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Detection of Nanometer-Scale Mixing in Phosphate-Glass/Polyamide-6 Hybrids by ^{1}H−^{31}P NMR

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The size of phosphate-glass (Pglass) particles dispersed in a polyamide-6 (PA6) matrix by melt blending has been characterized by ^{1}H−^{31}P solid-state nuclear magnetic resonance (NMR). ^{1}H spin diffusion from ∼75% of the ^{1}H in the glass to the polyamide is observed within 50 ms, indicating proximity on a 30 nm scale. Fast dephasing of a quarter of the ^{31}P magnetization by dipolar couplings to polyamide protons in ^{31}P{^{1}H} heteronuclear recoupling with dephasing by strong homonuclear interactions of protons (HARDSHIP) NMR shows that ∼25% of the Pglass is within 0.5 nm from the polyamide. This is confirmed by ^{1}H−^{31}P heteronuclear correlation NMR spectra with inverse $T_{2,H}$ filtering, which document relatively fast (1 ms) cross polarization from PA6 protons, identified by their upfield chemical shift and short transverse relaxation time $T_{2,H}$, to a significant fraction of ^{31}P in the glass. The ^{31}P spectrum associated with the polyamide ^{1}H reveals that the phosphate sites near the polyamide matrix are chemically altered but differently than previously observed in Pglass−polyethylene hybrids, where no such contact was proven. As expected, the ^{31}P sites that cross-polarize from the polyamide protons also exhibit pronounced dephasing in ^{31}P{^{1}H} HARDSHIP experiments. HARDSHIP experiments after cross polarization and ^{31}P spin diffusion experiments indicate that the ∼25% of phosphate that is within 0.5 nm from the polyamide is not dispersed in the polymer but on the surface of ∼10 nm diameter Pglass particles. This study represents the first conclusive evidence of intimate mixing of the hybrid components. Further, it suggests that this is an excellent model system for exploring new routes for driving organic polymers and inorganic glass to self-assemble into useful organic/inorganic hybrid materials.

Introduction

While conventional polymer blends and composites can more or less satisfy current material needs, the demand for advanced materials is still growing. In order to meet the material requirements for new applications, it is necessary to develop and evaluate novel materials like inorganic-glass/organic-polymer hybrids. Hybrid materials are broadly defined as synthetic materials containing both organic and inorganic components.[1,2] They can be further classified into (i) homogeneous systems derived from monomers or miscible components and (ii) phase-separated or heterogeneous systems.[1,2] Low-T_g phosphate glass (Pglass)/polymer hybrids are a good example of the latter. Phosphate glasses that display excellent water resistance and chemical durability are now readily available.[3,4] An example is tin fluorophosphate glass with a T_g of 125 °C.[5−7] Due to the low T_g of the Pglass component, these hybrids can be melt-processed conventionally with Pglass loadings as high as 60% by volume or 90% by weight, thereby eliminating the intractable viscosity problem inherent in conventional high-filler composition polymer composites.[8,9] Another advantage of these hybrids, which stems from both hybrid components being fluid during processing, is the unique morphologies, such as fibrils, droplets, and co-continuous networks, that can be generated due to the molecular-level (i.e., single-phase) mixing of the components.[8,10] The final morphology can be partially controlled through careful choice of processing parameters.[11] As the morphology greatly impacts the macroscopic properties, the “tunability” of the morphology presents the opportunity to design a hybrid to meet specific materials needs. Therefore, a better knowledge of hybrid miscibility and molecular dynamics, especially at the interface, and of the thermodynamics of hybrid phase separation is clearly desirable. The Pglass/polyamide-6 (PA6) hybrid system studied here provides an excellent opportunity to investigate new processing routes for controlling the self-assembly of organic polymers and inorganic phosphate glasses into useful materials.

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It is noteworthy that existing hybrid materials are almost exclusively silica-based polymer hybrids prepared via solution or sol−gel methods.[1,12,13] To our knowledge, very few applications of these methods to inorganic phosphate-based hybrid systems have been reported in the literature.[14] As pointed out by Niida and co-workers,[14] it is difficult to use the sol−gel method for the hybrid systems discussed in the present article because the samples from sol-gels are often porous and crack or severely contract to squeeze out the incorporated organics when the solvents evaporate from the gels. This article describes the characterization of a class of hybrid materials produced by a relatively new and facile (but radically different) method. These hybrids of ultra-low T_g inorganic phosphate glass and a polymer matrix combine in one material the excellent gas/liquid barrier properties and flame resistance of inorganic glasses with the mechanical toughness and ease of processing of organic commodity polymers for next-generation applications where either pure glass or polymer is not useable.

While the effects of interactions and miscibility on morphology have been studied for many different polymer blends,[15−17] there are relatively few investigations of the miscibility of polyamides with other polymers.[18,19] Miscibility is often enhanced in polymer blends or hybrid materials where there is a large potential for interactions between the components. Good polymer/glass adhesion is often achieved in conventional glass-filled polymer composites through coupling agents that promote interaction between the glass filler and polymer matrix.[20] In Pglass/polyamide hybrids, this may be unnecessary since it has been reported that certain Pglass compositions will bind amine groups to the glass surface.[21] This classical interaction facilitates a high degree of interaction between the PA6 and Pglass phases, thereby encouraging both miscibility in the melt and polymer/glass adhesion in the solid state. Urman and Otaigbe examined the interaction between Pglass and PA6 using melting point depression.[22] By using the Nishi−Wang equation[23] to describe the thermodynamics of this system, we were able to calculate a χ interaction parameter of -0.067, which indicated that the components were miscible in the melt. This was the first reported evidence of miscibility of an inorganic glass and an organic polymer. The high degree of interaction also facilitated a 10 K drop in the PA6 T_g (as measured by dynamic mechanical analysis (DMA)), as well as a plasticizing effect on tensile mechanical properties. Since the PA6 and Pglass are only miscible in the liquid (melt) state, the phase separation of the components can generate morphologies that are very suitable for nuclear magnetic resonance (NMR) studies.

Modern solid-state NMR can provide useful information on composition and size of domains in nanoheterogeneous polymer-based materials, even in the absence of long-range order. ^{1}H spin diffusion between ^{1}H dispersed in the Pglass and polyamide ^{1}H can prove mixing on a 30 nm scale.[24,25] Our recently developed ^{31}P{^{1}H} heteronuclear recoupling with dephasing by strong homonuclear interactions of protons (HARDSHIP) NMR method is particularly suited for determining the size and fraction of phosphate particles that are <15 nm in diameter.[26] In this ^{1}H−^{31}P recoupling experiment, the particle thickness is probed using the strongly distant-dependent dipolar couplings between the abundant ^{1}H spins in the polyamide and the ^{31}P nuclear magnets in the Pglass. Furthermore, if the fraction of interfacial phosphate sites is large enough, their ^{31}P spectrum can be read off at the polymer-proton frequency in a two-dimensional ^{31}P−^{1}H heteronuclear correlation (HetCor) experiment with ^{1}H−^{31}P cross polarization. All three experiments are demonstrated successfully on PA6/Pglass hybrid samples containing 10% Pglass by volume, and the fraction and size of the Pglass nanoparticles is estimated.

Experimental Section

Samples. The low-T_g Pglass used in the study has a molar composition of 50% SnF_2 + 20% SnO + 30% P_2O_5, a density of 3.75 g/cm^3, and a T_g of 125.7 °C. The glass was synthesized in our laboratory using procedures reported elsewhere.[27] The tin fluoride and tin oxide were supplied by Cerac Inc., and the ammonium phosphate was supplied by Sigma-Aldrich. The polyamide-6 used was Capron 8270 HS supplied by Allied Signal. The hybrids were prepared using a Thermo-Haake Polydrive Melt Mixer equipped with roller rotor blades. Prior to melt-mixing, the Polydrive mixer was heated to 250 °C and allowed to equilibrate for at least 20 min. The PA6 was added to the Polydrive first and allowed to mix for 5 min in order to obtain a homogeneous melt. The Pglass was then added, and the two components were allowed to mix together for 10 min. Hybrid samples containing 10% Pglass by volume were made for testing. The materials were collected in “chunks” from the Polydrive mixer and subsequently ground into fine particles using an IKA A11 basic laboratory mill for the NMR measurements.

NMR Parameters. The NMR experiments were performed using a Bruker DSX400 spectrometer at 400 MHz for ^{1}H and 162 MHz for ^{31}P. A Bruker 4 mm double-resonance magic-angle spinning (MAS) probehead was used for 13 kHz MAS ^{1}H−^{31}P NMR experiments, while 6.5 kHz MAS ^{1}H−^{31}P NMR experiments were performed with larger 7 mm sample rotors in a different Bruker double-resonance probehead. The ^{1}H and ^{31}P 90° pulse lengths were 4 μs. In direct-polarization (DP) ^{31}P experiments, recycle delays

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of up to 200 s were used. In ^{1}H and ^{1}H$-$^{31}P cross polarization (CP) experiments, including two-dimensional (2D) heteronuclear correlation (HetCor), the recycle delays were 5 s. The ^{1}H$-$^{31}P HetCor spectra were obtained with homonuclear frequency-switched Lee-Goldburg (FSLG) decoupling applied during t_1 evolution, followed by 1 ms of standard Hartmann$-$Hahn cross polarization for optimum sensitivity. The ^{1}H spin diffusion data were obtained using a dedicated ^{1}H NMR ("CRAMPS") probehead.

^{1}H Spin Diffusion. In order to detect spin diffusion from the small number of protons in the Pglass to the PA6 matrix, we have combined $T_{2,H}$ filtering with 2D exchange NMR. Before the spin diffusion time, this identifies the Pglass protons in terms of $T_{2,H}$ and their 7 ppm chemical shift. After the spin-diffusion time t_m, the sharp Pglass proton signal at 7 ppm is detected, and its intensity is quantified as a function of t_m. As ^{1}H magnetization diffuses into PA6, the magnetization in the Pglass, and thus the Pglass diagonal signal, is reduced. We record the intensity of the Pglass diagonal peak as a function of the spin diffusion time. The data were plotted after correction for $T_{1,H}$ relaxation during the spin-diffusion time.

After equilibration to equal magnetization per ^{1}H, the fraction of the total ^{1}H magnetization remaining in the Pglass is negligible, on the order of 0.01, due to the at least 10 times larger density of ^{1}H in the polyamide and 10 times larger amount of PA6. As a result, if the Pglass ^{1}H diagonal signal reaches a finite constant value, this value gives an estimate of the fraction of large Pglass particles (>30 nm).

HARDSHIP NMR. The Pglass particle thickness is probed using the strongly distant-dependent dipolar couplings between the abundant protons in the polyamide matrix and ^{31}P nuclei in the Pglass. This approach requires a pulse sequence that ensures heteronuclear dephasing only by the polymer protons but not by dispersed protons in the Pglass (which are probably due to H_2O). This is achieved by heteronuclear recoupling with dephasing by strong homonuclear interactions of protons (HARDSHIP),[26] which distinguishes between the polymer and Pglass-dispersed protons based on their different transverse ($T_{2,H}$) relaxation times. In short, the HARDSHIP pulse sequence alternates REDOR heteronuclear dipolar recoupling[28] for ~0.15 ms with periods of homonuclear dipolar $T_{2,H}$-dephasing that are flanked by canceling 90° pulses. The heteronuclear evolution of the long-$T_{2,H}$ protons in the Pglass is refocused after two recoupling periods. We have shown that for the strongly coupled, short-$T_{2,H}$ protons in the PA6 matrix, the heteronuclear dephasing rate depends simply on the heteronuclear second moment, not on the homonuclear interactions, even though no homonuclear decoupling is applied.[26] Simulations and experiments on model systems[26] show that the majority of ^{31}P spins within 0.5 nm from the interface with the polymer matrix will be dephased within 5 ms.

In these experiments, the 7 ppm resonance of the ^{1}H in Pglass was set on resonance. In order to minimize the effects of $T_{2,H}$ relaxation of the protons in Pglass, most HARDSHIP experiments were run with faster (13 kHz rather than 6.5 kHz) spinning that increases the $T_{2,H}$ relaxation time due to improved homonuclear decoupling by faster MAS. Recoupling for $2t_r = 154\ \mu$s alternated with 154 and 77 μs periods of $T_{2,H}$ relaxation (pulse sequence (d) in Figure 5 of ref 26, with $k = 1$).

Inverse $T_{2,H}$ Filtering. We will show below, using ^{1}H$-$^{31}P HetCor experiments, that cross polarization from PA6 protons to a significant fraction of ^{31}P is possible. The undesirable signal of ^{31}P cross-polarized from the ^{1}H dispersed in the Pglass can be reduced by an "inverse $T_{2,H}$ filter", which again relies on the differences in the $T_{2,H}$ relaxation of protons in the PA6 vs the Pglass. After a 0.3 ms $T_{2,H}$ filter, the polyamide-proton magnetization has been suppressed while the Pglass-proton magnetization is only slightly reduced. Subtracting out the CP signal of these long-$T_{2,H}$ protons from the total CP signal results in the "inverse-$T_{2,H}$-filtered" CP signal that mostly shows ^{31}P near the PA6 protons.

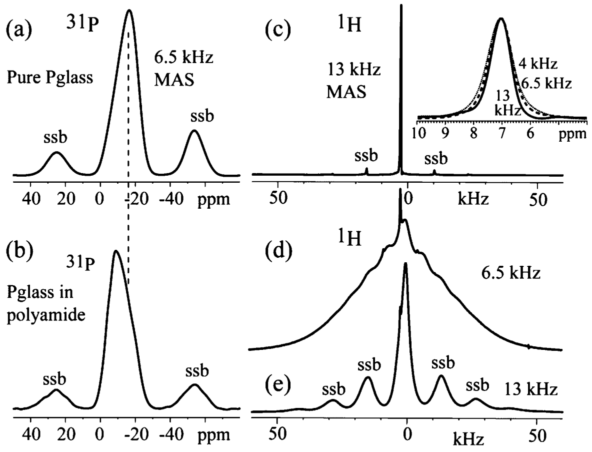

Figure 1. (a, b) ^{31}P and (c, d, e) ^{1}H NMR spectra of (a, c) pure Pglass and (b, d, e) a hybrid of 10% Pglass and 90% polyamide-6, at spinning frequencies of 6.5 or 13 kHz. Spinning sidebands are labeled "ssb". The inset in spectrum c shows the center band of the sharp 7 ppm signal of pure Pglass at spinning frequencies of 4, 6.5, and 13 kHz.

Due to the relatively weak ^{1}H$-$^{31}P couplings in the Pglass, the rf-field match condition for cross polarization is rather sensitive to small drifts in the amplifiers or probes. To avoid experimental artifacts, the match condition in HARDSHIP experiments with CP was carefully monitored.

Results and Discussion

Figure 1 shows the ^{31}P and ^{1}H NMR spectra of pure Pglass and a hybrid of 10% Pglass with PA6. A change in ^{31}P line shape is observed from pure glass to hybrid, but differently than previously reported for Pglass/LDPE hybrids.[2] The inhomogeneously broadened bands observed have been assigned to Q_1 phosphate species (dimers with one bridging oxygen) that are shifted upfield by a nonbridging fluorine.[2]

A sharp ^{1}H signal at 7 ppm is observed in the pure Pglass, Figure 1c, probably due to absorbed water. It is also seen in the hybrid, Figure 1d,e, but is small in area compared to the PA6 proton signal. The smaller line width corresponds to a longer $T_{2,H}$ relaxation time, which allows the sharp signal to be selected easily by a Hahn spin echo that serves as a $T_{2,H}$ filter.

Dispersed Pglass Fraction from ^{1}H Spin Diffusion. The distinct difference in the widths, or equivalently $1/T_{2,H}$ values, of the ^{1}H spectra of the Pglass and the PA6 matrix makes it easy to select the protons in the Pglass, whose magnetization survives for hundreds of microseconds, and observe the spin diffusion to the polyamide protons, during a time t_m, in terms of the changes of the detected spectrum. Small domains show fast equilibration.

Figure 2 shows the $t_m^{1/2}$-dependence of the Pglass ^{1}H diagonal signal in a $T_{2,H}$-filtered 2D exchange spectrum (see description above). For large Pglass domains (>30 nm), most of the $T_{2,H}$-selected Pglass ^{1}H magnetization would not reach the polyamide matrix within 100 ms. Thus, their signal after the spin-diffusion time would remain essentially unchanged.

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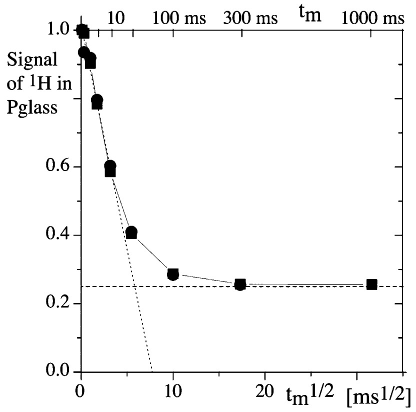

Figure 2. Spin diffusion from ^{1}H dispersed in the Pglass (10 vol %) to the PA6 matrix, obtained at 13 kHz MAS in a dedicated ^{1}H NMR probe head. The data were obtained with spin-diffusion times t_m between 0.1 ms and 1 s from two series of T$_{2,H}$-filtered two-dimensional ^{1}H NMR exchange spectra, with two different T$_{2,H}$ filters. The intensity of the diagonal signal of the Pglass protons (7 ppm, 7 ppm), corrected for T$_{1,H}$ relaxation, is plotted as a function of the square root of the spin diffusion time.

For small Pglass domains and correspondingly smaller distances between domains across the matrix, the ^{1}H magnetization of the Pglass diffuses significantly into the polyamide. If the Pglass ^{1}H diagonal signal retains a finite constant value, this value gives an estimate of the fraction of large Pglass particles ($>$30 nm). The plateau observed in Figure 2 indicates that about 75% of the Pglass is close enough to the protons of the PA6 matrix to equilibrate with them, and 25% is in larger domains. Since the proton density in the Pglass is low, spin diffusion certainly occurs with an effective diffusion coefficient of $<$0.8 nm^2/ms, the value found in rigid polymers.[29] Given the 20 ms time-scale of the spin diffusion, the data prove mixing of 75% of the Pglass with the PA6 on a $<$30 nm scale, conservatively estimated.

Dispersed Pglass Fraction from ^{31}P{^{1}H} HARDSHIP NMR. The size of phosphate nanoparticles can be probed further by ^{31}P{^{1}H} HARDSHIP NMR, which measures the dephasing of ^{31}P in the glass by polymer ^{1}H.[26] Figure 3a,b shows ^{31}P{^{1}H} HARDSHIP and ^{31}P{^{1}H} REDOR[28] dephasing curves for pure Pglass and for 10% Pglass in PA6, obtained at 13 kHz MAS. As desired, little HARDSHIP dephasing is observed in the pure Pglass (diamonds in Figure 3a), while REDOR dephasing (open inverted triangles) is fast due to the ^{1}H dispersed in the Pglass. In the hybrid material, see Figure 3b, quantitative ^{31}P{^{1}H} HARDSHIP after a long (50 or 200 s) recycle delay and 90°-pulse excitation (squares) shows fast initial dephasing by the polyamide protons, indicative of phosphates in intimate contact with the PA6 matrix. The plateau of 75% shows that the amount of Pglass within 0.5 nm from the polyamide matrix is ~25% of the total.

We can detect more pronounced HARDSHIP dephasing if we selectively enhance the signal from phosphates at the interface with the PA6 matrix. This can be achieved partially by using a short recycle delay of 5 s, which reduces the signal of the slower-relaxing interior phosphates. Indeed, more pronounced HARDSHIP dephasing is observed (open triangles in Figure 3b).

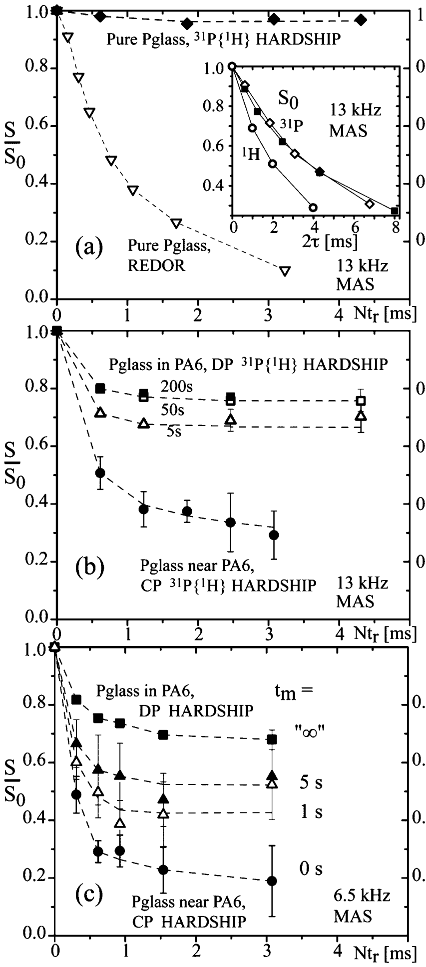

Figure 3. ^{31}P{^{1}H} HARDSHIP NMR data for estimating the size and fraction of Pglass nanoparticles in the 10% Pglass/PA6 hybrids. (a) ^{31}P-{^{1}H} HARDSHIP (diamonds) and ^{31}P{^{1}H} REDOR (open inverted triangles) data obtained for the pure glass, shown for reference. As desired, little HARDSHIP dephasing is observed in the absence of short-T$_{2,H}$ protons. The inset shows the proton-decoupled T$_2$ decay of ^{31}P S$_0$ signals in pure Pglass (open diamonds) and Pglass in the hybrid (filled squares) and the T$_{2,H}$ decay of protons in pure Pglass as a function of spin−echo time 2τ (open circles). (b) ^{31}P{^{1}H} HARDSHIP NMR data of the 10% Pglass/PA6 hybrids. Some data were obtained after 90°-pulse ^{31}P excitation, with recycle delays of 5 s (open triangles), 50 s (open squares), and 200 s (filled squares, quantitative), indicating that 23% of the phosphate is within 0.5 nm from the polyamide matrix. After selection of the phosphates near polyamide ^{1}H, by 1.8 ms CP after a 0.3 ms inverse T$_{2,H}$ filter, more pronounced HARDSHIP dephasing was observed, filled circles. (c) ^{31}P{^{1}H} HARDSHIP NMR after 0.3 ms inverse T$_{2,H}$ filtering and 1.8 ms CP, which selects ^{31}P near the interface, and ^{31}P spin diffusion from the interface during t_{sd} = 0.1 ms, 1 s, and 5 s. Spinning frequency: 6.5 kHz. The lines are guides to the eye.

The signal of the phosphates in close contact to the polyamide can be selected even more efficiently by cross polarization from the PA6 protons, whose magnetization can in turn be selected by the "inverse T$_{2,H}$ filter" described above. This magnetization is indeed strongly dephased by the PA6 protons in HARDSHIP experiments (Figure 3b, filled circles), to 40% within 2 ms. The $^1/_3$ of the magnetization that dephases more slowly probably originates from ^{1}H in the dispersed Pglass that have a shortened T$_{2,H}$, most likely due to proximity (within ~0.7 nm) to PA6 protons. A corresponding signal is observed at 7 ppm in the inverse-T$_{2,H}$-filtered ^{1}H−^{31}P HetCor spectrum presented below.

Interface-Interior Connectivity from ^{31}P Spin Diffusion. In phosphates, magnetization can be transferred from ^{31}P to

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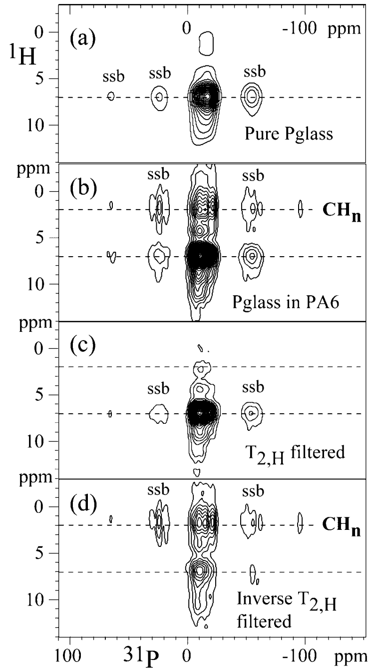

Figure 4. ^{1}H−^{31}P HetCor spectra of pure Pglass and the 10% Pglass/PA6 hybrid. ^{1}H homonuclear FSLG decoupling was applied during t_1 evolution, followed by 1 ms of Hartmann−Hahn cross polarization for optimum sensitivity. (a) Spectrum of pure Pglass. (b) Spectrum of the Pglass/PA6 composite, showing a new ^{1}H signal near 2 ppm, with multiple ^{31}P chemical shifts. (c) Same as b but after a 0.3 ms T$_{2,H}$-filter. The short T$_{2,H}$ of the 2 ppm signal confirms its assignment to the PA6 protons; hydrogen sites in the glass are so dilute that they have a much longer T$_{2,H}$. (d) Unscaled difference of spectra b and c, which retains the signals of short T$_{2,H}$ hydrogens as found in PA6. The spectra were acquired at 6.5 kHz MAS. Spinning sidebands are labeled "ssb".

^{31}P based on their magnetic couplings, over a ∼2-nm distance within 5 s. Inserting a ^{31}P spin diffusion period (t_m) into the inverse-T$_{2,H}$-filtered CP-HARDSHIP experiment, immediately after CP from ^{1}H to ^{31}P, enables such a transfer of the ^{31}P magnetization from the interfacial phosphates to the interior. The HARDSHIP dephasing is then indeed slowed down, see Figure 3c. These data were acquired in a larger rotor at a 6.5 kHz spinning frequency for increased signal and reduced effects of rf fluctuations on cross polarization.

After 5 s of ^{31}P spin diffusion (filled triangles), the asymptotic dephasing, due to sites in the interior that cannot be dephased on this time scale, is $^2/_3$ of the level without surface selection (HARDSHIP after DP under the same conditions, filled squares). This shows that the phosphates at the interface are within ∼2 nm from $^2/_3$ of the other phosphates, which is consistent with the ^{1}H spin diffusion data.

Pglass Surface Fraction Detected in ^{1}H−^{31}P HetCor NMR. The close proximity of a significant phosphate fraction to the polyamide can be confirmed in ^{1}H−^{31}P HetCor experiments, where they are manifested in ^{31}P signals correlating with polyamide ^{1}H resonance(s). Figure 4b shows this signal at 2 ppm in the ^{1}H dimension, as well as a strong 7 ppm peak of the ^{1}H in the Pglass, which is also seen in the pure Pglass, Figure 4a. The aliphatic PA6 protons are identified not only by their upfield chemical shifts (∼2 ppm), but also by their short T$_{2,H}$, which is characteristic of organic solids. A 0.3 ms T$_{2,H}$ filter added before the ^{1}H evolution time dephased the 2 ppm signal, while leaving most of the 7 ppm peak unaffected, see Figure 4c. The "inverse-T$_{2,H}$-filtered" difference of the full and the T$_{2,H}$-filtered HetCor spectrum is dominated by signals of protons with short T$_{2,H}$, i.e. of the polyamide. This spectrum, shown in Figure 4d, prominently shows the 2 ppm ^{1}H signal of the PA6 matrix. The residual 7 ppm peak is likely due to ^{1}H in the phosphate that are so close to the interface that their T$_{2,H}$ is shortened by dipolar couplings to PA6 protons.

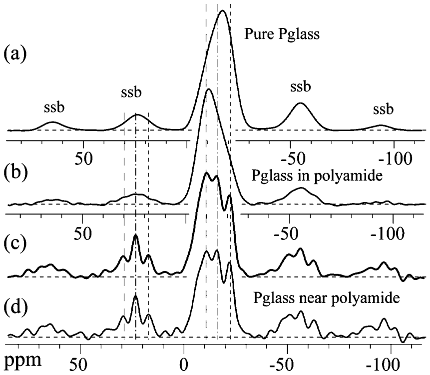

Figure 5. ^{31}P NMR cross sections from the ^{1}H−^{31}P HetCor spectra in Figure 4. (a) Pure Pglass, at the 7 ppm ^{1}H peak. (b) Pglass in PA6, at 7 ppm. (c) Pglass in PA6, at the aliphatic-H 2 ppm resonance. (d) Inverse-T$_{2,H}$-filtered spectrum of Pglass in PA6, cross section at the aliphatic-H 2 ppm resonance. Spinning sidebands, labeled by "ssb", show differences in the ^{31}P chemical-shift anisotropies of interfacial and interior sites in the Pglass.

Previously, Tischendorf et al.[2] tried to detect polymer-Pglass correlation signal in ^{1}H−^{31}P wide-line separation (WISE) NMR,[30] which is equivalent to HetCor without homonuclear ^{1}H decoupling. Without decoupling, the peak of ^{1}H in Pglass is ca. 2 ppm = 0.8 kHz, and the band of the PA6 protons ca. 40 kHz wide. Given the approximate 1:1 integral-intensity ratio of the 7 and 2 ppm bands in the ^{1}H dimension of the ^{1}H−^{31}P HetCor spectrum of Figure 4b, the polyamide proton peak height in ^{1}H−^{31}P WISE spectra would be 50 times lower than the Pglass proton peak. Therefore, this signal is effectively unobservable in a WISE experiment.

^{31}P Spectra of the Surface Pglass Fraction from ^{1}H−^{31}P HetCor NMR. In the inverse-T$_{2,H}$-filtered HetCor spectrum, the ^{31}P signal correlated with the polyamide ^{1}H peak at 2 ppm is exclusively due to the surface sites of the Pglass particles. The ^{31}P spectrum of these interfacial phosphates can thus be obtained as the cross section at the 2 ppm polyamide ^{1}H frequency. Figure 5c shows this cross section and compares it with the cross section at the Pglass ^{1}H-frequency of 7 ppm, Figure 5b, and the cross section from pure Pglass, Figure 5a. The cross section from the inverse-T$_{2,H}$-filtered HetCor spectrum, Figure 5d, shows the centerband region without interference from interior phosphates, but the sidebands are noisier.

While all the signals appear to fall within the range of Q$_1$ sites (phosphate dimers),[2] both the centerband and the sideband pattern of the interfacial component show pronounced differences compared to the other spectra. An upfield centerband with significant sidebands is seen. One of the downfield species has sharp sidebands of high

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(30) Schmidt-Rohr, K.; Clauss, J.; Spiess, H. W. *Macromolecules* **1992**, *25*, 3273.

intensity. Possibly, these are indicative of trans-amidation of polyamide nitrogen to interfacial phosphates.

Structural Model. The plateau in the ^{1}H spin diffusion data of Figure 2 shows that 75% of the Pglass is dispersed on a scale $<$30 nm. The HARDSHIP data of Figure 3b yield an (operationally defined) Pglass surface fraction of 23%. The thickness of this surface layer is $d_S \sim 0.5$ nm, since that is the "reach" of ^{31}P{^{1}H} HARDSHIP on the 5 ms time scale.[26] As indicated above, the ^{31}P spin diffusion data of Figure 3c show that at least $^2/_3$ of this surface layer is in close contact with the Pglass interior. This means that it does not consist of small clusters of phosphate dimers dispersed in the PA6 matrix, but that most of the Pglass forms particles containing many dozens of phosphate dimers.

The volume fraction of the 0.5 nm thick surface layer of the finely dispersed Pglass, $V_S/V = 23/75 = 31\%$, enables us to estimate the minimum size of the nanometer-scale particles. For a spherical particle of diameter d, the surface-layer volume fraction is

$$V_S/V = 1 - (d - 2d_S)^3/d^3 \qquad (1)$$

For a d = 10-nm diameter particle and a surface layer thickness of $d_S = 0.5$ nm, eq 1 gives $V_S/V = 0.27$, close to the 31% measured. The 10 nm diameter is also consistent with the ^{31}P spin diffusion results, since a 2 nm thick outer shell of a 10 nm diameter particle would contain 80% of its material, which is thus accessible to ^{31}P spin diffusion from the surface layer on the 5 s time scale. If the surface is rough, the particle size will be larger; however, the ^{31}P spin diffusion data, see Figure 3c, limit the particle diameter to $<$20 nm, since otherwise the protrusions of the particle surface would be too distant from the particle interior.

Conclusions and Outlook

Various advanced ^{1}H$-^{31}$P NMR experiments have shown conclusive evidence of a significant fraction, ~75%, of Pglass dispersed as ~10 nm diameter particles in the polyamide matrix of a hybrid material. We have documented ^{1}H spin diffusion out of the Pglass and fast dipolar dephasing of ^{31}P by the short-$T_{2,H}$ polyamide protons. Cross polarization from the short-$T_{2,H}$ polyamide protons to ^{31}P surface sites in Pglass was detected in HetCor and HARDSHIP experiments. Significant ^{31}P spin diffusion from the interfacial to the interior sites was observed. The bonding of the surface sites is varied and significantly changed from that of the interior. With a large organic−inorganic interfacial area established, we can now apply ^{13}C NMR to look for effects on the polyamide matrix, providing further insights into the structure and dynamics of the Pglass/polymer hybrid system. Further, we will use TEM to characterize the ~25% larger Pglass particles and confirm the NMR results.

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