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^{13}C Solid-State NMR Study of the Interfacial Region in Glass-Filled Polyamide-6 Composites

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ABSTRACT: ^{13}C-labeled (γ-aminopropyl)triethoxysilane (γ-APS) has been used to enhance the sensitivity and selectivity of solid-state ^{13}C NMR in an investigation of the interfacial region of microcomposite samples composed of polyamide-6 (PA6), glass microspheres, and γ-APS. As the interphase is crucial in determining the properties of a composite, we have focused our attention on this region with the goal of elucidating the adhesion mechanism. From the MAS spectra, some indication has been obtained for the occurrence of amide formation between the PA6 carboxylic acid end groups and the amines of γ-APS, but the evidence is not overwhelmingly strong. Several relaxation times, i.e., T_1 (^{13}C), T_2(^{13}C), $T_{1\rho}$ (^{1}H), $T_{1\rho}$(^{13}C), and T_{IS}(^{1}H$\rightarrow$^{13}C), of both γ-APS and PA6 have been studied as a function of sample composition, and their behavior can be explained on the basis of the presence of entanglements and interpenetration of the polysiloxane and polyamide networks. So the interpenetrating network mechanism and presumably also chemical bonding contribute to the adhesion between the PA6 matrix and γ-APS.

Introduction

The use of organosilane reagents to modify inorganic surfaces has found widespread application in reinforced polymer composites. These reagents have been reported to give a composite of better mechanical and electrical properties, to give enhanced resistance to ingress by chemicals, and also to improve rheological properties.[1-4]

Several spectroscopic techniques have been applied to study these composite systems including FT-IR, Raman, NMR, and ESCA.[1,2,5,6] However, the small relative volume of the interfacial region often results in it being obscured by the bulk of the filler and/or polymer in spectroscopic measurements. To avoid this problem, various strategies have been explored including radioisotopic labeling of the coupling agent,[7] isolation of the filler from the composite,[8] examining interdiffusion of protonated and deuterated polymers with secondary ion mass

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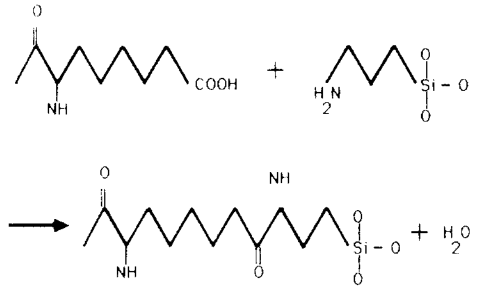
Scheme I
Reaction of Amine of γ-APS with Carboxylic End Group of PA6



spectrometry (SIMS),[9] studying the pretreated filler before incorporation into the composite,[8] etc. Another possibility, which to our knowledge has not yet been explored, is to use a selectively ^{13}C-enriched coupling agent as a probe for the investigation of the interfacial region by ^{13}C solid-state NMR.

A widely used coupling agent is (γ-aminopropyl)triethoxysilane (γ-APS) because it has the possibility of chemically bonding with both the inorganic surface and with reactive functionalities in a polymer.[6] For the system studied here, polyamide-6 (PA-6) and glass microspheres (beads), previous investigations[8] have established that a significant amount of the γ-APS reacts with silicon Q^2 and Q^3 sites on the surface of the glass microspheres. Also, it was found that γ-APS on the surface of the beads polymerizes to form networks.

We now want to address the problem of the interaction between PA-6 and γ-APS. Chemical bonding between PA-6 and γ-APS, although possible, may occur only to a limited extent, therefore it cannot be the main factor for the enhancement of the interaction between the matrix and the filler. The improvement of composite properties due to the presence of the coupling agent can then be provided by the interpenetrating network (IPN) theory, which proposes entanglement of polymer chains in a polymerized network of coupling agent at the filler surface with the matrix polymers.[1] The interfacial layer of polysiloxane is assumed to have an irregular structure; recent models suggest a fractal structure.[10]

To simultaneously address the issues of sensitivity and adhesive mechanism, γ-APS has been synthesized with ^{13}C at the γ position, [γ-^{13}C]-γ-APS, i.e., adjacent to the amine.[11] Preliminary work has shown that when the amine reacts with a carboxylic acid to form an amide (see Scheme I), there is an upfield shift of 1.5 ppm of this carbon resonance.[8] Therefore, if reaction with carboxylic end groups of PA6 does occur, it should be reflected in the resonance characteristics of this carbon.

Experimental Section

We have studied several samples which are compositions of glass microspheres, ^{13}C-enriched γ-APS, and low molecular weight PA6. The report of the synthesis of a ^{13}C-enriched precursor to γ-APS[12] has recently been followed by the details of the synthesis[11] of the [γ-^{13}C]-γ-APS, which was used in these experiments. The PA6 employed in the composite samples was of low molecular weight ($M_w = 7000$, $M_n = 4650$, $M_z = 9900$, $M_w/M_n = 1.5$; end group analysis: $\epsilon_{COOH} = 266$ mequiv kg^{-1}, $\epsilon_{NH_2} = 298$ mequiv kg^{-1}). Methanol extraction of the PA6 was used to remove residual monomers and oligomers. The glass beads were small, 5 μm in diameter, to maximize surface area and number of reaction sites. Two samples of glass beads were prepared by treating them with [γ-^{13}C]-γ-APS as follows: to a toluene solution (5 mL) of [γ-^{13}C]-γ-APS (10% w/w for glass beads 1 or 0.5% w/w for glass beads 2) 0.5 g of glass microspheres and 3 M equiv of water, based on [γ-^{13}C]-γ-APS, were added. The mixture was stirred for 1 h at room temperature, and the glass beads were filtered off and dried under vacuum at 100 °C for 1 h. The amount of [γ-^{13}C]-γ-APS present at the surface of the glass microspheres was estimated by comparison to nonenriched samples, which were prepared by using the same procedure, by thermogravimetric analysis (TGA) and solid-state NMR. The estimated loading of the pretreated glass beads by [γ-^{13}C]-γ-APS is 8.4% by weight for glass beads 1 and 0.5% by weight for glass beads 2.

The composites were prepared by placing 0.3 g of the glass microspheres which had been pretreated with [γ^{13}C]-γ-APS (composite I with glass beads 1 and composite II with beads 2) and 0.7 g of PA6 in a sealed vessel which was then evacuated and flushed 3 times with N_2 before immersion in an oil bath at 220–230 °C. The mixture was heated with continuous stirring until it melted and then stirred in its melted state for 5 min. After removal from the oil bath, the sample was allowed to cool to room temperature, removed from the vessel, ground in the presence of dry CO_2(s), and dried under vacuum at 100 °C for 8 h. Also, two samples were prepared for which the glass beads were extracted from the composites: extracted glass beads I from composite I and extracted glass beads II from composite II. The glass beads were isolated from the microcomposite by dissolving the PA6 matrix in trifluoroethanol (TFE). The insoluble fractions were isolated by filtration and were extracted twice with TFE in order to ensure complete solution of any soluble material. These insoluble fractions were dried under vacuum at 100 °C for 1 h.

NMR Spectroscopy. The NMR spectra were measured at room temperature on a Bruker CXP 300 spectrometer equipped with an Aspect 3000 computer and with a Bruker double-bearing CP/MAS probe. The 90° pulse lengths were 3.4–4.25 μs in length for ^{13}C and ^{1}H nuclei. Some of the data presented here were collected with cross-polarization (CP),[13] as shown in Figure 1a. The mixing time was typically 1.5 ms.

Recycle delays were 2 s long, and the magic angle spinning (MAS) frequency was either 3.7 or 4.0 kHz. Phase cycling and spin temperature alternation were used to minimize artifacts.[14] Adamantane was used to optimize experimental parameters and as an external secondary chemical shift reference (38.56 ppm for the methylene resonance relative to TMS[15]). The Bloch decay spectra were measured with a modification of the DEPTH pulse sequence[16] to minimize the background signal from the probe, as shown in Figure 1b. The recycle delay for these experiments was generally 1 s.

Five relaxation parameters were measured for the samples, although not all parameters were determined for all samples. The ^{13}C T_2 was measured with an echo technique, shown in Figure 1c, in which the interval τ is an integral multiple of the rotor period.[15]

The ^{13}C relaxation time in the rotating frame, $T_{1\rho}(^{13}\mathrm{C})$, was measured with the pulse sequence of Figure 1d.

The magnetization decays in the $T_2(^{13}\mathrm{C})$ and $T_{1\rho}(^{13}\mathrm{C})$ experiments are fitted with a sum of exponentials:

$$M(\tau) = \sum_i M_{0i} e^{-\tau/T_i} \tag{1}$$

where T_i is an individual T_2 or $T_{1\rho}$.

The values for the transfer time of magnetization from ^{1}H to ^{13}C, $T_{CH} \equiv T_{IS}$, and of the proton $T_{1\rho}$, $T_{1\rho}(^1\mathrm{H})$, were determined in a combined experiment according to the pulse sequence of Figure 1e. The intensities of several ^{13}C lines as a function of τ were fitted by

$$M(\tau) = \sum_i \frac{1}{A_i} M_{0i} e^{-\tau/T_{1\rho i}(^1\mathrm{H})}(1 - e^{A_i\tau/T_{\mathrm{IS}i}}) \tag{2}$$

where

$$A_i = 1 - T_{\mathrm{IS}i}/T_{1\rho i}(^1\mathrm{H})$$

The final relaxation parameter to be measured was $T_1(^{13}\mathrm{C})$, the spin–lattice relaxation time. For the pretreated beads 1, an inversion recovery experiment in combination with CP was used, as shown in Figure 1f. Not indicated in the pulse sequence

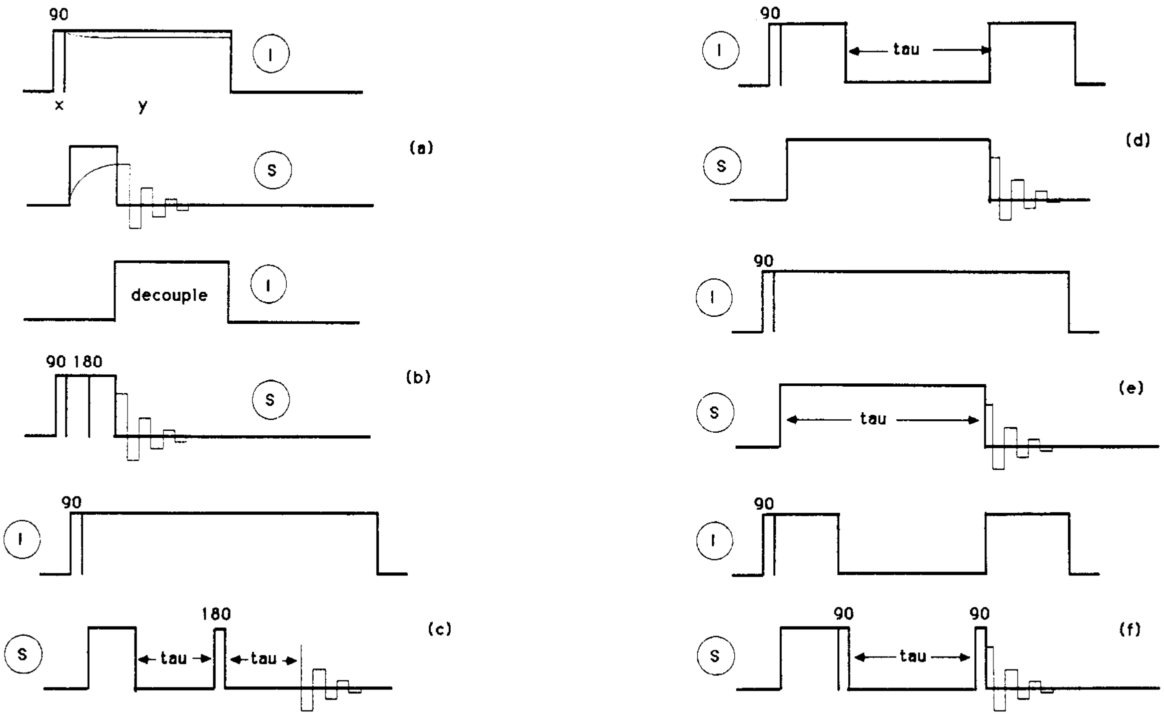


Figure 1. Various pulse sequences used: (a) standard cross-polarization experiment; (b) DEPTH pulse sequence to eliminate probe background; (c) $T_2(^{13}C)$ measurement, τ is an integral multiple of the rotor period; (d) $T_{1\rho}(^{13}C)$ measurement; (e) T_{IS} and $T_{1\rho}(^1H)$ measurement; (f) $T_1(^{13}C)$ experiment, not indicated is the pulsed proton saturation during the delay τ.

of Figure 1f is the proton saturation during the delay τ by a pulsed, resonant radio-frequency field. For composite I and the beads extracted from it, Torchia's pulse scheme[17] was used, a modification of Figure 1f. The ^{13}C magnetization decays were in that case fitted by eq 1.

The relaxation data were fitted with a minimization procedure using the MINUIT package from CERN.[18] The fits to the data which are shown in Figures 7 and 8 are semilog plots for clarity of presentation; however, the fitting was done by using the measured intensities and not the logarithm of the intensities.

It is important to note the mathematical difficulty of the fitting procedure. The worst case is the variable mixing time experiment (26 data points) which was fitted with eq 2, which has six independent parameters in the case of two $T_{1\rho}(^1H)$ and two T_{IS} values. Approximate starting values for the ^1H $T_{1\rho}$ were known from a determination on pure PA6 using a variable-length spin lock to the protons before a cross-polarization step of fixed length. We made careful searches to test the reliability and stability of the procedure with respect to false minima or nonphysical solutions. For example, one or more of the parameters were fixed, and the fitting procedure was repeated iteratively. The possibility of including additional components was explored, and we concluded that the additional parameters either increased the uncertainty in the other parameters unacceptably, were too small to be significant, or gave physically unreasonable values.

Results and Discussion

Spectra. 1. ^{13}C Spectra of Pretreated Beads. Figure 2 shows the Bloch decay and CP spectra of the glass beads loaded with 8.4% ^{13}C-enriched γ-APS; only a single line is observed from the enriched position in γ-APS. The Bloch decay spectrum is 5 times more intense than the CP spectrum; also, the width of the line and the peak positions are different (43.1 ppm for the Bloch decay and 42.7 ppm for the CP line). In addition, the line width of the Bloch decay is a function of the recycle time, 275 Hz for 1.5 s and 245 Hz for 0.5 s. This all suggests a multicomponent structure for the polysiloxane layer with different mobilities and relaxation times. The more mobile components are mainly represented in the Bloch decay spectrum, the more rigid parts in the CP spectrum.

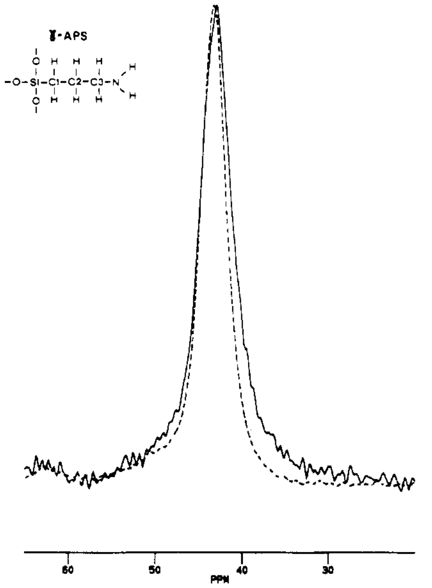


Figure 2. Bloch decay and CP MAS ^{13}C NMR spectra of γ-APS (enriched with ^{13}C at position C_3) on glass micropheres (glass beads 1). The dashed line represents the Bloch decay spectrum, the solid line the CP spectrum.

2. ^{13}C Spectra of the Composites. Figures 3 and 4 show CP and Bloch decay spectra of composite I, with glass beads loaded with 8.4% [γ-^{13}C]-γ-APS and of composite II, with glass beads loaded with 0.5% [γ-^{13}C]-γ-APS, together with the corresponding spectra of the beads isolated from the composites. The enhancement of the 43 ppm line due to the ^{13}C-enriched γ-APS is obvious when the spectrum from the enriched composite I is compared with the spectra of a nonenriched composite, shown in Figure 1 of ref 8. Obviously, the enhancement of the 43 ppm resonance is more pronounced in the case of the extracted beads from composite I than in the composite itself. The spectra in Figures 3c,d and 4c,d unambiguously prove that by the procedure of the extraction of beads from the composites not only γ-APS but also poly-

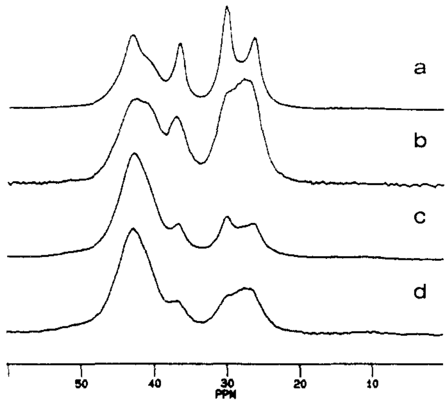


Figure 3. CP and Bloch decay ^{13}C spectra (aliphatic region) of composite I and extracted beads I: (a) CP MAS spectrum of composite I; (b) Bloch decay MAS spectrum of composite I; (c) CP MAS spectrum of beads extracted from composite I; (d) Bloch decay MAS spectrum of beads extracted from composite I.

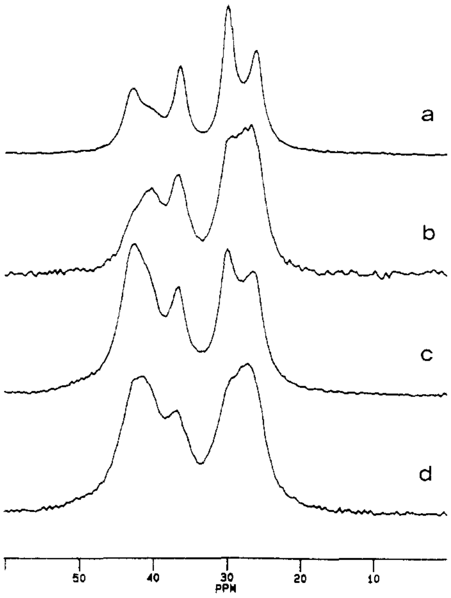


Figure 4. CP and Bloch decay ^{13}C MAS spectra (aliphatic region) of composite II and extracted beads: (a) CP MAS spectrum of composite II; (b) Bloch decay MAS spectrum of composite II; (c) CP MAS spectrum of beads extracted from composite II; (d) Bloch decay MAS spectrum of beads extracted from composite II.

amide chains come along with the beads, presumably for the reason that they are chemically and/or mechanically attached to the glass surface.

The width at half-height of the $[\gamma\text{-}^{13}\text{C}]$-$\gamma$-APS can be obtained by subtracting the Bloch decay spectrum of the nonenriched composite from that of composite I. The width of 410 Hz so obtained is considerably larger than that of the pretreated beads outside the composite (275 Hz) (Figure 2). This must be due to a broad distribution of chemical environments in the composite, which either does not exist in the pretreated beads or is averaged out by the mobility of the APS units on the surface of the beads. This aspect will be investigated in the next section via spin relaxation measurements.

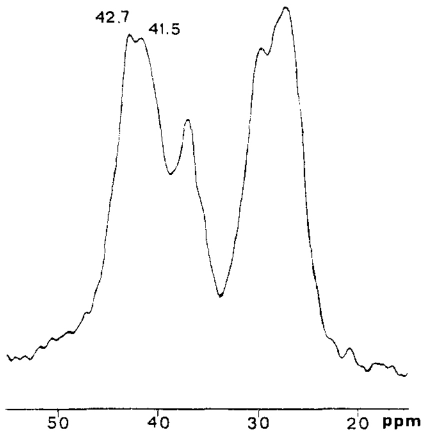


Figure 5. Bloch decay MAS ^{13}C spectrum of extracted glass beads II after collecting 58 450 FIDS and resolution enhancement (LB = -80 Hz, GB = 0.3).

The existence of a possible chemical bonding between $[\gamma\text{-}^{13}\text{C}]$-$\gamma$-APS and the PA6 can be detected by a change in chemical shift of the enriched carbons, as mentioned in the Introduction. Composite II, with the lowest amount of $[\gamma\text{-}^{13}\text{C}]$-$\gamma$-APS, is the best sample in which to look for such a shift because for this sample one might hope that a significant fraction of the total number of APS amine groups has reacted with the PA6 carboxylic end groups. At the level of loading in this sample (0.5%), geometrical arguments suggest that up to 50% of the γ-APS may have reacted with PA6. Figure 4d shows the spectrum of the extracted beads from composite II; in Figure 5 the spectrum from the same sample is given, to improve the S/N, from 58 450 Bloch decays collected at 1.5-s intervals and after resolution enhancement. Although the two peaks in Figure 5 at 41.5 and 42.7 ppm and the related upfield line broadening may indicate that chemical bonding has occurred between some of the amines of the γ-APS and the PA6 carboxylic end groups, the evidence is not completely convincing.

^{13}C Spin Relaxation. To investigate whether the insertion of the pretreated glass beads in the composites affects the mobility of the poly(APS) chains at the surface of the glass beads, several relaxation times of the carbons at the enriched position in γ-APS have been measured: T_2, $T_{1\rho}$, the cross-polarization time T_{IS}, and T_1. Also, the proton $T_{1\rho}$ has been determined. The ^{13}C T_2 spin–spin relaxation time is sensitive to the average distance between the nuclear dipole moments and to the motions of the internuclear vectors and therefore depends on sample density and rigidity. For a sample with molecular motion, the T_2 will be longer than for a more rigid sample. The ^{13}C $T_{1\rho}$ is notoriously difficult to interpret since in principle this relaxation time is sensitive to both spin–lattice and spin–spin relaxation processes. In this respect, ^{13}C enrichment of a sample forms another complication.

1. **Pretreated Glass Beads.** The results of the relaxation measurements on the pretreated glass beads with a loading of 8.4% $[\gamma\text{-}^{13}\text{C}]$-$\gamma$-APS are summarized in the first column of Table I. Although a multicomponent character of the ^{13}C T_2 cannot be excluded, the experimental data can be fit in a satisfactory way with eq 1, and only two different values for T_2 (see Figure 6a, where the data and the fitting curve are shown on a semilogarithmic scale).

The longer T_2 is assigned to the more mobile fraction of γ-APS, based upon the mobility argument given above and the narrower line width observed at shorter recycle delays. For the ^{13}C $T_{1\rho}$ data, again only two terms adequately fit the experimental data (Figure 6b). The two different $T_{1\rho}$ values are assigned to a mobile and rigid component of γ-APS, again based upon line width: the longer ^{13}C $T_{1\rho}$ corresponds to a narrower line and a more mobile phase. Figure 7a shows the experimental data from the experiment that is used to determine T_{CH} and $T_{1\rho}(^1\mathrm{H})$, see Figure 1e; the mixing time was varied from 0.005 to 30 ms. The best fit of eq 2 to these experimen-

Table I
Relaxation Times of the Different Samples at 43 and 40 ppm

relaxation time	pretreated beads 1 γ-APS (43 ppm)		composite I				extracted beads from composite I				pure PA6	
			γ-APS		PA6		γ-APS		PA6			
	rigid	mobile	43	40	43	40	43	40	43	40	43	40
$T_2(^{13}C)$, ms	3.4 ± 1.0	11 ± 2	3.7 ± 0.3	4.6 ± 0.3	7.8 ± 0.7	4.6 ± 0.3	2.7 ± 0.9	2.6 ± 0.2	6.7 ± 1.0	5.4 ± 0.3	6.4 ± 0.6	4.0 ± 0.5
$T_{1\rho}(^{13}C)$, ms	6.9 ± 1.5	35 ± 5	4.0 ± 1.7	3.3 ± 1.7	33 ± 8	25 ± 8	3.1 ± 0.9	3.1 ± 0.9	27 ± 3	30 ± 5	40 ± 14	11 ± 6
T_{IS}, μs	28 ● 5	307 ± 25	24.9 ± 1.0	25.9 ● 1.0	164 ± 10	174 ● 25	24.1 ± 0.9	22.0 ± 0.9	336 ± 60	281 ± 60		
$T_{1\rho}(^1H)$, ms	12.5 ± 0.3	12.5 ± 0.3	3.6 ± 0.6	3.1 ± 1.1	14.5 ± 2.3	9.9 ± 1.0	3.1 ± 1.0	3.6 ± 1.0	8.2 ± 1.0	8.0 ± 1.0	13.6 ± 1.2	
$T_1(am)(^{13}C)$, s	0.58 ± 0.05	0.23 ± 0.11	0.64 ± 0.20	0.56 ± 0.18		5.3 ± 3.1	0.54 ± 0.30	0.59 ± 0.29		4.5 ± 1.9		1.1 ± 0.3
$T_1(cr)(^{13}C)$, s					11 ± 5				4.7 ± 1.9		138 ± 14	

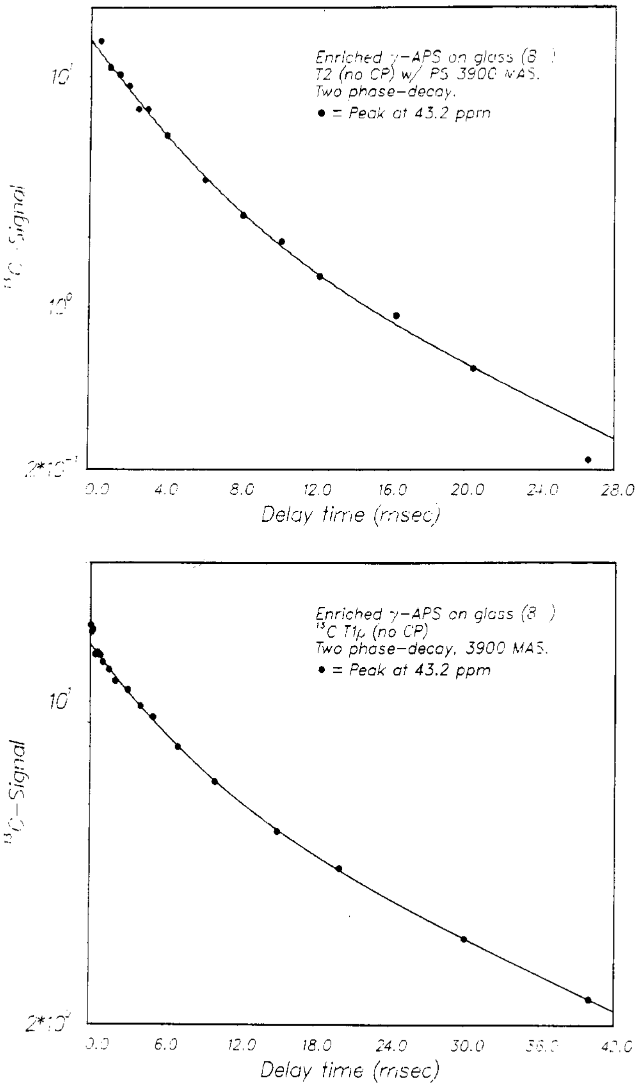


Figure 6. $T_2(^{13}C)$ (a, top) and $T_{1\rho}(^{13}C)$ (b, bottom) data points for the carbon in the enriched position in γ-APS (pretreated glass beads 1) and the fit (solid curve).

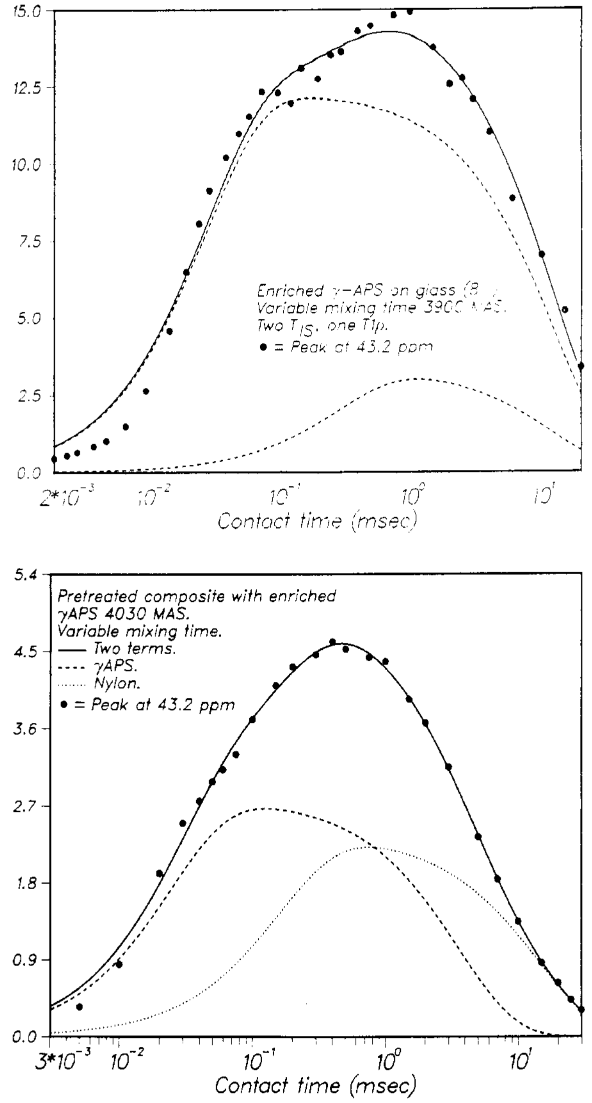


Figure 7. T_{CH} and $T_{1\rho}(^1H)$ data points and numerical fit for the ^{13}C NMR line at 43 ppm of pretreated glass beads 1 (a, top) and of composite I (b, bottom).

tal data was obtained with two values for T_{CH} and one for $T_{1\rho}(^1H)$. Again we interpret these results on the basis of the existence of a mobile and a relatively rigid fraction of γ-APS. Table I also shows that for the ^{13}C T_1 two different values are found.

The amounts of the rigid and mobile fractions of γ-APS at the surface of the beads, as determined from the numerical fits, vary with the type of relaxation time studied. For spin–spin relaxation times such as T_2 and T_{IS}, about 25% of the γ-APS on the beads belongs to the mobile fraction. From the spin–lattice relaxation experiments, it is found that the rigid and mobile fractions are roughly equal in size. This difference can be a consequence of the frequency distribution of the motions in the mobile fractions.

From the previous study,[8] it followed that upon treatment of the glass beads with γ-APS Si–O–Si linkages are formed between γ-APS and the glass surface on the one hand and between γ-APS molecules on the other hand. The γ-APS units therefore polymerize and form a network, parts of which are immobilized by the chemical bonding to the surface of the glass beads. These immobilized fractions we consider to be the rigid parts from the relaxation study. The mobile and rigid fractions of the γ-APS network are spatially close since, because from the $T_{1\rho}(^1H)$ measurements a single value is found, ^1H spin diffusion apparently is able to average local differences.

2. Composite I and Extracted Glass Beads. The same relaxation time measurements as discussed above for the pretreated glass beads have been performed for composite I, with glass beads treated with 8.4% [γ-^{13}C]-γ-APS, and for the glass beads extracted from this composite. From the spectra of the nonenriched composite, see Figure 1 of ref 8, it is clear that the line from the enriched position in [γ-^{13}C]-γ-APS will overlap with both the line from C_1 carbons of crystalline PA6 at 43 ppm and the line from C_1 carbons of amorphous PA6 at 40 ppm. For both samples, the composite and the extracted beads, we can therefore expect for the relaxation measurements of the lines at 40 and 43 ppm contributions from three components: PA6 (crystalline PA6 at 43 ppm and amorphous PA6 at 40 ppm), and "rigid" and "mobile" γ-APS. It appeared, however, that after convergence was reached one of the three terms was either negligibly small or gave a negative relaxation time. The best result for each relaxation time and each chemical shift (40 and 43 ppm) was obtained with a two-term fit which yielded two relaxation times, one for [γ-^{13}C]-γ-APS and one for PA6, see Table 1 and Figure 7b. It is gratifying to see that the [γ^{13}C]-γ-APS relaxation times, determined from measurements at 40 and 43 ppm, nicely agree.

By comparing the relaxation time data of [γ-^{13}C]-γ-APS of the pretreated beads with those of composite I and of the extracted beads, we conclude that for [γ-^{13}C]-γ-APS in the composite and extracted beads only those relaxation times are found which we assigned in the case of the pretreated beads to the "rigid" parts. Apparently, the mobility of the mobile fraction of [γ-^{13}C]-γ-APS on the pretreated beads is severely restricted by the presence of PA6 in the composite. An indication of this was already obtained from the increase in the line width of [γ-^{13}C]-γ-APS in going from the pretreated beads to the composite (see above). Although our experiments cannot give a clear answer, we believe that such a restriction in the local mobility of the γ-APS networks cannot exclusively be due to chemical bonding of γ-APS with PA6. Entanglements and interpenetration of the γ-APS and PA6 are believed to be the main cause of the disappearance of the mobile γ-APS fraction in the composite.

Another striking result is that in the composite two different values for $T_{1\rho}$ ^{1}H are found for γ-APS and PA6. Apparently, the entanglements and interpenetration do not lead to a mixing intimate enough that ^{1}H spin diffusion[19] can average the difference. In the last two columns of Table I, relaxation data are presented for pure PA6. Clearly, the addition of pretreated beads to PA6 to make a composite, has an effect, especially on the T_1 value of crystalline PA6. We assume that either the presence of beads in the composite makes the crystalline regions so much smaller that spin diffusion between carbons in amorphous and crystalline regions starts to decrease the crystalline T_1 and increase the amorphous carbon T_1 or that the crystalline regions are disrupted and therefore have become less rigid.

Attention is also drawn to the $T_{1\rho}(^1\mathrm{H})$ value for pure PA6 (13.6 ms at 43 ppm), which equals that of PA6 in the composite. However, in the extracted beads this relaxation time has decreased to 8.2 ms. It is tempting to believe that this points to a beginning of spin diffusion between PA6 and γ-APS in the extracted beads.

Conclusions

The polysiloxane ^{13}C-enriched γ-APS layer on the surface of the glass microspheres shows, due to the selective ^{13}C enrichment, a single ^{13}C NMR line. Relaxation time measurements clearly demonstrate the two-component character of this line. A more rigid fraction of γ-APS, presumably near the glass surface, with a relatively broad line and a more mobile outer layer with a narrower line can be distinguished.

Composite preparation broadens the [γ-^{13}C]-γ-APS line in the upfield direction. This may be caused by amide formation between the PA6 carboxylic acid end groups and the amines of the γ-APS. This is suggested by the observation of a small splitting in the line of γ-APS in the sample of glass microspheres, loaded with 0.5% γ-APS, separated from the composite. Although evidence for chemical bonding between γ-APS and PA6 is not overwhelming, the change in relaxation times of γ-APS upon composite forming clearly demonstrates strong intermolecular γ-APS and PA6 interactions. In particular, it is observed that the mobile fraction of γ-APS on the surface of the glass microspheres outside the composite is stiffened by insertion into the PA6 matrix. This is attributed mainly to chain entanglements and interpenetration of polysiloxane and polyamide networks. The interpenetration, however, seems superficial since proton spin diffusion cannot average the different proton $T_{1\rho}$ values for protons in the γ-APS layer and in PA6.

The final conclusion is therefore that ^{13}C NMR shows some evidence of chemical bonding between γ-APS and PA6 but that chain entanglements and interpenetration of networks also play a role in the adhesion between PA6 and γ-APS.

References and Notes

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