Hydrated Calcium Silicate and Poly(vinyl alcohol): Nuclear Spin Propagation across Heterogeneous Interfaces

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Spin-diffusion NMR techniques were applied to the description of a heterogeneous interphase of composite materials formed by the hydration of calcium orthosilicate and poly(vinyl alcohol) (MDF cements). Hydrogen relaxation times were measured by magnetization transfer to ^{29}Si and ^{13}C atoms and indicate the degree of interaction between the organic and inorganic phases. Magnetization diffusion through the interfaces, measured by T_{1H} and $T_1\rho_H$ relaxation times, seems effective, showing that the phases are intimately mixed and restricted defective regions are interposed between the bulk organic and the inorganic phases. On the other hand, some components of the hydrogen relaxation times, observed in both the ^{13}C and the ^{29}Si domain, identify an extended interphase. The distances travelled by the magnetization in homogeneous domains of the polymer are limited, being confined to the 4−90 nm range.

Introduction

One of the main features of high-resolution solid-state NMR[1−5] for the characterization of materials is the detailed observation of the structure of multiple phases and defects from the complementary points of view of different resonance frequencies. A very favorable case occurs when the substance contains a few different spin-active nuclei, these being useful markers or probes to collect information about a particular phase.[6−9] When a composite material contains an organic and an inorganic phase, the phases can be identified by *rare* isotopes, e.g., by carbon-13 or silicon-29.[10−12] Nevertheless, *abundant* nuclei, such as hydrogen, act as good magnetization conductors, connecting the facing phases by the phenomenon of magnetization propagation. As a consequence, magnetization transfer across interfaces gives a measure of the degree of cohesion between the phases. Thus it is necessary to consider the interplay of three nuclei when heterogeneous phases are present: rare nuclei mark each phase, retaining high resolution, and the abundant nucleus, that participates in both phases, conveys the phase-interaction information.

This idea led us to develop a project focused on the interaction between inorganic and organic phases by NMR techniques.[13−27] Several techniques contributed to the determination of interface quality at the molecular level in composite materials. Infrared spectroscopy played an active role in obtaining molecular information on the interfaces, especially those showing hydrogen-

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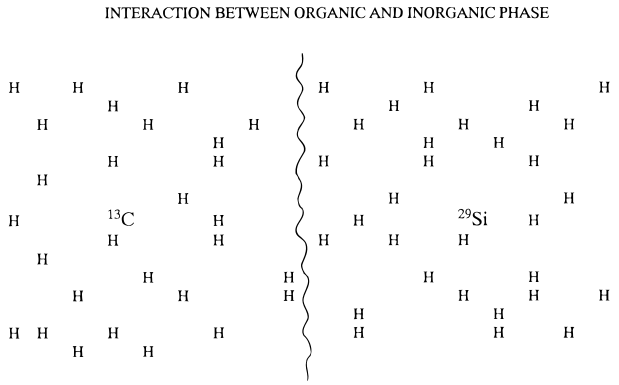

Figure 1. Organic–inorganic interface where rare nuclei are dispersed as probes for the measurement of the magnetization residue in the hydrogen domain.

bond connectivity.[28,29] On a larger scale, microscopy is the preferred technique, although it often lacks resolution as a result of limited image contrast. In the field of polymer morphology, NMR techniques have been used for collecting information at both the molecular and the extended scale, where the determination of interphase organization and phase dimensions of semicrystalline polymers and polymer blends determine the properties of the materials.[30–35]

From the technical point of view, our work is based on an analysis of hydrogen relaxation times. The bath of hydrogen nuclei is highly crowded, and there is diffuse interaction that extends to both the organic and inorganic phases. During the magnetization propagation (*spin diffusion*),[36–38] the magnetization crosses the interfaces and the relaxation properties of the hydrogen are, to some extent, averaged. Cross polarization experiments appended at the end of the proper pulse sequences bring about the transfer of magnetization from the hydrogen domain to the rare nuclei (details and sequences are given in the experimental section). The relaxation times (T_1 and $T_{1\rho}$ of the hydrogen nucleus[13–29]) can thus be selectively measured from several points dispersed in the matrix. ^{29}Si and ^{13}C act efficiently as phase-selective detectors of the residue of hydrogen magnetization existing at a given time (Figure 1). Much of this magnetization lies in a boundary region where an equilibration of magnetization occurs; thus the hydrogen relaxation properties must be the same.

The present research concerns the interactions between calcium orthosilicate (a reactive component of Portland cement and conventionally called C_3S, Ca_3SiO_5),[39] and a polymeric binder (poly(vinyl alcohol))[40–42] after the hydration process. It could have some impact on the evolution of Macro Defect Free (MDF) cement based materials[43–47] which are produced in such a manner that the polymer fills the voids between the hydrated particles and imparts improved mechanical properties, also as a result of the good adhesion of inorganic particles. ^{29}Si and ^{13}C MAS NMR have already been proved unique tools for identifying the connectivity, conformation and packing properties of inorganic[48–54] and organic (especially polymeric)[55–57] phases. Thus the aspects addressed by the present study go beyond the determination of domain size and interface quality, including both the identification of the chemical modification of the components and a search for NMR evidence of chemical interactions between molecules in vicinal phases.

Experimental Part

Materials. Reference poly(vinyl alcohol) (PVA) was purchased from Fluka (average $M_n = 72\,000$); mp = 265 °C; viscosity (4% in water, 20 °C) = 24–32 mPa s; degree of polymerization = 1600; degree of hydrolyzation = 97.5–99.5 mol %. An 80% hydrolyzed poly(vinyl alcohol)–poly(vinyl acetate) copolymer (PVAC) was purchased from Nippon Synthetic Chemical Industry Co. Ltd. Japan (Gohsenol KH-17s); degree of polymerization = 300–3000; viscosity (4% in water, 20 °C) = 32–38 mPa s. The microstructure of poly(vinyl alcohol) acetate was determined by ^{13}C and ^{1}H NMR in solution.[58–63]

The synthesis of C_3S was carried out using stoichiometric quantities of calcium carbonate and SiO_2 (silica). The mixture was repeatedly ground and heated at 1450 °C until equilibrium conditions were reached. The obtained powder was characterized by X-ray diffraction (XRD) and optical microscopy.

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The powder was then mixed with an 80% hydrolyzed poly(vinyl alcohol)−poly(vinyl acetate) copolymer PVAC and distilled water and then pressed at 80 bar and heated at 353 K for 10 min (pressed sample). Some of this sample was subjected to further curing at 353 K for 24 h (cured sample).[64−66] Both the flat sheets of the composite (pressed sample) and the cured sample were analyzed by MAS NMR. No differences in behavior were observed. The composition of the samples was as follows: sample A: 10 g of C_3S with 1 g of PVAC. Sample B: 10 g of C_3S with 7 g of PVAC, both undergoing the abovementioned processing with w/c (water to C_3S) ratio = 0.1. Sample C: 10 g of $Ca(OH)_2$ with 0.7 g of PVAC and excess water. Sample D: 10 g of C_3S with H_2O (w/c = 0.5) treated for 1 month. Sample E: 10 g of C_3S with H_2O (w/c = 0.1) in the presence of PVAC without pressing and heating. Sample F: 10 g of C_3S with H_2O (w/c = 0.1) treated for 3 h. Sample G: 10 g of C_3S with H_2O (w/c = 0.1) treated for 3 h and subsequently pressed at 80 °C. Samples D−G were quenched with acetone after the treatment.

X-ray Diffraction. X-ray diffraction profiles of the powders were obtained by a Siemens D5000 diffractometer, using Cu Kα radiation and diffracted-beam monochromator.

Solid-State NMR. NMR high-resolution ^{13}C and ^{29}Si MAS NMR spectra were run at 75.5 and 59.6 MHz, respectively, on a CXP300 Bruker instrument operating at a static field of 7.04 T. A MAS Bruker probe was used with 7 mm ZrO_2 rotors spinning at a standard speed of 4−5 kHz. For cross-polarization (CP) spectra, the best contact time was 1 ms for ^{13}C and 1.5 ms for ^{29}Si. A high-power proton decoupling (DD) field of 15 G was applied, the delay between pulses being 5 s for CP MAS. For each spectrum about 5000−10000 transients were collected. For MAS without cross polarization, a 90° pulse for carbon of 4 s was used; quantitative MAS experiments were performed by applying a delay time of 400 s.

The resolution for carbon was checked on glycine (line width at half-height = 26 Hz). Crystalline polyethylene (PE) was taken as an external reference at 33.63 ppm from tetramethylsilane (TMS).[67] The resolution for silicon was checked on Q_8M_8 sample (trimethylsilyl ester of octameric silicic acid, $Si_8O_{20}H_8$). Q_8M_8 sample was also used as the second standard, assigning the ^{29}Si chemical shift of the trimethylsilylgroups to +11.5 ppm from TMS.[48]

Sequence Description and Space-Domain Determination. The main part of the NMR characterization is done through the measurement of relaxation times and chemical shift. The direct measurement of different proton relaxation times is unsuitable due to the poor resolution of proton spectra while multipulse techniques such as CRAMPS distinguish only a few spectrum regions (those of the aromatic, vinyl, and aliphatic protons).

The experiments proposed here are able to measure spin-diffusion among protons in the high-resolution mode (Figure 2). Proton relaxation times in the rotating frame $T_{1\rho H}$ were measured indirectly by varying the length of a ^1H spin-lock period prior to a fixed $^1H \rightarrow {}^{13}C$ (or $^1H \rightarrow {}^{29}Si$) cross-polarization contact period. Proton relaxation times in the laboratory frame T_{1H} were measured by applying an inversion recovery sequence to the ^1H and successively transferring the proton magnetization to the rare nuclei by cross-polarization contact period.

In heterogeneous materials spin-diffusion evens out the differences in local magnetization because, in solids, $T_1 > T_2$.[36−38] However, this evening-out occurs, via a flip-flop mechanism, only if enough time is left for nonequilibrium magnetization to flow within the material. The distance covered by the propagation of magnetization, which is correlated to the strong dipolar coupling between hydrogens, is given by the formula

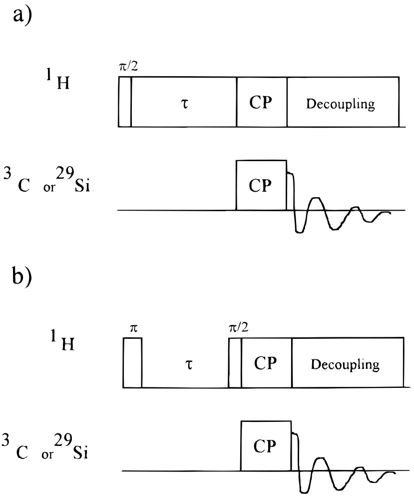

Figure 2. Pulse sequences applied to obtain high-resolution spectra and the measurement of abundant nuclei relaxation times. Pulse sequence applied for the measurement of the relaxation times in the rotating frame ($T_{1\rho H}$) (a), and in the laboratory frame (T_{1H}) (b).

$$\langle L^2 \rangle = nD\tau$$

where D is the diffusion coefficient, n = 2, 4, 6 for diffusion in 1, 2, and 3 dimensions, and τ is the time for the diffusion. The diffusion coefficient D is angular dependent.[38] At very high magic angle spinning speeds the dipolar coupling is, in principle, reduced to zero, and therefore spin diffusion should be quenched. However, the relatively slow mechanical spinning (4−5 kHz) applied in our experiments, slightly affects the strong homonuclear coupling. The spin diffusion coefficient measured by Douglass and Jones[37] for *n*-alkanes is 6.2 × 10^{-16} m^2/s in the laboratory frame; about the same value was found by Packer based on polyethylene lamellae thickness.[32] We can assume that in our polymer system the diffusion coefficient corresponds to that of polyethylene, the proton density being almost coincident. In the presence of a spin-lock field along the *x* axis, D was calculated to be half of that in the laboratory frame, since spin diffusion is proportional to $(3 \cos^2 \theta - 1)$.[38] Thus, in our polymer system, the T_{1H} values (of the order of a few seconds) allow a diffusion of magnetization over a maximum distance of 140 nm. On the contrary, $T_{1\rho H}$ values (about 5 ms) are influenced by heterogeneity on the scale of a few nanometers.

If no such diffusion coefficient is available for a given material, the average hydrogen density and the value of spin−spin relaxation times must be taken into account according to the expression[36−38]

$$\langle \mathrm{L}^2 \rangle \cong \langle l^2 \rangle T_i / T_2$$

where T_i is the measured relaxation time, T_2 the spin−spin relaxation (assumed approximately of the order of 10 μs). In the hydrated silicate phase l can be considered to be a few angstroms.

Results and Discussion

Water-soluble poly(vinyl alcohol)−poly(vinyl acetate) copolymer (80% deacetylated, PVAC) was adopted as the starting polymer. Under the alkaline conditions of preparation (see Experimental Part), poly(vinyl alcohol) acetate deacetylates to form poly(vinyl alcohol), while orthosilicates undergo a condensation reaction (Scheme 1).[68−71] Chemical shift and relaxation measurements

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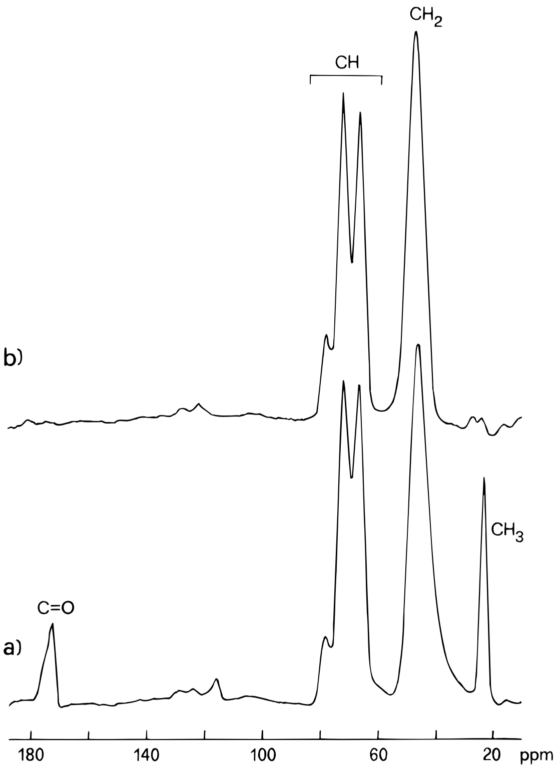
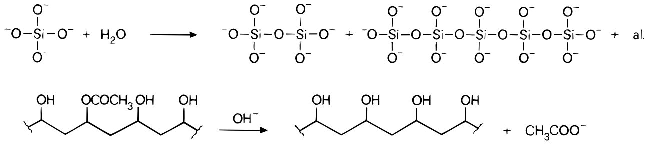


Figure 3. The 75.5 MHz ^{13}C CP MAS NMR spectra of (a) PVA and (b) PVAC. CP mixing time = 1 ms. No window functions were applied.

Scheme 1. Polymers and Oligomers Formed in the Organic and Inorganic Phases during the Hydration Process



of PVA and PVAC were performed so that they could be taken into account when assessing the properties of the composite. The extent of deacetylation of PVAC was also determined.

Figure 3a,b show the ^{13}C MAS NMR spectra of PVAC and PVA, respectively. To optimize the response of the ^{13}C MAS NMR spectra and possibly approach quantitative conditions, several contact times were investigated using ^{1}H−^{13}C cross polarization (CP). In pure PVA the strongest signal intensity occurred at a contact time of 1 ms, whereas for acetate signals of PVAC it was revealed to be shifted to longer times. On comparing the CP MAS spectrum, collected at the mixing time of 1 ms, and the MAS spectrum of PVAC, obtained under quantitative conditions (recycle times 400 s), complete coincidence can be seen. Integration of the PVAC signals indicates that methyl and carboxyl amounts are approximately 20% with respect to the methine and methylene peaks, in both the MAS and CP MAS spectra.

It should be noted that ^{13}C MAS NMR spectra are especially informative about hydrogen bonding. High-resolution NMR techniques in the solid state were first applied to atactic poly(vinyl alcohol) by Terao et al.,[72−76] who observed that the methine carbon CH gives rise to three peaks (from 60 to 80 ppm) which are found to resonate at lower fields than the solution signals. These authors concluded that this effect can be ascribed to the amount of intramolecular hydrogen bonds in the mm and mr triads.[75,76]

Proton Spin Diffusion in the ^{13}C Domain. Spin−lattice relaxation times of the polymer proton in the laboratory frame as well as relaxation times in the rotating frame of the pure polymers (PVAC and PVA) were measured.[77−79] Since T_{1H} and $T_{1\rho H}$ are not specific properties of single protons (methyl, methylene, etc.) but are overall properties that are affected by strong dipolar interactions, allowing the diffusion of magnetization, the pure polymers show a single value for T_{1H} and $T_{1\rho H}$ (Tables 1 and 2).

^{13}C CP MAS analysis of sample B (C_3S + 70% PVAC) showed that complete deacetylation occurred (Figure 4).[68−71] A highly crystalline hemihydrate calcium acetate $Ca(COOCH_3)_2$ was formed which shows four signals at 188.7, 185.5, 181.33, and 177.5 ppm, assigned to the carboxyl group. These are characterized by equal intensity (within experimental error). A doublet with an intensity ratio of 1:3 for the CH_3 groups (24.2 and 23.4 ppm) is also present, consistent with an overlap of three resonances out of four. The spectrum of crystalline calcium acetate was first shown by Harris et al.[80] Results from NMR determinations indicate the existence of at least four nonequivalent crystallographic sites for the acetate groups in the unit cell. However, the assignment of the four peaks in the carboxyl region is not univocal.

The T_{1H} sequence (see Experimental Part) selectively records the polymeric poly(vinyl alcohol) phase or the crystalline phase of calcium acetate within the composite, the domain size of these phases being definitely larger than the distance travelled by spin-diffusion within this time scale. Figure 4 shows spectra for sample B obtained with the pulse sequence utilized for measuring T_{1H} at different intervals. If the system was homogeneous in this time scale (domain size of less than 140 nm), we would have found the same T_{1H} value for all the peaks present in the spectrum. In fact the T_{1H} values measured for the polymeric phase in the composite are about 5 s and are similar to the T_{1H} values found in the pure poly(vinyl alcohol) polymer taken as reference (Table 1). On the other hand, the crystalline phase of calcium acetate shows proton relaxation times of 0.5 s. Thus it can be concluded that the crystalline phase of the calcium acetate separates out for domain sizes of the order of 20 nm, whereas the polymeric domain size is, on the average, greater than 140 nm.

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Table 1. Proton Relaxation Times in the Laboratory System (T_{1H}), Transferring Proton Magnetization to ^{13}C and ^{29}Si by CP MAS NMR Sequence in Pure PVA, in Pure PVAC, in 10% PVAC + C_3S (Sample A) and in Hydrated C_3S (Sample D) (Values Affected by a 10% Error)

		T_{1H} (s)						
		PVA	PVAC	10%PVAC + C_3S (sample A)		C_3S hydrated 1 month		
assignment	δ (ppm) ^{13}C	from ^{13}C	from ^{13}C	from ^{13}C	from ^{29}Si	from ^{29}Si	δ (ppm) ^{29}Si	assignment
CH_3	22.5		3.4					
	25.7			1.3				
CH_2	45.4		3.4					
	46.4	6.0		1.7				
CH	65.7	5.9	3.4	1.7				
	71.2	5.9	3.4	1.6				
	76.3			n.d.[a]				
	77.4	5.8	3.2					
C═O	168.3			n.d.				
	171.8		3.3					
	184.2			1.0				
					1.2		−72.5	Q^0
					1.1		−77.9	new species
						0.23	−79.0	Q^1
					1.0		−79.7	Q^1
					n.d.	0.22	−85.3	Q^2

[a] Not determined.

Table 2. Proton Relaxation Times in the Rotating Frame ($T_{1\rho H}$), Transferring Proton Magnetization to ^{13}C and ^{29}Si by CP MAS NMR Sequence in Pure PVA, in Pure PVAC, in 10% PVAC + C_3S (Sample A) and in Hydrated C_3S (Sample D) (Values Are Affected by a 10% Error)

		$T_{1\rho H}$ (ms)								
		PVA	PVAC	10% PVAC + C_3S (sample A)				C_3S hydrated		
assignment	δ (ppm) ^{13}C	from ^{13}C monoexp	from ^{13}C monoexp	from ^{13}C biexp	rel %	from ^{13}C monoexp	from ^{29}Si monoexp	1 month from ^{29}Si monoexp	δ (ppm) ^{29}Si	assignment
CH_3	22.5		5.5 ± 0.1							
	25.7			0.2 ± 0.2 4.8 ± 0.3	19/81	4.3 ± 0.3				
CH_2	45.4		5.6 ± 0.1							
	46.4	5.9 ± 0.1		n.d.[a]		4.6 ± 0.2				
CH	65.7	5.6 ± 0.1	5.3 ± 0.1	1.6 ± 0.4 5.9 ± 0.7	31/69	4.4 ± 0.2				
	71.2	6.0 ± 0.1	5.6 ± 0.1	1.5 ± 0.6 6.0 ± 0.8	27/73	4.6 ± 0.2				
	76.3			n.d.		n.d.				
	77.4	6.2 ± 0.1	n.d.							
C═O	168.3			n.d.		n.d.				
	171.8		6.00.1							
	184.2			0.6 ± 0.8 14 ± 3	75/25	5.4 ± 0.7				
							4.8	1.66	−72.5	Q^0
							3.4		−77.9	new species
								1.53	−79.0	Q^1
							4.0		−79.7	Q^1
							n.d.	1.95	−85.3	Q^2

[a] Not determined.

The ^{13}C CP MAS spectrum of sample A (C_3S + 10% PVAC) (Figure 5) revealed deacetylation and the formation of an amorphous phase of calcium acetate identified by a broad peak at 184.2 ppm. The ^{13}C CP MAS spectrum of sample C (not shown) also revealed amorphous calcium acetate, this being the only product of the deacetylation. The methyl signal appears broadened and its maximum intensity at 25.7 ppm lies at lower fields than in the PVAC methyl carbon resonance. The residual peak at 168.3 ppm was assigned to calcium carbonate by comparison to pure calcite.[81]

T_{1H} and $T_{1\rho H}$ relaxation time measurements were performed on sample A. The relaxation times were calculated through a nonlinear best fitting. It is worth recalling that proton $T_{1\rho}$ relaxation times were also measured by exploiting contact time dependence on cross-polarization phenomenon (not shown);[2] the $T_{1\rho H}$ values are virtually coincident.

T_{1H} relaxation times of the polymer in the composite material are less than 2 s, quite short compared to the reference polymeric compunds (Table 1). Figure 6 shows the semilogarithmic graph of the peak at 65.9 ppm, from which it clearly stands out that the T_{1H} relaxation time of the composite is reduced compared to that of the PVAC copolymer. A single-exponential decay is shown. This would indicate the homogeneity of the phases for domain sizes below 90 nm.

By contrast, $T_{1\rho H}$ measurements indicate the occurrence of two components in the presence of hydrated C_3S (Table 2). The longest one is almost equivalent to the value of pure PVAC (5.5 ms). This value indicates that, in this phase, the polymer relaxation dominates, as independently confirmed by ^{29}Si results. The other one (lower than 2 ms) is assigned to the small domain sizes of the polymer approximating the inorganic component. The 2 ms component represents a minor part in the domain size distribution.[82] The intensity of the signals measured by applying the $T_{1\rho H}$ pulse sequence is illustrated in a semilogarithmic form in Figure 7. On the other hand, on Table 2 the $T_{1\rho H}$ values, as obtained

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(81) Papenguth, H. W.; Kirkpatrick, R. J.; Montez, B.; Sandberg, P. A. *Am. Mineral.* **1989**, *74*, 1152.

(82) Stejskal, E. O.; Schaefer, J.; Sefcik, M. D.; McKay, R. A. *Macromolecules* **1981**, *14*, 275.

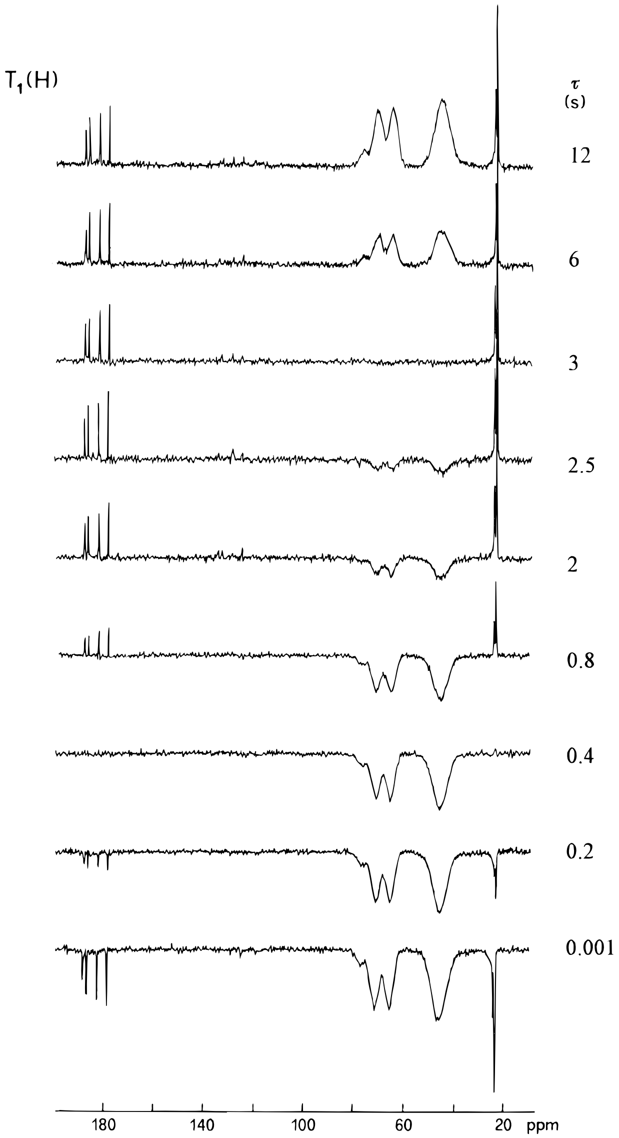

Figure 4. The 75.5 MHz ^{13}C CP MAS NMR spectra of 70% PVAC + C_3S (sample B) at different delay times for the measurement of T_{1H} (see Figure 2). CP mixing time = 1 ms.

by a monoexponential fitting procedure, are also reported. The values are slightly reduced with respect to the T_{1pH} values of the pure PVAC, confirming that a minor part of the polymer is affected by the presence of the inorganic phase.

From the ^{13}C point of view, it can be affirmed that based on T_{1H} values, a large part of the domain sizes of pure polymer in the composite are less than 90 nm. On the other hand, we were able to identify, on the basis of the $T_{1\rho H}$ values, a few domain sizes of less than 4 nm for the fast component and quite a number >4 nm for the slow one. In a few words, most size domains range between the domains associated to the T_{1H} and $T_{1\rho H}$ values, i.e., the distribution is estimated as being restricted to within 4−90 nm.

Proton Spin Diffusion in the ^{29}Si Domain. Experiments aimed at studying contact times as well as T_{1H} and $T_{1\rho H}$ relaxation times on the composite material C_3S + 10% PVAC (sample A) were carried out by transferring the proton's magnetization not only to the ^{13}C nucleus but also to the ^{29}Si one. In this way we were able to detect the hydrated phase of C_3S (C−S−H),[67] despite the low concentration. The low concentration of C−S−H is due to the short hydration times and low H_2O content (w/c ratio = 0.1). T_{1H} and $T_{1\rho H}$ were measured on hydrated pure C_3S, and the values were taken as a reference to determine domain size of the phases (Tables 1 and 2). T_{1H} and $T_{1\rho H}$ values in hydrated pure C_3S proved to be approximately 0.2 s and

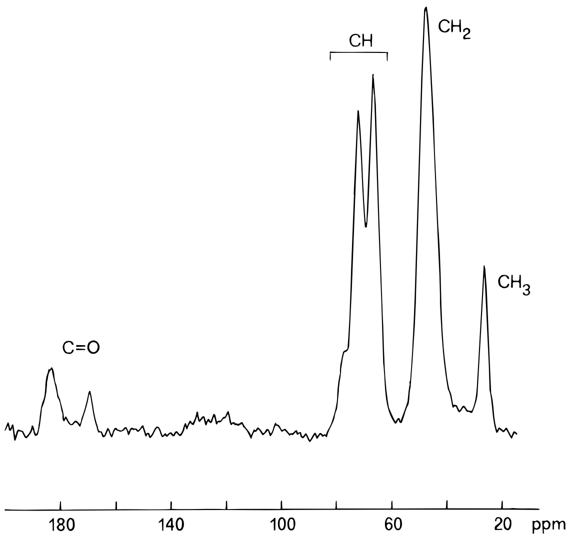

Figure 5. The 75.5 MHz ^{13}C CP MAS NMR spectrum of 10% PVAC + C_3S (sample A). CP mixing time = 1 ms. Line broadening refinement (LB = 30) was applied.

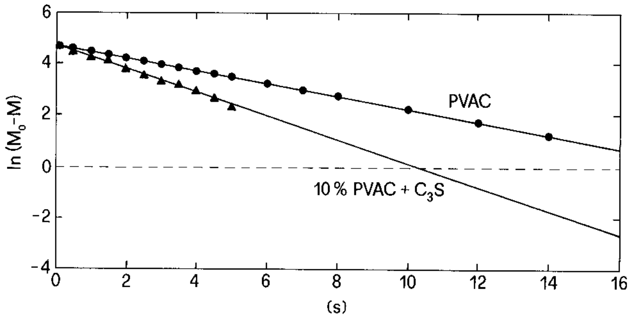

Figure 6. Logarithmic scale of the intensity magnetization ($M_0 - M$). M_0 equilibrium magnetization and M intensity of the peak at appropriate time. Each point (circles and triangles) refers to the peak at 65.7 ppm and a given for PVAC and 10% PVAC + C_3S samples, respectively. The lines represent the behavior of the T_{1H} relaxation. T_{1H} is the reciprocal of the measured slope of the lines.

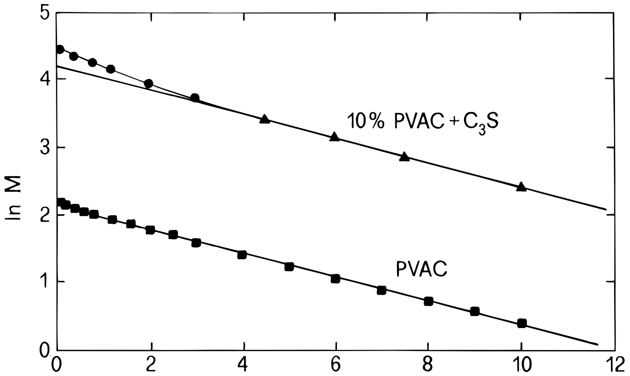

Figure 7. Variation of logarithm magnetization M at specific times τ. Each point (circles and triangles) corresponds to the intensity of the peak at 65.7 ppm for 10% PVAC + C_3S and PVAC samples, respectively. The lines represent the behavior of the T_{1pH} relaxation. T_{1pH} is the reciprocal of the measured slope of the lines.

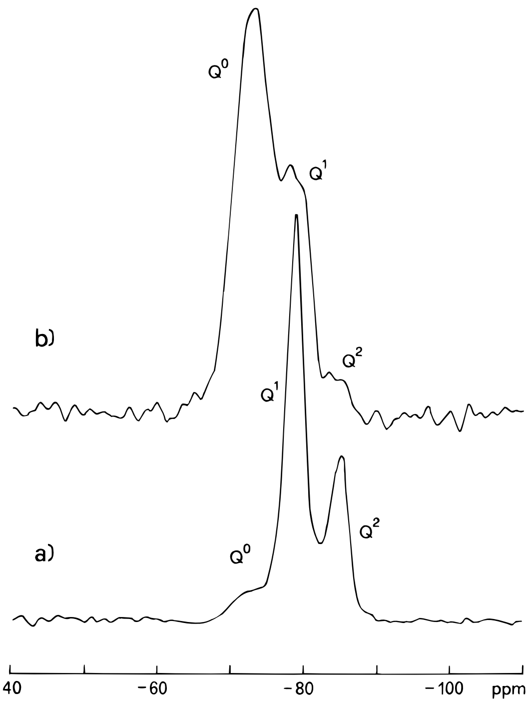

Figure 8. The 59.7 MHz ^{29}Si CP MAS spectra: (a) 1 month hydrated C_3S sample (sample D); (b) 10% PVAC + C_3S (sample A). CP mixing time = 1.5 ms.

1.5 ms for each species, respectively.

As regards the composite material, T_{1H} and $T_{1\rho H}$ values obtained by direct ^{29}Si observation turned out to be substantially increased ($T_{1H} = 1$ s and $T_{1\rho H} = 4$ ms) and very close to the values found in the same material on transferring the proton's magnetization to ^{13}C (polymeric phase observation; Tables 1 and 2). It can therefore be concluded that, as regards T_{1H}, there exists a phase homogeneity in terms of both polymer and C−S−H. The virtual coincidence of the component of the hydrogen relaxation times measurements in the composites, as observed by both ^{13}C and ^{29}Si, suggest the correctness of the experiments and the unequivocal identification of the physical object. The $T_{1\rho H}$ values determined through ^{29}Si observation indicates that most of the hydration process is produced at the contact with the polymer.

On the composite material (sample A) ^{29}Si CP MAS NMR spectrum was executed with a contact time of 1.5 ms (Figure 8b). The distribution of the Q^0, Q^1, and Q^2 species differed from that expected for the hydration of the pure inorganic phase.[54] C_3S hydrated with 0.5 water to C_3S ratio was examined for comparison (sample D; Figure 8a). We found that the Q^0 species in sample A predominates. The Q^0 species is associated with the C_3S grains which, although not polymerized, are close to hydrogen atoms.[54]

A cross-polarization study enhanced the apparent resolution at increased contact times (Figure 9). A more careful observation indicated that this effect is due to the progressive disappearance of a signal at −77.9 ppm. This signal cross polarized efficiently just at short mixing times. The remaining and well-resolved peaks at 8 ms mixing times correspond to Q^0 and Q^1 species. We assumed that the new peak could be assigned to the hydrated C−S−H species interacting with the deacetylated polymer. Our assumption is strengthened by the fact that even when C_3S reacted with H_2O in the presence of PVAC without pressing and heating (sample E) the peak at −77.9 ppm occurs, whereas there was no evidence of this peak in the ^{29}Si CP MAS NMR spectra of samples F and G (without the polymer).

Conclusion

The measurement of hydrogen relaxation times in different molecular neighborhoods of ^{29}Si and ^{13}C atoms allowed us to define the degree of interaction between the organic and inorganic phases. This aspect was investigated by a novel methodology for the field of heterogeneous interfaces, exploiting a regime of rapid magnetization diffusion across the heterogeneous interface.

Magnetization diffusion through the interfaces seems effective as regards the $T_{1\rho H}$ measurements measured by the magnetization transfer to ^{29}Si. The values obtained appear to indicate that the C−S−H phase is greatly affected by the presence of the polymer at a 5 nm scale. Thus most of hydrated inorganic phase lies in close contact with the polymer phase. The relaxation measurements, as measured by the ^{13}C, show a relatively wide extension of the polymeric phases.

A direct communication of magnetization through the interface indicates good adhesion between the various substrates. In a general model, where efficient spin diffusion occurs only in rigid and dense materials, a barrier to the magnetization propagation could consist of soft and mobile pieces of materials that present long T_2's and a low proton density. Such a barrier would occur when loose interphases are interposed in between two neat phases. On the other hand an efficient spin-diffusion through the interfaces indicates that a limited amount of such defective regions are interposed between the bulk organic and the inorganic phases.

From the ^{13}C analysis of T_{1H} relaxation times of samples containing 10% polymer (sample A), a mixing

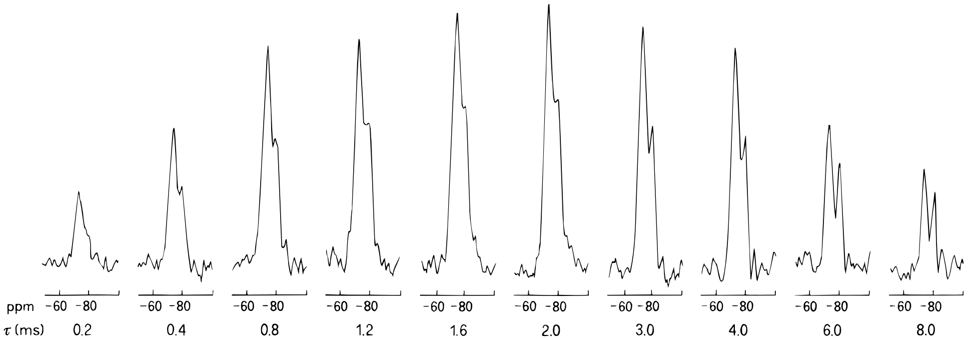

Figure 9. 59.7 MHz ^{29}Si CP MAS spectra at defined contact times of 10% PVAC + C_3S (sample A).

of the phases with a formation of domains smaller than about 90 nm was found, whereas the analysis of $T_{1\rho H}$ relaxation times revealed a small number of polymer domain sizes smaller than 4 nm. Thus distances travelled by the magnetization in homogeneous domains are shown to be confined to the 4−90 nm range. The dimensional results obtained from such measurements can be considered consistent with the observation by electron microscopy of a minor presence of large domains. Complete deacetylation and the formation of a crystalline phase of calcium acetate became apparent through spin-diffusion experiments in samples of a high polymer content. It can be demonstrated that calcium acetate is segregated to regions of the order of 20 nm, and the polymeric phase to regions larger, on average, than 140 nm.

Through silicon analysis a new signal, due to the interaction with the polymer, becomes evident in C−S−H. This new peak with a chemical shift at −77.9 ppm was found to be different from those of the Q^0 and Q^1 structures. Our conclusion is that this peak can be assigned to the silicate species occurring near the polymer. ^{29}Si CP MAS spectra of the sample containing 10% PVAC + C_3S showed the presence of a large amount of Q^0 orthosilicate and the formation of a small amount of oligomers, evidenced by the Q^1 and Q^2 peaks. These results have led us to conclude that there exists a major interaction of the polymer with the inorganic matrix of hydrated C_3S.

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