$_d$ cross-linked
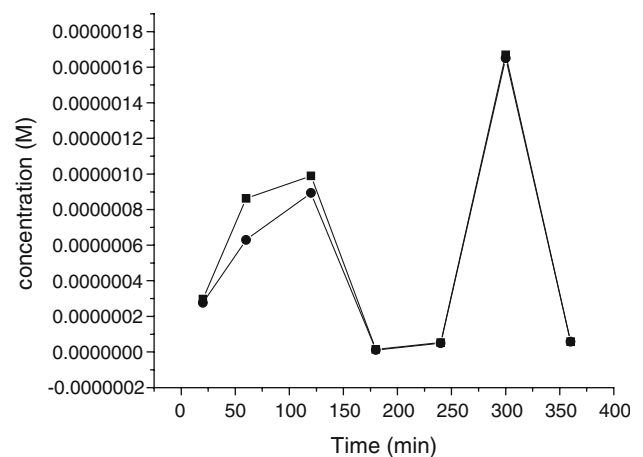

Fig. 4 Results from pH cycling for coatings cross-linked with DETA. (■) Coating cycled from pH 2.5 to pH 6.0, (●) coating cycled from pH 11.0 to pH 6.0

approach has been established previously for layers of organic polymers on nanoparticle silica [12].

The result of this measurement is shown in Fig. 7. The isoelectric point for the EDA cross-linked coating is approximately 10.20, and is entirely different from that observed for uncoated silica particles [12].

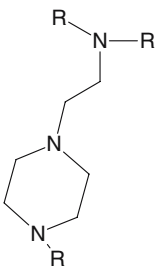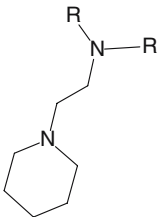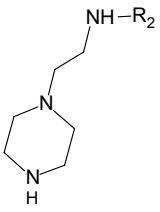pKa determination for cross-linked materials

Using ACD/pka software accessed through ACD/I-labs, we computed the pKa's for various moieties representing the likely products of the epoxy-amine cross-linking reaction (Table 1). From this work, it is clear that as the amines become more substituted their pKa's drop, making them better nucleophiles. Fully substituted cross-linkers were found to be fully deprotonated at pH 8.59 for AEP_d, 7.78 for AEP_z, 7.69 for EDA and 7.41 for DETA.

Epoxide consumption measurements

To identify the species present in the matrix following film preparation, epoxide consumption was studied for both monoliths and coatings using ^{13}C solid-state NMR, Raman and infrared spectroscopy. The absence of peaks in the solid-state ^{13}C-NMR spectra at 50 and 44 ppm and 1250 cm^{-1} in the Raman indicate that all of the epoxide groups have been consumed in the monoliths [14].

Raman spectroscopy of the coatings demonstrates that the epoxide groups remain for slightly longer period than those in the monoliths. The coatings exhibited peaks at 1250 cm^{-1} for up to 96 h after the coatings were visually dry. IR spectroscopy confirms this result and suggests that mostly tertiary amines remain indicating completion of the epoxide amine cross-linking. Previous results by Vreugdenhil et al. on a similar coating support this result [15].

Table 1 Amine-containing components and their respective pKa's

Component	Derived from	pK_{a1}	pK_{a2}	pK_{a3}
$R_2NCH_2CH_2NRCH_2CH_2NHR_2$	DETA	2.16 ± 0.50	7.04 ± 0.19	7.41 ± 0.19
$R_2NHCH_2CH_2NHR_2$	EDA	5.38 ± 0.21	7.69 ± 0.50	
	AEP_z	2.22 ± 0.50	6.11 ± 0.19	7.78 ± 0.25
	AEP_d	5.96 ± 0.19	8.59 ± 0.20	
$R_2NCH_2CH_2NHCH_2CH_2NHR$	DETA	2.22 ± 0.50	7.05 ± 0.50	8.86 ± 0.19
$R_2NCH_2CH_2NHR$	EDA	5.78 ± 0.50	8.81 ± 0.19	
	AEP_z	2.33 ± 0.50	7.57 ± 0.50	9.45 ± 0.25

These results were obtained using ACD/pka v. 8.02 via the ACD/I-lab service) [13]
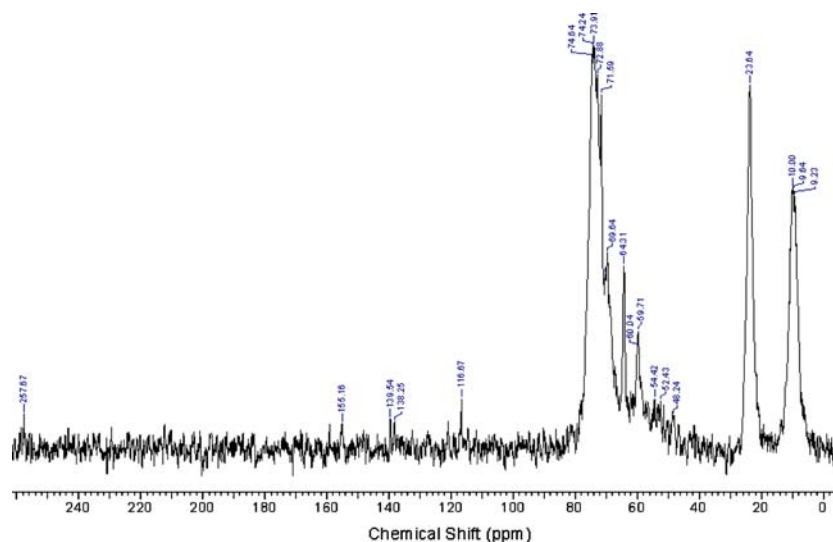
Discussion

Characterization of amine moieties in the material

Solid-state ^{13}C NMR and Raman spectroscopy of monoliths of these materials indicate that all epoxides are consumed in the final material (Fig. 5). Raman spectroscopy of the coatings suggests that the epoxides are present initially after coatings are prepared. However, within 96 h, all epoxides are consumed. The difference between these two results can be accounted for by the significantly longer drying time required for monoliths versus coatings (1 h vs. 3 min) allowing for longer interaction time between the epoxide groups and the cross-linking amines. The epoxide consumption for the coatings as a function of amine cross-linker is shown in Fig. 6. These results show that over a period of 48 h most of the epoxide groups are consumed: 80% for DETA cross-linked materials, 70% for EDA and 100% for AEP$_z$. After 96 h, all epoxides in all coating formulations are consumed.

Raman investigations of the epoxide consumption, AEP$_z$ was the most efficient cross-linker requiring only 24 h to reach complete epoxide consumption. The epoxide–amine cross-linking mechanism is a nucleophilic attack of the epoxide group by the lone pair of electrons on the amine, as more amines become functionalized during the cross-linking reaction they become better nucleophiles. However, as the amines react with the epoxides in the sol–gel coating, steric hindrance of the bulky groups attached to the epoxides are expected to slow down the rate of the reaction. Additionally, increasing rigidity of the cross-linked solid reduces the mobility of the epoxide and amine groups.

Wet adhesion and cross-linker hydrophobicity

As previously mentioned, the wet adhesion of the coatings is of particular importance for elucidating the triggered-release mechanism. IR and Raman results indicate that all epoxide groups are consumed suggesting that the coatings are densely cross-linked and should ideally act as efficient water barriers [16, 17]. However, wet adhesion experiments for the AEP$_z$ cross-linked coatings demonstrated poor wet adhesion over the entire pH range, with the coating bubbling due to water penetration and eventually delaminating entirely from the substrate. This behaviour was not observed for the three other coating systems studied.

The success of the DETA and EDA cross-linked is not unexpected. However, the durability of the AEP$_d$
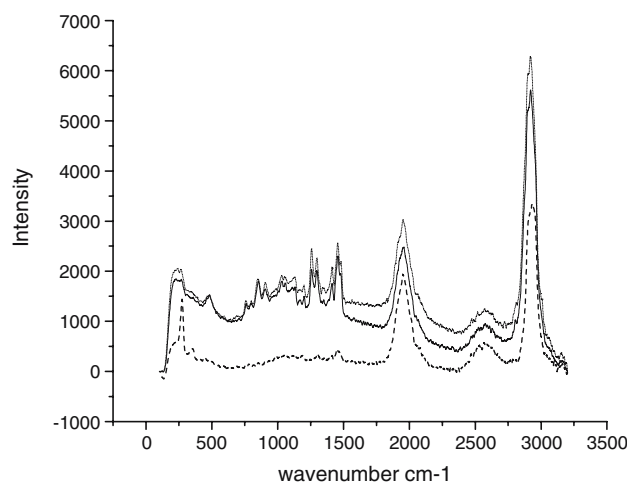
Fig. 6 Raman spectra for AEPZ (dashed line), EDA (dotted line) and DETA (solid line) cross-linked coatings 48 h after cross-linking

Fig. 5 ^{13}C Solid state NMR for EDA cross-linked monolith

cross-linker system was somewhat unanticipated given the similarities between AEP$_z$ and AEP$_d$. One explanation is that the performance differences between AEP$_z$ and AEP$_d$ cross-linked coatings could be due to an increase in the hydrophilicity of the materials given that AEP$_z$ is a more hydrophilic molecule with an additional secondary amine in its 6-member ring (Fig. 1). This hydrophobic/hydrophilic difference is also suggested by the triggered-release results for AEP$_d$ (Fig. 3) where release from this coating was approximately 1/3 less than that observed for AEP$_z$ formulated coatings. As demonstrated by Avnir's work on MTMOS and VTMOS materials [18], we ascribe this difference to the fact that the hydrophobic nature of the cross-linker will result in a slower ingress of water into the material. AEP$_z$ on the other hand releases the most additive due to an increase in hydrophilicity allowing for more facile ingress of water into the coating.

Cross-linker dependent triggered-release

The triggered-release profiles for EDA, DETA, AEP$_d$ and AEP$_z$ coatings are shown in Fig. 2. Overall, the release profiles share the same general horseshoe shape; however, the results of the triggered-release experiments demonstrate that the use of different cross-linkers can be used to subtly tune the triggered-release profile of the material. This is most readily apparent in the dependence of release minima for the different formulations. This occurs at pH 5.0 for materials cross-linked with DETA and AEP$_z$ and pH 6.0 for EDA and AEP$_d$ cross-linked materials. As well, the EDA and AEP$_z$-triggered release profiles have an asymmetric appearance with more additive being released at basic pH than at acidic. DETA and AEP$_d$ have profiles that are more symmetrical. A comparison between DETA's release profile and TMOS only release coating emphasizes the responsiveness of the cross-linked coatings (Fig. 3). Uncross-linked TMOS-GPTMS also shows no responsiveness to their chemical environment in the release profile.

We have used a number of tools to characterize the coatings and clarify the triggered-release dependence on the amine cross-linker. The only difference between the materials investigated in this work was the cross-linker used in the formulation. Although the rate of epoxide consumption varied slightly as a function of the amine used, all coatings achieved complete epoxide consumption within 96 h. IR spectroscopic studies suggest the presences of mostly tertiary amines in all cross-linked coatings rather than secondary or primary amines. In light of the fact that the amines in the

coating dominate the electrostatics of the system and the triggered release mechanism is primarily an electrostatic one, an investigation of the charge states associated with the coating was conducted.

The electrostatics of the coating were studied using two approaches. First, zeta potential was used to study the behaviour of silica particles coated with a model of the EDA cross-linked coating. These results are presented in Fig. 7. The isoelectric point for the modeled material occurs at pH 10.20. The four coatings studied differ only in the amine used to cross-link them. The ratio of silane precursors and the formulation conditions are the same in every case. The isoelectric point of the silica particles is known to be 2.3 [12] and primarily silica-coated materials have similar acidic behaviour. The basic isoelectric point observed for these sol–gel-derived materials clearly indicates that the charge state of the coating is dominated by the amines used in the cross-linking process.

In an effort to identify the electrostatic behaviour of the different moieties that may be present in the coating as a result of the epoxy amine reaction, the pK_a was calculated for the cross-linkers themselves and several likely epoxy-amine reaction products as suggest by IR and Raman results [13]. These species are shown in Table 1. The calculated pKa's suggest that each of the coatings are fully deprotonated and therefore neutral above pH 8.5. This is lower than the pH predicted using zeta potential, which was a pH of 10.2. Given the assumptions in each of these models, it is likely that the true isoelectric point for the coating falls somewhere between the zeta potential result and the pKa calculations. Both models are useful in bracketing
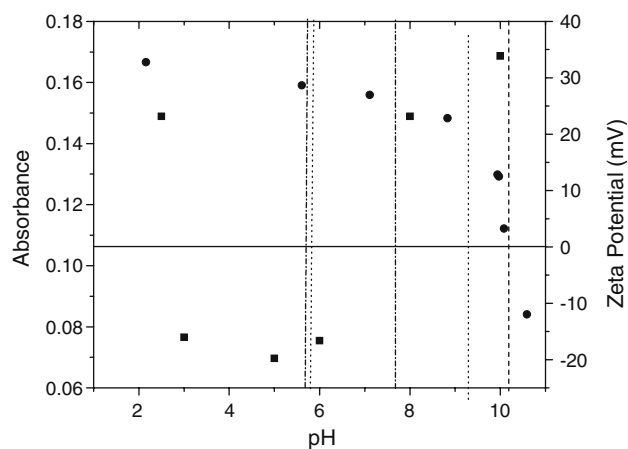

Fig. 7 Zeta Potential results for the 1:3 coating terminated with N,N,N'-trimethylethylenediamine. The isoelectric point is indicated with the dashed line, overlaid with the leaching profile of the EDA cross-linked coating

the electrostatic behaviour of the cross-linked sol–gel materials and demonstrating the important role of the amines in the triggered-release process.

If we consider all of the electrostatic data for the coatings and the molecular additive methyl orange, the electrostatic interaction becomes clear (Fig. 7). Methyl orange is zwitterionic between pH 2.5–3.0 and become negatively charged around pH 4.0; it carries this negative charge over the rest of the triggered release pH range. From both the pKa result and the zeta potential measurements, we know that the coating is positively charged between pH 2.5 and 3.0. We expect little interaction between the coating and the additive in this range and uninhibited release of the additive from the coating. EDA and AEP_d coatings are expected to be fully positively charged until approximately pH 5.38 for EDA and 5.96 for AEP_d. These pHs correspond well with the triggered release minima observed for the coating cross-linked with EDA or AEP_d. DETA and AEP_z on the other hand loose their first proton at pH ~2.0 an additional proton is lost by these amines at approximately pH 7.04. As the pH increases, the epoxy-amine cross-links undergo further deprotonation resulting in the coating carrying no charge. In this region, an increase in the amount of methyl orange released from the coating is observed as the electrostatic interaction between coating and additive decreases.

Due to the fact that electrostatic interactions dominate the triggered release behaviour, these cross-linked sol–gel materials should continuously respond to their immediate chemical. In order to evaluate this aspect of their release behaviour pH cycling experiments were carried out on each of the coatings. In these experiments, coatings were cycled between moderate and extreme pHs. Extreme pH exposure produced the expected maximum release. Cycling the samples to moderate pH resulted in minimal release (Fig. 4). Release profiles from these experiments demonstrate that the materials respond continuously to their local pH, independent of the pH to which they had previously been exposed. This novel behaviour indicates that little to no coating degradation occurs during the release experiments and further emphasizes the continuing responsiveness of the materials to their current chemical environment.

Conclusion

This work demonstrates the role that amine cross-linkers play in the triggered release of molecular additives from alkylalkoxysilane sol–gel coatings. The results of this work expand the proposed electrostatic mechanism previously described by us for a single amine cross-linker [9]. A thorough study of the iso-electric point of the coatings has been performed using zeta potential measurements and computation of pK_a's for a variety of species potentially present in the material. These studies, in combination with the release profiles for the coatings cross-linked with DETA, EDA, AEP_z and AEP_d, allow for a satisfactory elucidation of the release mechanism. Cross-linking efficiency of the four amines has also been characterized providing a better understanding of the coatings matrix. The pH cycling experiments have highlighted the continuous responsiveness of these coatings to their immediate chemical environment. This work permits us to readily identify new additives and to estimate their triggered release behaviour. This knowledge will be applied to the triggered release studies of additives selected for their target applications. It is hoped that with a full understanding of triggered release, it will be possible to precisely tune these materials to release additives only under very specific environmental conditions and that these materials will remain continuously responsive primarily by selecting the appropriate cross-linking agent.

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