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NMR Studies of Enriched Species at Interfaces

by

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A review of the use of NMR at interfaces of solid surfaces is made. Special attention is focussed on the use of 2-H, 13-C, and 15-N isotopes in studies of Polymers and silane surfaces active agents on solid surfaces

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1.0 Introduction

The full power of magnetic resonance techniques has yet to be unleashed on composite interfaces. These techniques have been applied to bulk systems or solutions to address a myriad of structural and dynamical problems in chemistry, biochemistry, physics, and materials science. The reasons for their limited application in composite interfaces are mainly two-fold. NMR is an inherently insensitive technique, and discrimination between interfacial and bulk material is often difficult or impossible. Analysis of composite interfaces becomes possible only if both of these problems are successfully addressed. On the other hand, there are several reasons why NMR is well suited in the study of interfacial properties. One of the most significant is that the optical clarity of the sample in an NMR experiment is not important in contrast to optical techniques such as infra-red, uv-visible and fluorescence. While optical studies can yield valuable information on single layers of surface material, they generally can not probe internal interfaces or regions of a composite material.

NMR can probe the interfacial structure and dynamics using a variety of different nuclei and selection of the proper nucleus allows different properties of the system to be studied.(1) These properties include the determination of which atoms are directly bonded to a surface or to how different groups move on the surface. Differences in interfacial mobility may also necessitate that different types of NMR experiments be performed. Mobile species at a gaseous or liquid interface may require solution techniques, while solid-state NMR techniques are usually required at solid interfaces or interphases. These solid techniques can vary greatly in both how they are performed and in the information that is obtained.(2)

The NMR sensitivity arises from the relative populations of nuclear spins in excited and ground NMR (Zeeman) states; they are almost equally populated. This inherent lack of sensitivity is exacerbated by the fact that much of the effective sample volume is taken up by the two or more separate bulk phases making the interfacial concentration low. In order to increase the number of interfacial NMR nuclei in the sample, it is advantageous to use a model substrate with a high surface area. While this limits the systems which can be studied, there are a variety of high surface area materials which are representative of those used in composites.

A further concern is the ability to distinguish the interfacial material from the two bulk phases. Contrast is often difficult to achieve because one of the bulk phases usually has an elemental composition similar to the interfacial material. For example, both the interfacial material and the surface modifier of a fiber or bulk matrix polymer may be composed of carbon, hydrogen, nitrogen and oxygen. For a composite made from one polymer and a fiber, the molecules at the interface have the same chemical composition as the polymer or fiber. One useful way to overcome this problem is through use of isotopically labelled molecules selectively placed at the interface.

The purpose of the present work is to give an overview of how selective NMR probes can be used to study the structure and dynamics of interfacial regions in composite materials. Emphasis will be on isotope enriched molecules used to improve both sensitivity and contrast, thus allowing the interface to be probed without interference from bulk material. The focus of the review will be on determining the properties of interfacial species used as surface modifiers and adhesion promoters.

2.0 Practical NMR Considerations

There is abundant literature on the use of NMR spectroscopy to solve problems related to the structure and dynamics of chemical species.(2-3) In order to assist the reader unfamiliar with these techniques, some of the basic principles and phenomena are discussed.

Atomic nuclei posses spin angular momenta which are characterized by the spin quantum number, I, (set by nature for a given nuclear species) in positive half integer values (i.e. 0, 1/2, 1, 3/2 ...). Species with I = 0 (^{12}C, ^{16}O, ^{28}Si, ^{32}S) are not NMR active because they do not posses such a nuclear magnetic moment while species with I = 1/2 (^{1}H, ^{13}C, ^{19}F, ^{29}Si, ^{31}P) and I > 1/2 (^{2}H, ^{14}N, ^{27}Al) do. Spins with I > 1/2 also posses a nuclear quadrupole moment which may couple with the electric field gradient at the nucleus to change lineshapes and relaxation behavior of the nuclei.

The nuclear magnetic moment is proportional to the nuclear angular momentum by the magnetogyric ratio, γ (usually in rad/T/s), whose value is different for each different nucleus. The frequency at which an NMR experiment for a particular nucleus is done is called the Larmor frequency, ν (in Hz), given by: $\nu = |\gamma|H/2\pi$ where the proportionality to the magnetic field strength. H (T, 1 Tesla = 10,000 Gauss) is noted. Typical NMR magnets produce fields from about 1 T to 14 T making ν in the range of 10 to 600 MHz for typical values of $|\gamma|$. Table I contains a partial listing of nuclei relevant to this chapter along with their isotope abundance, relative sensitivity and Larmor frequencies.

<Table I>

From the entries in Table I, several things are apparent. NMR frequencies are in the radio-frequency range and transitions have energies which are much less than the thermal energies in the system except at very low temperatures (a few degrees Kelvin!). This results in nearly equal populations of ground and excited states at typical laboratory temperatures. Since the NMR signal intensity is normally proportional to the population difference, this limits the sensitivity of the technique. The number of excess nuclei in the ground state (in the high temperature limit) is proportional to the field strength H. Generally, higher fields result in higher sensitivity, although other factors which come into play which means that higher fields do not necessarily mean better spectra.(2) These additional factors are incorporated into the noted values for relative sensitivity. The sensitivity at natural abundance would be the product of the relative sensitivity times the natural abundance.

The natural abundance factor in Table I identifies some nuclei which offer opportunities for enrichment. When the natural abundance is low, the background for that particular nucleus is small. Unfortunately, the effort involved in producing enriched isotopes increases with atomic number; consequently, the least expensive isotope is deuterium, although enrichment with carbon or nitrogen is common in several fields of chemistry.

It is also apparent in Table I, that the NMR frequency is different for different isotopes of the same atom. The familiar chemical shift is generally only a small perturbation on these frequencies. For example, for protons, ^1H, this amounts to only 10 ppm of the value of ν. The fact that protons and deuterium, for example, have such widely different frequencies, assures no overlap between them. The breath of NMR frequencies for different nuclei, plus the need for enhanced sensitivity, also means that switching from one nucleus to another is generally not trivial.

It is appropriate to note that the techniques used to study interfacial materials can generally be classified as solution, magic angle spinning (MAS), and wide-line (WL) NMR experiments. MAS is often used along with cross-polarization (CP) to protons which (usually) enhances sensitivity. Although these methods overlap in some cases, they generally require different hardware to perform. For solid materials, CP-MAS is usually effective for ^{13}C while ^2H usually requires WL techniques.

3.0 Surface Modifiers

Surface modifiers are used in a variety of situations and for a number of applications and are small molecules which are interfacially active. The use of coupling agents in composites is well documented.(4) These materials form a bridge between the fiber and the organic matrix. The most common of these are the organosilanes where siloxane bonds are formed between glass or glass-like fibers and organic resins. Use of these materials in small amounts at the interface produces composites with enhanced ability to retain physical properties when subjected to environmental conditions which would otherwise degrade them. An important example of this is the strength of glass fiber-epoxy composites in the presence of water. It is important to note that this behavior is not limited to inorganic fibers or organic matrices. The details of the mechanisms for the enhancement of physical properties are not entirely clear, but NMR techniques have significantly improved our knowledge of these systems.

A second area of importance for silane and related species is in chromatographic analyses.(5)

Both the chemical structure of the material at the interface and its mobility are believed to play a role in the effectiveness of the surface modification. The modification of mainly silica supports may allow the stationary phase to be tailored for the separation needed. This tailoring may involve both the type of functional groups present for "chemical" effects, the amount of the material at the interface, and its mobility. The physics and chemistry of both of these applications are similar.

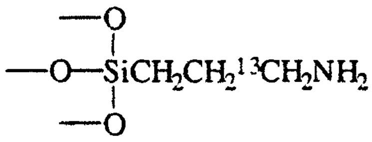
NMR has been a very powerful tool for the determination of structure and bonding which occurs between the solid and interfacial species. Generally, silanes start out as either mono-, di- or tri-chlorosilanes, although methoxy- or ethoxysilanes are also effective. Upon treatment with water, hydrolysis occurs with the production of an intermediate silanol species. These can then react with a variety of surfaces or they can self condense to form a variety of siloxane linkages. For silane agents used on silica, proof of Si-O-Si bond formation can be provided by ^{29}Si CP-MAS NMR techniques.(6,7) The formation of the bond with the surface causes a change in the shift of the Si chemical shifts so that the surface-O-Si bonds can be distinguished from the R-Si-O-Si-R groups where the R's represent three nonsurface groups (possibly different) from the coupling agent. With ^{29}Si NMR, it is also possible to distinguish the functionality of the silane in terms of the number of organo- and silanol groups.(6)

The use of ^{29}Si NMR would be enhanced by the use of isotopically enriched surface specific probes. However, these are not necessary for silane surface modifiers on silica if cross polarization is used since the vast majority of silicon atoms in these samples are *inside* the silica, and are generally not close enough to protons to cross polarize effectively. In contrast, the surface or near-surface silanes, and the silane agents themselves are relatively proton rich. Consequently, the spectra obtained under conditions of CP-MAS are inherently surface selective. Most studies to date have used silica gel (6,7) with surface areas ranging from 200 to 800 m^2/g, although few studies have been reported on amorphous silicon dioxide (8) and cab-o-sil silica (9,10) with surface areas from 200 to 400 m^2/g. Hoh et al. (8) mixed coupling agent with epoxy resin and found that the composition affected the efficiency of the cross polarization process in coupling agent-surface and coupling agent-resin systems.

To date it appears that no studies have reported the use of enriched ^{29}Si in surface studies. Their use would be important for achieving enhanced sensitivity for Si containing species at interfaces on substrates with lower surface area. The possibility for using unlabelled species in composites exists. The current limitation is cost and availability of the labelled species.

Carbon-13 NMR has also been used to probe the structure and dynamics of interfacial material. The mobility of short alkyl chains bound to silica surfaces is such that on the NMR timescale they are effectively solid-like and require CP-MAS for resolution of individual chemical moieties in the absence of solvents. For short chains with functional groups such as aminopropylsilane on silica surfaces, all three unique carbons can be resolved using CP-MAS.(11) A number of other coupling agents have also been studied in this way.(11-13) The spectra are of good enough quality, allowing the probing of molecular motion, curing, and surface adsorption effects at natural abundance levels provided high surface area supports are used.

In order to probe the behavior of the coupling agent in composite materials, aminopropylsilane has been enriched with ^{13}C.(14) The γ-position was labelled and this coupling agent:



$$\begin{array}{l} \quad\;\; -O \\ \quad\quad\; | \\ -O-SiCH_2CH_2{}^{13}CH_2NH_2 \\ \quad\quad\; | \\ \quad\;\; -O \end{array}$$

was adsorbed onto 5mm glass spheres in two different amounts. Carbon-13 spectra were then taken of the coupling agent on the glass beads, i) alone, ii) in a composite with low molecular weight nylon-6, and iii) after extraction of the polymer with trifluoroethanol. The enrichment was high enough that good quality spectra could be obtained on these relatively "large" particles. At the surface-air interface, only the resonance due to the labelled species at 43 ppm was observed although at least two components of different mobility were found to contribute to the signal intensity. Upon mixing with nylon-6 in the melt, the room temperature spectrum of the composite showed the superposition of resonances from the labelled interfacial species plus those of the polymer as seen in Figure 1. The C_1 carbon of the nylon overlapped with the coupling agent resonance, but it was still possible to deconvolute the contributions to the relaxation behavior of each to some degree. After extraction of the free nylon in the composite, the resulting ^{13}C spectrum (Figure 1) showed the definite contribution of the coupling agent at 43 ppm plus nylon resonances due to material which had not been extracted. The fact that a considerable amount of polymer was not removed from the glass beads suggested a strong interaction between the polymer and the treated glass surface. This may be due to hydrogen bonding or carboxylic acid end groups through surface-amine salt formation.

<Fig. 1>

Relaxation measurements on the coupling agent's labelled carbon suggested that the presence of the polymer reduced its mobility. Chemical-shift changes provided additional evidence for bonding between the coupling agent and the polymer, but this bonding did not appear to be enough to account for the changes in the mobility observed. A combination of bonding and intermixing of the polymer and coupling agent probably accounts for the observed mobility changes, although evidence for an interpenetrating network was not found.

For longer chain alkylsilanes adsorbed on and attached to silica surfaces, differences in mobility as a function of chain length have been observed with CP-MAS techniques.(15,16) Generally, the rates for segmental reorientation increase as the carbon position from the surface increases. Unfortunately, as the chain lengths increase, it is increasingly difficult to distinguish the different alkyl segments because many of the carbons have very similar chemical shifts that result in a broad envelope of resonances.

In order to chemically distinguish carbons on alkyl chains with similar chemical shifts, Gilpin and Gangoda synthesized a variety of ^{13}C enriched silanes(5, 17-20) for use as chromatographic surface modifiers. Enrichment of 25-50% ^{13}C also increased the sensitivity of the NMR experiment for the surface-bound species. Their initial experiments on labelled C_9 and C_{10} alkyl silanes (17) demonstrated that the mobility of species reacted at the interface and dried was sufficient to yield spectra in the NMR "liquids" mode, although the quality of the spectra was not good. It was possible to identify a motional gradient with those nuclei further from the surface exhibiting increased mobility. Surface-bound species from trichlorosilanes were also more restricted than those from monochlorosilanes, as expected because of the increased number of sites for bonding in the trichlorosilanes.

The addition of solvent to ^{13}C labelled surface-bound alkyl silanes significantly increased their mobility compared to that of the dry state.(18) This allowed the measurement of spin lattice relaxation times (T_1) for the segments labelled. It was found that surface coverages affected the mobility of the adsorbed layers.(18) The relaxation times for bound silanes also correlated with solvent viscosity.(19) In different solvents, the T_1 behavior of the labelled dodecyldimethylchlorosilane varied linearly with the reciprocal of the solvent viscosity for each of two groups of solvents. The separation of the solvents into two different groups was thought to be due to differences in the penetration of the solvent into the alkylsilane layers. This was suggested to affect the contribution of the "total and segmental" motion of the silane in the different types of solvents.(19) T_1 results are shown in Figure 2. The apparent energies of activation for the T_1 process were also measured for the dry (ca. 13 kJ/mol) samples and compared to those soaked with ethylene glycol (15 - 19 kJ/mol), and carbon tetrachloride containing materials.(20) The solvent-wet materials also showed greater sensitivity to the position of the ^{13}C label on the silane. These results suggested to the authors that the silanes were more orientationally ordered in the presence of solvents than in their absence.

<Fig. 2>

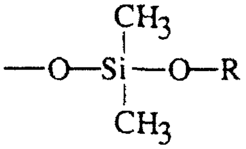
In order to probe the surface viscosity and solvent penetration of acetonitrile into surface-bound octadecylsilane, Ellison and Marshall (21) used deuteroacetonitrile as an NMR probe. Both ^{14}N and ^{2}H NMR were used and the T_1's measured as a function of the type of silica gel and composition of modifier. The T_1 results were interpreted as due to two motionally distinct species in fast exchange. From their analysis, they obtained a surface viscosity of the C_{18} layer corresponding to about 13 times higher than that of the bulk solvent viscosity. The effects of added D_2O were also probed and the water mobility results were dependent on the amount of surface coverage of silanol.

Along similar lines to Gangoda and Gilpin, Van Alsten (22) used ^{13}C methyl-labelled dodecyldimethylchlorosilane which was adsorbed onto silica gel. In the presence of various solvents, the measured T_2 of the probe was significantly greater than that estimated from the line widths. This suggested that the line widths were dominated by the superposition of resonances from different environments of the alkylsilanes. Again the T_1 decreased with increasing solvent viscosity and the verification that the system was in the fast motional regime was made by variable temperature studies. Van Alsten plotted T_1 linearly with solvent viscosity, but a reciprocal viscosity relationship is better statistically. This is shown in Figure 2 along with the data from Gilpin and Gangoda (GG).(19) Although the Van Alsten (VA) data was taken at 308 K and the GG data at "ambient" temperature, there is good agreement between the two sets, confirming the dependence of the motion on the solvent viscosity and solvent penetration.

Van Alsten also added poly(dimethyl siloxane) to his labelled silica gel samples in the presence of deuterocyclohexane. The isotopic labelling allowed the bound alkylsilane to be studied in the presence of an overlayer of polymer. At low coverages of polymer, the T_1 of the probe at the interface actually increased, indicating of greater motional freedom possibly due to the conformational changes of the alkylsilane in response to the presence of the polymer. At higher polymer concentrations, the T_1 decreased, went through a minimum and then increased with further addition of polymer. This is consistent with the environment of the alkylsilane becoming more motionally restricted as more polymer was added. The minimum is probably that expected where the molecular motion is on the order of the carbon Larmor (resonance) frequency. In contrast, the mobility of the adsorbed polymer (and its T_1) increased as the amount of adsorbed polymer increased. This was consistent with the view that at low coverages, the polymer was in a relatively flat conformation on the surface. As the coverage increased, the number of segments in the more mobile loops and tails also increased.

Nitrogen-15 is an isotope which could have applicability in a variety of systems, but to date no studies have appeared on its use in interfacially bonded species. Of particular importance are nitrogens in coupling agents such as aminosilanes, and in polymers such as nylons and polyimides. It would not be surprising to see this nucleus used in interfacial systems soon because it is not difficult to incorporate synthetically and ^{15}N spectra have good chemical resolution in the solid state.

The use of deuterium has the advantages of being relatively easy to introduce, with a wide range of methodologies exist for its incorporation. It is also inexpensive compared to other isotopes. Kelusky and Fyfe have used deuterium labelled alkoxysilanes to probe mobility in the presence and absence of solvents.(23) They reacted perdeuteroalkoxydimethoxychlorosilanes with silica gel and observed deuterium NMR lineshapes. The coupling agents studied had the general formula:

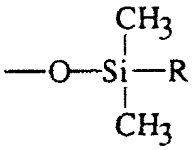


$$-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\mathrm{R}$$

and included R = $-CD_3$, $-CD_2CD_3$, $-CD(CD_3)_2$, $-(CD_2)_7CD_3$, and $-(CD_2)_{15}CD_3$. At room temperature for the dry, treated surface, the deuterium NMR lineshapes consisted of the superposition of more than one unresolved resonance. As the distance from the silicon increased, the width of the resonances decreased. This is indicative of increasing mobility of the alkyl CD's further away from the surface. These spectra broadened with decreasing temperatures indicating slower motions.

In the presence of common solvents, the narrowing of the resonances, compared to bulk, was also observed due to the faster motions present. At lower temperatures, the dry and hexane solvated surface-bound C_8 alkoxysilane indicated a significant motional gradient within the chain. This was evidenced by separation of the powder patterns into rigid and more mobile, but not isotropic, portions. Although this study identified the potential for using deuterated chains and probing its mobility, the overlap of the resonances from different deuterons made it very difficult to separate the contributions of each. Quantitative interpretation was impossible.

In order overcome the problems associated with overlapping resonances, a few studies have described the use of selectively labelled silanes adsorbed and bonded to surfaces.(10, 24-30) Gangoda et al. have labelled alkyldimethylchlorosilanes in different positions. The resulting materials were reacted with silica gel. The general structure of these was:



$$\text{—O—}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{Si}}}}\text{—R}$$

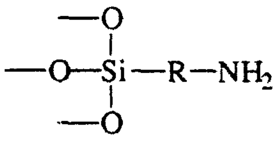
where R ranged from C_{10} to C_{12} and the position of the label varied. In addition, a trimethylalkylsilane was prepared which should have been incapable of covalently bonding to the silica gel surface without siloxyl functionality. Spectra obtained for various species are shown in Figure 3.(24) The labelled compounds are designated by $C_x(Dy)$, where x is the total length of the R group and y is the position of the deuterium label with carbon number 1 next to the silicon. It was observed that the bonded silanes had much more restricted mobility , than associated silanes. The mobility also increased as the distance from the point of attachment increased. No serious attempt to fit the lineshapes to a quantitative model was made, although spin lattice relaxation times were calculated for the bound species and found to be consistent with the trends indicated by the lineshapes.

<Fig. 3>

Deuterium labelled $C_{12}(D11)$ was also used to probe the surface mobility of the bound modifier in the presence of various species.(25) These included simple and binary solvent systems, surfactant solutions and nematic liquid crystals. Methanol and hexane made the silane move relatively fast, compared to the dry state. In a water/methanol mixture the mobility was similar to that of the dry state. A surfactant solution slowed the silane more than in the dry state and a further reduction of the mobility was found in the presence of the nematic liquid crystal The line width was also found to vary linearly with the relaxation times of the label in the presence of the various media. In general, the line shapes obtained for all of the deuterated species mentioned so far are similar to those in Figure 3 although the widths vary significantly with environment.

Several deuterated C_{18} species were studied by Zeigler and Maciel.(26) They studied $C_{18}(D9,10)$ and $C_{18}(D1)$ as a function of temperature, loading and the presence of solvents. Simulations of the lineshapes were made: anti-gauche jumps and more complicated motions were required to simulate the experimental data. The effect of loading was determined at two levels referred to as "low" and "high". The mobility of the silanes was decreased for the high loadings as compared to the low loadings. The labels in the 9-10 positions were also more mobile than those in the 1 position, consistent with the expected motional gradient extending out from the surface. The solvents cyclohexane and acetonitrile were found to significantly increase segmental mobility, while water increased it only marginally. Quantitative rates for reorientation were provided with the use of a computerized spectral simulation program.

In our laboratory we have focused on the use of deuterium labelled coupling agents such as aminoalkylsilanes. The focus has been on trifunctional silanes such as those used in composites. Their structure is shown below:



$$—O—\overset{\overset{—O}{|}}{\underset{\underset{—O}{|}}{Si}}—R—NH_2$$

where the R groups are $C_3(D3)$ and $C_4(D4)$. These have been specifically deuterated in the side-chain position using deuterium gas and the alkyl-cyano silane (27):

$$(CH_3CH_2O)_3Si(CH_2)_nCN \xrightarrow{D_2/Ni} (CH_3CH_2O)_3Si(CH_2)_nCD_2ND_2 \xrightarrow{H_2O} (CH_3CH_2O)_3Si(CH_2)_nCD_2NH_2$$

where n is 2 or 3. Hydrolysis of the siloxane groups yields silanols which can bond to the surface as well as polymerize. The adsorption isotherms for the aminopropylsilane have been determined and, this material has been put on silica surfaces at sub-monolayer and multi-layer levels. An example of this is shown in Figure 4 for aminopropylsilane at various coverages.(10) It was found that at sub-monolayer coverages, the mobility of the surface-bound coupling agent was greater than that at monolayer coverage. At higher coverages, the mobility of the material starts to resemble that of the bulk material made by condensing the coupling agent alone. Even though the effects may seem small; they are measurable and reproducible. Simulation of the spectra provide information on the rates and types of motion present. While the motion of the silane can not be uniquely determined by simulation; strong "circumstantial" evidence is often convincing of the mechanism for motion.

<Fig. 4>

The picture that emerges for a composite interface formed from these coupling agents is one with an initial siloxane layer which is relatively rigid in behavior. At multilayer levels, this interphase approaches the mobility of the polymerized polymer product. Thus with one coupling agent alone, the coupling agent multilayer is graded in terms of mobility. This may be critical in the determination of mechanical properties of the interface and hence the entire composite. The effect of the mobility of the interface is currently under exploration in the author's laboratory.

In order to test the effect of a relatively small change in structure, the aminobutylsilane coupling agent was labelled and studied in the same way as that reported for aminopropylsilane. At low to monolayer coverage, the behavior of both coupling agents was the same. However, at multilayer coverages, the polymer layer from the aminobutylsilane species had significantly more mobility. Since the chemistry of both materials is almost identical, differences in the performance of the two materials when used in composites would most likely be related to small differences in mobility.

Finally, the deuterium label provides the contrast necessary to probe the mobility of the bonded layer in the presence of an overlayer of polymer. Figure 5 shows that the deuterated aminobutylsilane on silica was reduced in mobility when bismaleimide was reacted over it.(28,30) The broader powder pattern is indicative of the presence of slower motions. The quality of the spectra could be improved at higher field strengths than those used (ν = 31 MHz). In addition, comparison of the spectra with simulations suggest that the mechanism of motion changes with the addition of polymer. On the surface alone, the spectra of the labeled coupling agents are consistent with anisotropic rotational motion combined with three-site conformational jumps. When an overlayer of polymer is present, the rotational motions appear to be frozen out and the spectra are consistent with the presence of only the more restrictive conformational jumps. Thus the mechanism of motion, in addition to the rate of motion, changes significantly in the presence of a polymer.

<Fig. 5>

4.0 Conclusions

The use of isotopes and NMR can significantly enhance our understanding of interfacial reactions, and dynamics of molecules at interfaces. Use of isotopes can enhance sensitivity and contrast needed for interfacial studies. The use of ^{13}C and ^{2}H are especially helpful and, for certain systems, the use of ^{15}N may be important. Labelling with ^{29}Si would probably be too expensive because of the high cost of the enriched isotope precursors. In general, selective labelling is particularly useful for determining the rate and mechanism of motion present. For composite materials, the mobility of the interface may be probed, but more development in the mechanics of interfaces is needed in order to translate this knowledge into important breakthroughs in composite materials. The future of the use of isotopes at interfaces looks very bright and improved composite materials should result as we further our understanding the basic properties of interfaces.

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References

1. F. D. Blum, Colloids Surf., 45, 361 (1990).
2. C. A. Fyfe, Solid State NMR for Chemists, CFC Press, Guelph, Ontario, 1983.
3. F. A. Bovey, Nuclear Magnetic Resonance Spectroscopy, 2nd Ed., Academic Press, New York, 1988.
4. E.D. Pleuddemann, Silane Coupling Agents, 2nd Ed., Plenum Press, New York, 1991.
5. R.K. Gilpin and M.E. Gangoda, J. Chromat., 21, 352 (1983).
6. D.W. Sindorf and G.E. Maciel, J. Am. Chem. Soc., 105, 3767 (1983).
7. E. Bayer, K. Albert, J. Reiners, M. Nieder, and D. Muller, J. Chromat., 264, 197 (1983).
8. K.-P. Hoh, H. Ishida, J.L. Koenig, Polym. Composites, 11, 121 (1990).
9. J.W. De Hann, H.M. Van Den Bogaert, J.J. Ponjee, and L.J.M. Van De Ven, J. Colloid Interface Sci., 110, 591 (1986).
10. H.-J. Kang and F.D. Blum, J. Phys. Chem., 95, 9391 (1991).
11. C.-H. Chiang, N.-I Lui, and J. L. Koenig, J. Colloid Interface Sci., 86, 26 (1982).
12. D.E. Leyden, D.S. Kendall, and T.G. Waddell, Anal. Chim. Acta, 126, 207 (1981).
13. A.M. Zaper and J.L. Koenig, Polymer Composites, 6, 156 (1985).
14. T.P. Huijgen, H. Angad Gaur, T.L. Weeding, L.W. Jenneskens, H.E.C. Schuurs, W.G.B. Huysmans, and W.S. Veeman, Macromolecules, 23, 3063 (1990).
15. D.W. Sindorf and G.E. Maciel, J. Am. Chem. Soc., 105, 1848 (1983).
16. R.C. Zeigler and G.E. Maciel, J. Phys. Chem., 95, 7345 (1991).
17. M.E. Gangoda and R.K. Gilpin, J. Magn. Reson., 53, 140 (1983).
18. R.K. Gilpin and M.E. Gangoda, Anal. Chem., 56, 1470 (1984).
19. R.K. Gilpin and M.E. Gangoda, J. Magn. Reson., 64, 408 (1985).
20. M.E. Gangoda, R.K. Gilpin, and B.M. Fung, J. Magn. Reson., 74, 134 (1987).
21. E.H. Ellison and D.B. Marshall, J. Phys. Chem., 95, 808 (1991).
22. J. Van Alsten, Macromolecules, 24, 5320 (1991).

23. E.C. Kelusky and C.A. Fyfe, J. Am. Chem. Soc., 108, 1746 (1986).

24. M. Gangoda, R.K. Gilpin, and J. Figueirinhas, J. Phys. Chem., 93, 4815 (1989).

25. M. Gangoda, R.K. Gilpin, Langmuir, 6, 941.(1990).

26. R.C. Zeigler, G.E. Maciel, J. Am. Chem. Soc., 113, 6349 (1991).

27. H.-J. Kang, W. Meesiri, F.D.Blum, Mater. Sci. Eng., A126, 265 (1990).

28. F.D. Blum, W.Meesiri, H.-J. Kang, J.E. Gambogi, J. Adhesion Sci. Tech., 5, 479 (1991).

29. F.D. Blum, R.B. Funchess, W. Meesiri, in Solid State NMR of Polymers, Mathias, L., Ed.; Plenum Press, New York, 1991, p271-281.

30. J.E. Gambogi and F.D. Blum, Macromolecules, 25, 4526 (1992).

Table I. Partial Listing of NMR Active Nuclei

Isotope	Abundance %	I	Relative Sensitivity[a]	ν (MHz) at 1 T
^{1}H	99.98	1/2	1.000	42.58
^{2}H	0.0156	1	0.00964	6.536
^{13}C	1.108	1/2	0.0159	10.70
^{14}N	99.64	1	0.00101	3.08
^{15}N	0.365	(-)1/2[b]	0.00104	4.32
^{19}F	100.	1/2	0.834	40.06
^{29}Si	4.70	(-)1/2[b]	0.0785	8.46

a- for equal number of nuclei at constant field.

b- the negative sign indicates that these nuclei precess in the opposite sense. The consequences of this are beyond the scope of this work.

Figure Captions

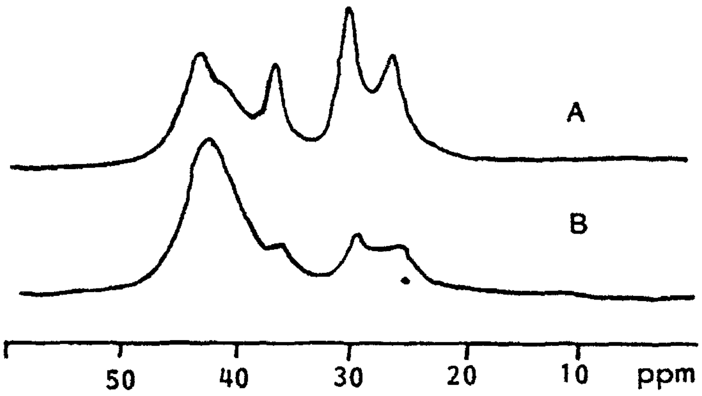
Figure 1. CP-MAS ^{13}C spectra of labelled (γ-^{13}C) aminopropylsilane on glass beads, 8.4% (w/w), in the presence of nylon-6. A) the composite spectrum, B) that obtained after extracting most of the polymer from the treated beads. (Reprinted in part with permission from reference 14. Copyright 1990, American Chemical Society.)

Figure 2. Variation of ^{13}C T_1 relaxation times of methyl-labelled dodecyldimethylchlorosilane bound to silica gel in the presence of various solvents as a function of reciprocal solvent viscosity: (VA) - $(CD_3)_2SO$, C_6D_6, D_2O, $CDCl_3$; (GG-1) - $(CD_3)_2SO$, CCl_4, C_2C_{14}, C_6D_6, $CDCl_3$; (GG-2) $C_4D_8O_2$, CD_3OD, CD_3CN, $(CD_3)_2CO$. (The solvents are listed in each set in order of decreasing viscosity. After references 19 and 22)

Figure 3. ^2H NMR spectra of deuterium-labelled alkylsilanes on dry silica gel, a) trimethyl-C_{10}(D4), b) dimethyl-C_{12}(D12), dimethyl-C_{12}(11), c) dimethyl-C_{10}(D4), d) dimethyl-C_7(D1). (Reprinted with permission from reference 24. Copyright 1989, American Chemical Society.)

Figure 4. Deuterium NMR spectra and simulations of deuterium-labelled C_3(D3) aminopropylsilane on silica. The material was deposited with solution concentrations of A) 0.5%, B) 1.0%, C) 2.0%, D) 3.5% and E) 10%; 2% corresponds to approximately monolayer coverage. (Reprinted with permission from reference 10. Copyright 1991, American Chemical Society.)

Figure 5. Deuterium NMR spectra of deuterium-labelled C_4(D4) aminobutylsilane on silica, A) treated surface and B) treated surface overpolymerized with bismaleimide. (Reprinted in part with permission from reference 28. Copyright 1991, VSP, Inc.)



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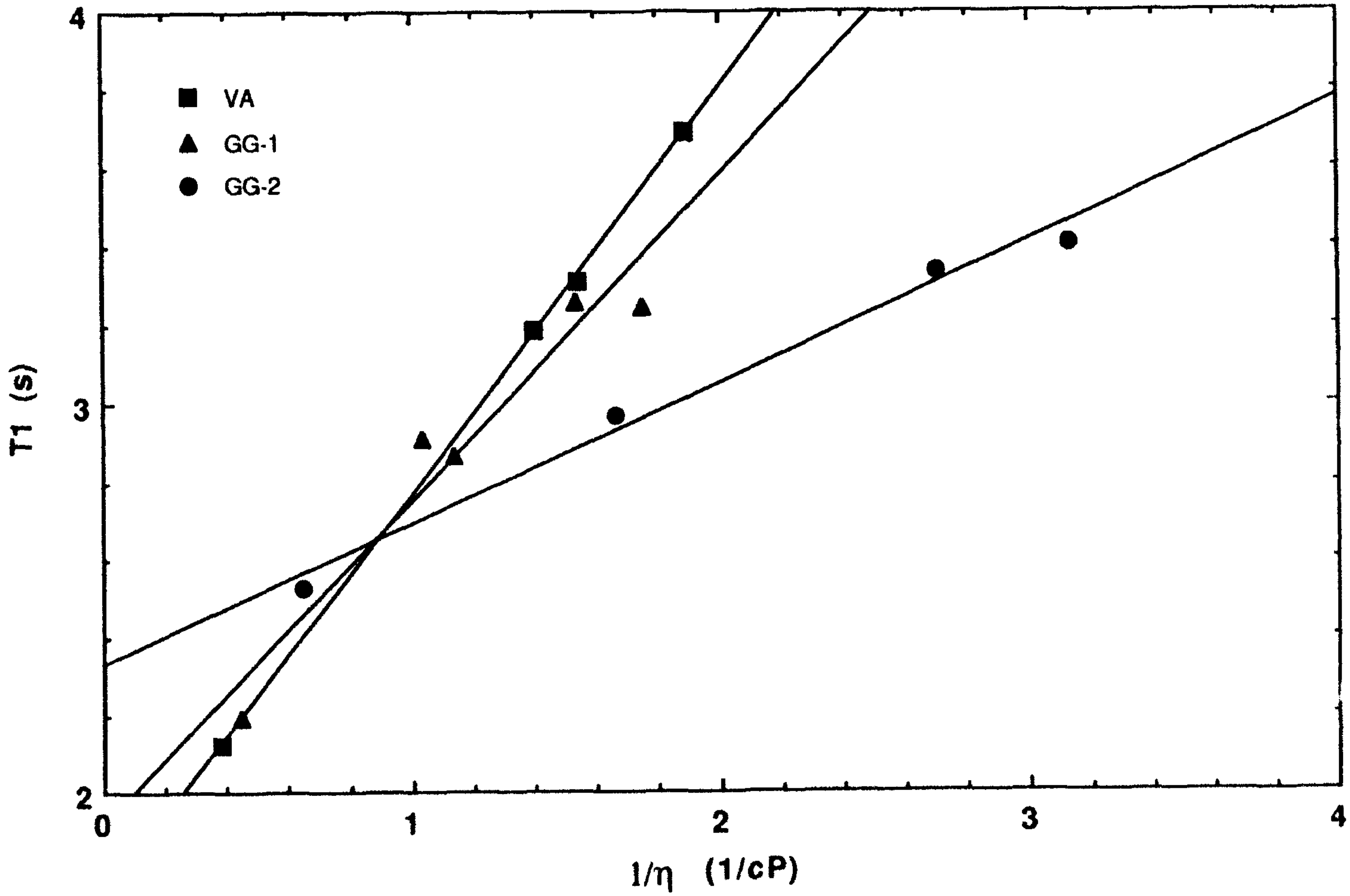

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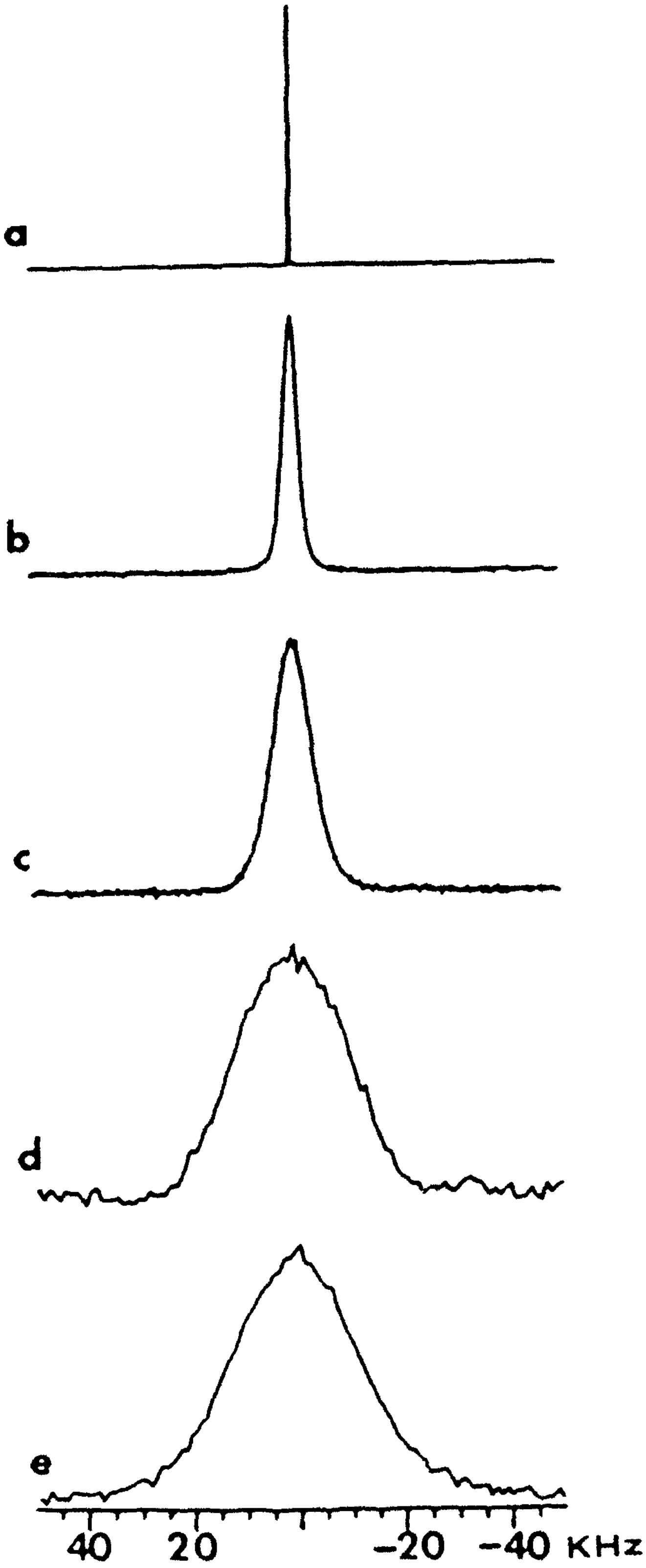

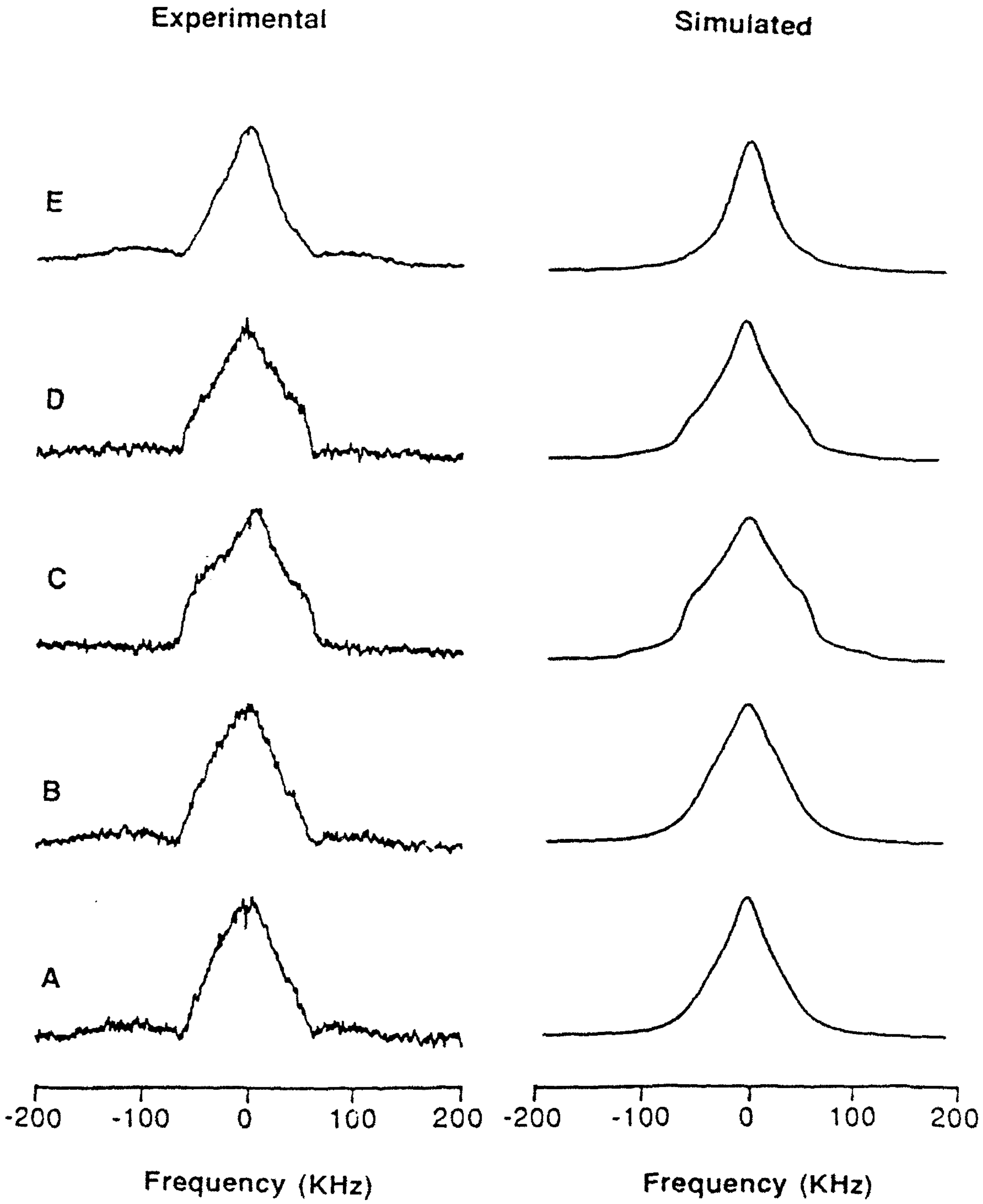

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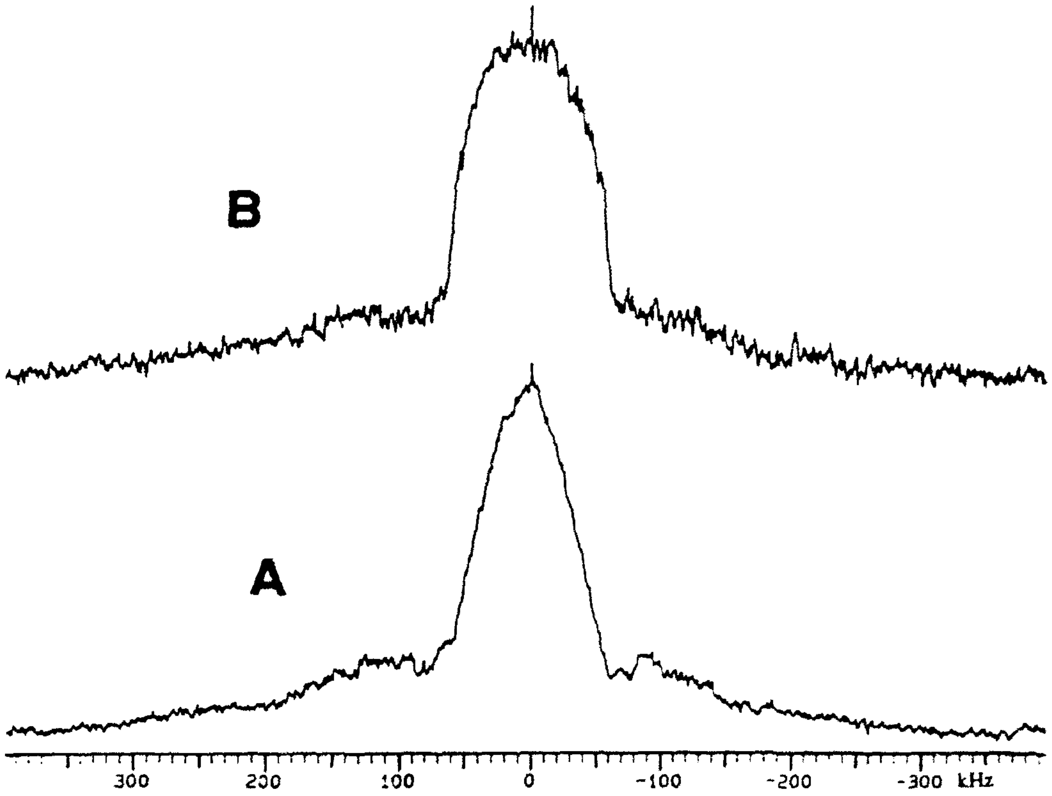

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