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Reactions in polyethoxysilane coatings using solution and solid-state ^{29}Si NMR spectroscopy

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Solution and solid-state ^{29}Si nuclear magnetic resonance (NMR) spectroscopy was used to follow the prehydrolysis and subsequent film formation of a polyethoxysilane mixture. Significant differences in intensity of the Q_2 resonances in the cross-polarization and dipolar decoupled spectra suggest a mobile phase is present in the cured film. Incorporation of solvent in the film is observed directly by ^{13}C cross polarization magic-angle-spin (CP MAS) NMR. The NMR results support the conclusions reached from a parallel chemical study.

1. Introduction

Polyethoxysilanes are used as protective coatings for stonework and with zinc in rust-proofing paints [1]. The protective action stems from the hydrolysis of the polyethoxysilane leading to an impervious three-dimensional matrix. Owing to the fluid nature of the applied materials, pores in the structure whilst penetrated and thus coated, are not blocked by the resulting layer with the result the surface can still breathe.

In view of the amorphous nature of the silicate matrix resulting from hydrolysis of the polyethoxysilanes little is known about the polymeric structure of the matrix. Indeed the effect of varying the prehydrolysis step and the curing conditions on the structure of the resulting film, is not properly understood at the atomic level. Recently, solid state ^{29}Si NMR spectroscopy has been shown to be extremely useful in studying the silicate polymerization reactions involved in the hydration of calcium silicates [2–5] where the product is again amorphous. An advantage of the polyethoxysilane hydrolysis is that the initial changes take place in a highly concentrated solution allowing the use of solution ^{29}Si NMR spectroscopy to characterize the changes in the silicate species during the early stages of the reaction [6, 7].

The utility of ^{29}Si NMR rests upon the sensitivity of the ^{29}Si NMR chemical shift to the degree of condensation of the silicate species. If the local environment around each silicon is $\mathrm{Si(OR)}_{4-x}\ (\mathrm{OSi})_x$, commonly represented by the symbol Q_x, then the resonances corresponding to $x = 1$ to 4 lie in distinct regions with only a minor degree of overlap depending on the exact local environment [8–9].

We report here preliminary ^{29}Si NMR studies of changes in the solution species as a result of the partial hydrolysis of polyethoxysilanes and alterations in the nature of the silicate film produced during curing as a function of curing time. The dependence of the nature of the film on the pH and the presence of Zn(II) ions during curing was also examined.

2. Materials and methods

Polyethoxysilane (Silbond 40, Stauffer Chemical Company) was used as supplied. Partial hydrolysis to the notional extent of three ethoxy groups per silicon was carried out by taking 45.0 g Silbond 40 and 49.8 g ethoxy-ethanol together with 5 ml of distilled water and 0.22 ml of 0.05 M HCl. Prior to curing the pH was adjusted to 5.7 or 1.0 and for one series of experiments zinc chloride was added to give a 3 mM concentration of zinc(II). A suitable amount of each liquid sample was placed in a Petri dish to give a film thickness of 75 μm. The curing was then allowed to take place at a constant humidity of 80% and at a temperature of 25° C. Portions of cured film were removed at various times and vacuum dried prior to NMR examination.

The solid state NMR spectra were collected on a Bruker CXP200 spectrometer operating at 39.7 MHz for ^{29}Si, 50.32 MHz for ^{13}C and 200.13 MHz for ^{1}H. Solution ^{29}Si NMR spectra were obtained using the SERC NMR Service at the University of Warwick. For the solid state NMR spectra, MAS [10] at 3.5 kHz was employed to average the anisotropic spin interactions and give high resolution NMR spectra. MAS was carried out using an Andrews-type rotor made of Delrin packed typically with 0.5 g of sample. Deuterated plexiglass rotors were used for the ^{13}C CP MAS spectra. High power proton decoupling was used to remove proton dipolar broadening. Cross polarization [11] experiments were performed using an

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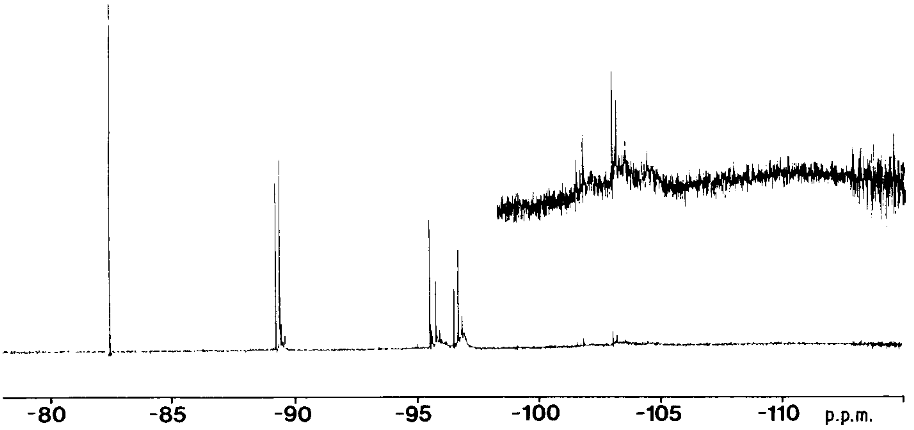

Figure 1 79.46 MHz ^{29}Si NMR spectrum of Silbond 40. A total of 470 transients were acquired using a 30 sec recycle delay.

optimum contact time of 1 m sec for ^{29}Si and 2 m sec for ^{13}C. No changes in relative intensities were found in the cross polarization spectra as a function of the contact time nor in the dipolar decoupled spectra as a function of recycle delay.

3. Results and discussion

The solution ^{29}Si NMR spectrum of the starting polyethoxysilane (Fig. 1) demonstrates well the value of ^{29}Si NMR spectroscopy for following polymerization reactions of silicates. At low field, $\delta = -82.4$ p.p.m., is the resonance corresponding to Q_0 silicon nuclei indicative of a monomeric tetraethoxysilane [12]. As the integrated intensity of this resonance is roughly 16% of the overall intensity the Silbond 40 is clearly shown to contain a significant fraction of polymers as the Product Information Bulletin states [13]. This was also supported by a GC/MS examination of SILBOND 40 which provided evidence for volatile polymers containing up to five silicon atoms. The next resonances upfield at around $\delta = -89.5$ p.p.m. correspond to Q_1 units, that is the end units of a polymer either a simple dimer or of a longer chain polymer. At least two Q_1 resonances can be resolved. These arise because the chemical shift of the Q_1 resonance is sensitive to the length of the polymer chain [12]. In the absence of specific data correlating the actual chemical shift to the chain length a more complete assignment is not possible. Similarly at least two resonances are seen in the Q_2 region at $\delta = -96$ p.p.m., these resonances however appear to be grouped onto two sub regions which we may tentatively assign as cyclic middle units and acyclic chain middle units [14]. An interesting feature of the spectrum are the resonances at $\delta = -103$ p.p.m. which can be assigned to Q_3 branching units. The simplest interpretation is that branched chain polymers are present although more condensed species such as a trigonal prismatic hexamer or cubic octamer may also be present as observed in aqueous silicate solutions [15].

Partial hydrolysis causes major changes in the solution ^{29}Si NMR spectrum, (Fig. 2). Two effects are apparent, first significant changes take place in the chemical shifts and second the resonance line-widths increase. The changes in chemical shift correspond to the formation of new species as hydrolysis of the ethoxyl to hydroxyl groups occurs followed by the polymerization of the hydroxylated silicates. Changes in the resonance line-widths can be attributed to either an increase in the spin–spin relaxation time T_2 or to a distribution of chemical shifts. A spin echo experiment demonstrates that the apparent line-width can not be due to a short T_2 and must arise from a distribution of chemical shifts indicating the heterogeneous nature of the polymers in solution. The effect of the substitution of ethoxy groups by hydroxyl groups in a hydrolysis is to cause a small downfield shift in the ^{29}Si chemical shift of around 1–2 p.p.m. per group. Consequently the absence of a resonance at ~ -80 p.p.m. implies the concentration of any monomeric species is negligible. The absence of monomers follows from their greater reactivity. Thus rapid hydrolysis has taken place to monosilicic acid followed by a fast polymerization. The low intensity of the Q_1 resonance at -86 p.p.m. suggests that few end units are present which is quite surprising implying either the formation only of cyclic polymers or of very long acyclic polymers. Two groups of Q_2 resonances are present corresponding to hydroxylated middle units, Q_2(OH), and ethoxy middle units Q_2(OEt) clearly showing that the

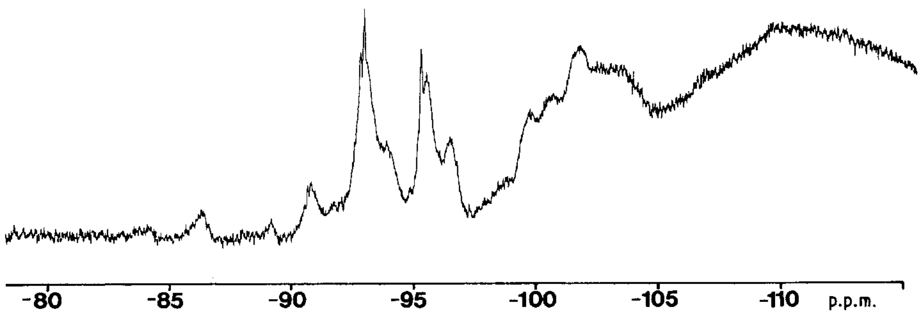

Figure 2 79.46 MHz ^{29}Si NMR spectrum of the prehydrolysed Silbond 40. A total of 3260 transients were acquired using a 30 sec recycle delay.

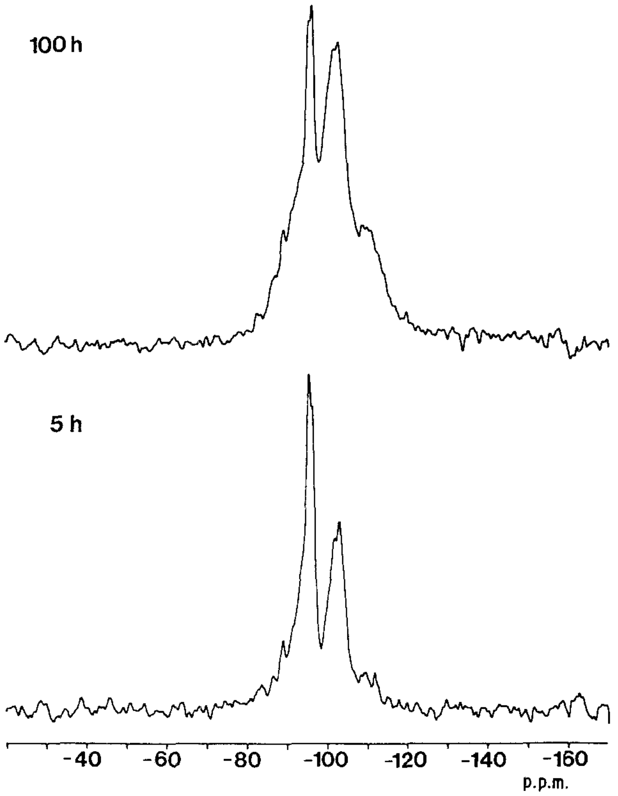

Figure 3 39.73 MHz solid-state ^{29}Si MAS NMR spectrum of the cured film after 5 and 100 h. About 2000 transients were acquired with high power proton decoupling and a recycle delay of 10 sec.

hydrolysis has occurred under conditions of insufficient water as indeed was the case. Reactions involving the monomeric units have led to two effects. The first is to cause an increased chain length as shown by the lower Q_1 intensity and the second is to cause increased branching as shown by the significant Q_3 resonance. This conflicts to a certain extent with ideas put forward concerning the hydrolysis of tetraethoxysilanes in sol-gel processes [16, 17] where it is suggested that long acyclic unbranched polymers are formed. No evidence is seen for Q_4 units. Provided that the resulting Q_4 units are low in molecular weight we would expect to see them, since non-viscous silica sols can be produced which give essentially only Q_4 resonances in the solution ^{29}Si NMR spectra [18].

During the curing stage a solid film is formed which gradually hardens. Under the above curing conditions the film is first evident after 5 h and is essentially completely hard by 100 h. The solid state ^{29}Si NMR spectra of the solid film samples taken as a function of the curing time are shown in Fig. 3. The cross polarization spectra are shown in Fig. 4. The most striking feature highlighted by a comparison of the conventional dipolar decoupled and CP spectra is the much lower intensity of the Q_2 resonance in the CP spectra. Whilst intensities may be distorted in a CP experiment because the extent to which enhancement occurs will depend on the local proton concentration surrounding each silicon nucleus and the strength of the dipolar coupling [19] it is not likely that the Q_2 resonance will be adversely affected relative to Q_3 and Q_4 resonances in a rigid lattice solid. The lack of enhancement of the Q_2 resonance in the CP experiments is thus indicative of motion of these middle units. This motion might be quite restricted, for example if the Q_2 units form part of the matrix, but with a correlation time such that coupling of the ^{29}Si spin to the ^1H spin bath is possible allowing efficient rotating frame relaxation of the ^{29}Si spins [20]. Alternatively, the Q_2 resonances may be in a relatively fluid region, for example if solution is trapped in the matrix, and capable of rapid isotropic reorientation so that the dipolar coupling necessary for CP is effectively averaged to zero. Evidence that a significant fraction of the Q_2 resonance is not part of the matrix is provided by the solid state ^{29}Si NMR spectrum of the high molecular weight fraction present in the solution prior to the formation of the film, Fig. 5. This fraction was obtained by removing the

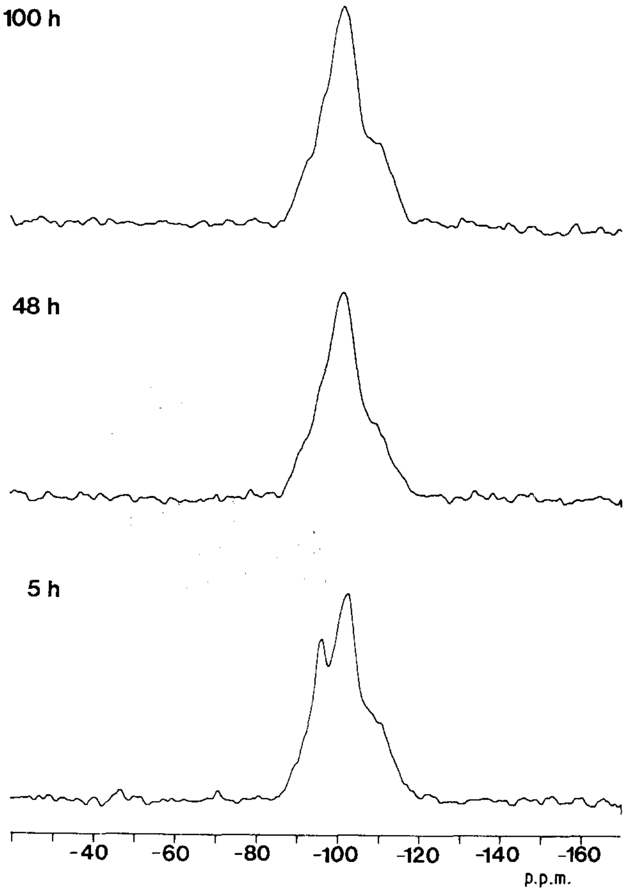

Figure 4 39.73 MHz solid-state ^{29}Si CP MAS NMR spectrum of the cured film after 5, 48 and 100 h. Roughly 400 transients were acquired using a contact time of 2 m sec and recycle delay of 3 sec.

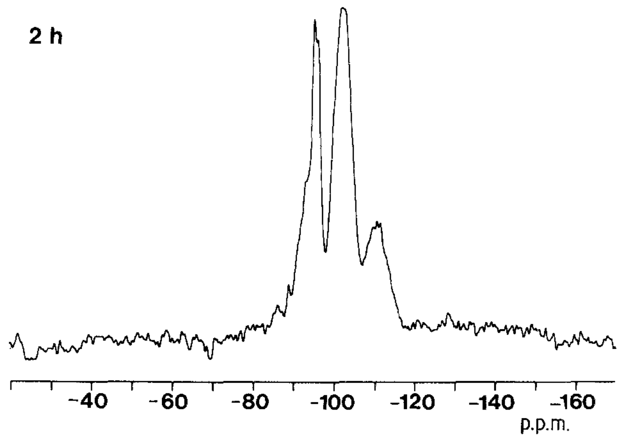

Figure 5 Dipolar decoupled 39.73 MHz solid-state ^{29}Si MAS NMR spectrum of the solid fraction obtained from the curing mixture by rotary evaporation after 2 h reaction.

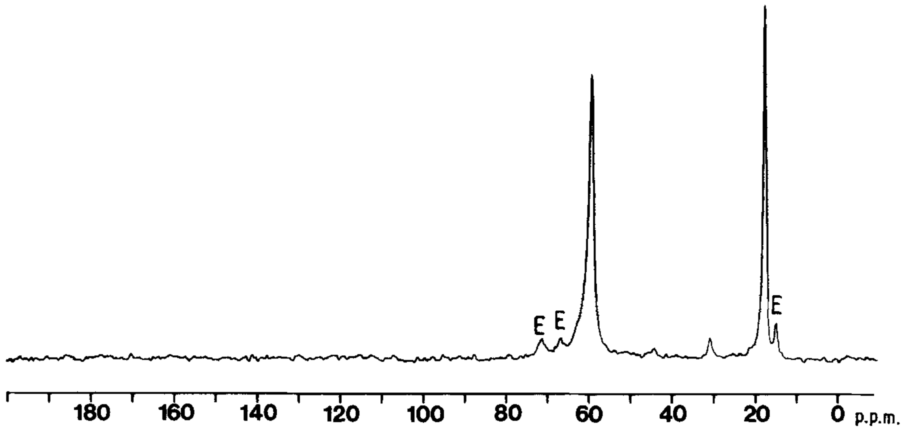

Figure 6 50.32 MHz solid-state ^{13}C CP MAS NMR spectrum of 5 h cured film. E denotes resonances assigned to 2-ethoxyethanol. 2780 transients were acquired using a contact time of 1 m sec and a 3 sec recycle delay.

solvent from the reaction mixture after only 2 h of reaction by rotary evaporation. Here the Q_2 resonance is only half as intense as in the 5 h spectrum and the Q_4 resonance is more intense.

This leads to the following model for the formation of the film. After the initial polymerization to long acyclic chains in the prehydrolysis step, further polymerization of the chain occurs to give a three-dimensional matrix as indicated by the intense Q_3 resonance. However, since the Q_4 resonance is relatively low in intensity the matrix must be quite open. As a consequence of the open character of the matrix some of the long chain polymer is trapped within the matrix leading to the sharp Q_2 component. Evidence that solvent and hence polymer can be incorporated into the film is strikingly provided by the ^{13}C CP MAS spectrum of the film after 5 h (Fig. 6). The resonances labelled E and occurring at 71.5, 66.8 and 14.9 p.p.m. can be assigned to 2-ethoxyethanol with the surprising feature that these resonances, associated with a liquid phase, are seen in the CP spectrum at all. The fact that cross-polarization is possible shows that not only is solvent present but also that it is locked rather rigidly into the matrix. Solvent is still present even after 100 h since these resonances are still present with the same relative intensity to the $SiOCH_2CH_3$ ^{13}C resonances in the film after 100 h. An alternative explanation for these resonances is that a transesterification reaction has occurred on the polymer leading to an ethoxyethoxyl silanol group. Interestingly, the $SiOCH_2CH_3$ resonances at this stage confirm that the silicate is still not fully hydrolysed even in the essentially set film.

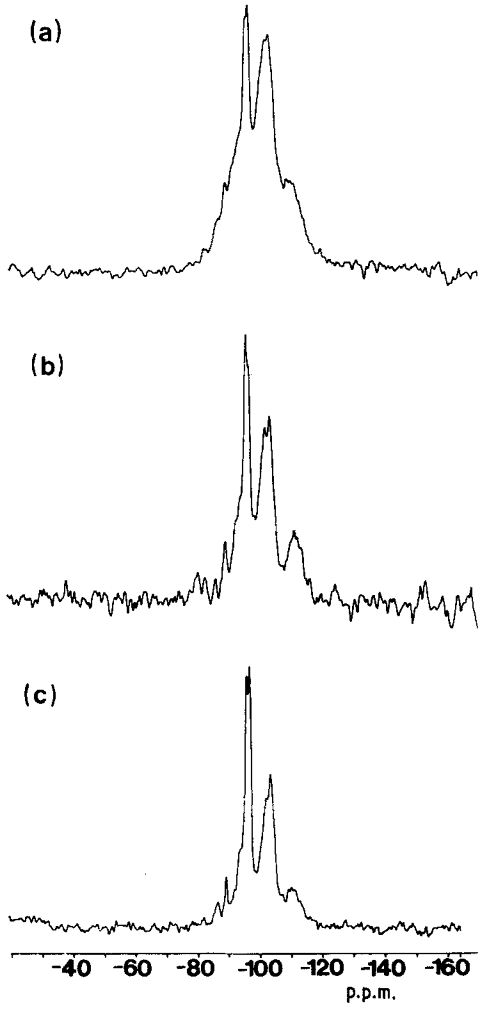

Figure 7 Dipolar decoupled 39.73 MHz solid-state ^{29}Si MAS NMR spectrum of the cured film after 100 h under different conditions. (a) pH 5.7 with zinc(II), (b) pH 1.0 without zinc(II), (c) pH 5.7 without zinc(II).

Changes in the film as a function of the setting time are difficult to see apart from the clear reduction in intensity of the narrower Q_2 resonance. It is unclear whether this indicates a reaction between the matrix and incorporated material or simply less incorporation in the film as the setting proceeds. However, because the intensity of the Q_4 resonance increases from the 5 h to 100 h cured film further reactions with the film would seem to be occurring leading to a more fully polymerized and less open network. The changes are also reflected in the CP spectra where only the matrix itself is seen.

The conclusions derived from the ^{29}Si NMR study complement the results obtained from our independent chemical analysis (which measured the ethoxy/silicon ratio) of the silicate matrix during film formation. Indeed, kinetic results obtained during the chemical study indicate a biphasic process in which the polymer is formed in solution by rapid hydrolysis and condensation reactions followed by a much slower, and incomplete, solid-state reaction. Parallel physical measurements, which determined hardness and resistance to abrasion, clearly indicated that the quality and long-term durability of the film was directly dependent on the length of time for which the initial fluid phase persisted. This latter observation is consistent with the notion that the longer the film remains fluid, the greater chance there is of producing high MW fully hydrolysed materials. Thus, if solvent is lost too quickly by evaporation, un-reacted material can be trapped within the precipitated polymer matrix and hence, any further reaction will be slow. Consequently, if the solid-state stage occurs too soon, low MW silicate polymers form and a softer, less durable, coating will be produced.

The effect of pH and the addition of zinc(II) ions as a Lewis acid catalyst on the form of the solid matrix is shown in Fig. 7. The presence of zinc(II) accelerates the polymerization reaction significantly. In fact the 100 h pH 5.7 spectrum in the absence of zinc(II) is very similar to the 5 h spectrum at the same pH with zinc(II). They both show a significant incorporation of incompletely polymerized material. The pH 1.0 matrix is intermediate showing a greater degree of polymerization than at pH 5.7 but less than with zinc.

4. Conclusion

The results presented illustrate qualitatively how ^{29}Si NMR spectroscopy, both solution and solid-state, can be used to study the hydrolysis and polymerization reactions of polyethoxysilane-based coatings. In particular we can conclude the following observations. Partial hydrolysis leads to a long chain polymer which may be branched together with more condensed networks but very few fully condensed silicate units, $Si(OSi)_4$. On forming the film the initial partially hydrolysed solution is incorporated into the matrix. As the curing proceeds so the degree of polymerization of the matrix increases leading to a less open network. Less solution appears to be present in the longer cured samples though whether this represents a reaction between the matrix and trapped solution or simply the trapping of less solution is unclear. Although the zinc(II) ions accelerate the film formation, the nature of the solid matrix formed and its trapping of solution are similar. Likewise decreasing the pH to 1.0 to compensate for the absence of zinc(II) causes a faster reaction than at pH 5.7 but the compensation is only partial.

Acknowledgements

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