# Promotion of the γ-Phase of Polyamide 6 in Its Nanocomposite with Phosphate Glass

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**ABSTRACT:** The effect of tin fluorophosphate-glass (Pglass) nanoparticles on the polyamide-6 (PA6) matrix in Pglass/PA6 hybrids has been investigated by $^{13}C$ solid-state nuclear magnetic resonance (NMR). The crystallinity determined by direct-polarization $^{13}C$ NMR combined with longitudinal relaxation-time ($T_{1C}$) filtering varied between 31 and 44%. $T_{1C}$-filtered $^{13}C$ spectra with cross polarization clearly showed resonances of both the α- and γ-crystalline phases of PA6, typically at ratios near 45:55, while the similarly processed neat polymer contained only the α-phase. This suggests that the Pglass promotes the growth of the γ-crystalline phase. © 2008 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 46: 857–860, 2008
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## INTRODUCTION

The hybrid materials formed by melt-blending of polyamide-6 (PA6) with low-$T_g$ tin-fluorophosphate glass ("Pglass") exhibit favorable processing and mechanical properties as well as chemical resistance.[1,2] These materials belong to a relatively new class of advanced materials that provide a facile route, via molecular-scale mixing of the hybrid components in the liquid state, to afford novel structures, morphologies and properties that are impossible to achieve with other available methods. These inorganic glass-polymer hybrids are important industrial materials because their properties can be tuned to satisfy a wide range of applications.[2]

An improved understanding of the molecular structure together with the information on chemical compatibility of the hybrid components should extend the versatile, low-cost, and convenient strategy to a wide variety of inorganic materials and organic polymers to yield new materials. Our previous nuclear magnetic resonance (NMR) investigation of a hybrid containing 10 wt % Pglass showed intimate contact of 75% of the Pglass with the polymer matrix on the 10-nm scale, thus proving the formation of a nanocomposite.[3] In this article, we report the effect of the Pglass on the crystallinity and crystalline structure of the PA6 in the hybrid material, probed by $^{13}C$ NMR spectroscopy. PA6 has two stable crystalline phases,[4–6] labeled α- and γ-phase, and a metastable β-phase that is thought to be an intermediate structure between the α- and γ-crystals.[6] The α-phase is thermodynamically most stable and obtained by slow cooling from the melt or annealing in superheated water.[7] The crystals of the γ-phase can be obtained by iodine treatment of the α-phase and by high-speed melt spinning.[5] The γ-phase has also been observed in PA6-clay nanocomposites,[8] where it appears to be nucleated near the silicate surfaces.[9] The effect of the crystal modification

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on the mechanical properties of the polyamide is significant, as seen by the very different tensile stress–strain curves for the two phases.[10] While the α-phase imparts improved stiffness and barrier properties, the β and γ-phases provide much better ductility and draw ratios, which are desirable for fiber and film applications.[10] In $^{13}C$ NMR, the α- and γ-phases exhibit distinct peak patterns, in particular well-resolved signals at 43.2 and 39.8 ppm, respectively.[8] Using quantitative $^{13}C$ NMR with direct polarization, we quantify the mass fractions of the crystalline phases in several hybrids and in a neat PA6 reference material subjected to the same processing steps.

## EXPERIMENTAL

### Samples

The low-$T_g$ Pglass was synthesized according to procedures reported elsewhere.[2,11] It 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 approximately 126 °C. The tin fluoride and tin oxide were supplied by Cerac, and the ammonium phosphate was purchased from Sigma-Aldrich. The PA6 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 to obtain a homogenous melt. The Pglass was then added, and the two components were allowed to mix together for 10 min. Hybrid samples containing 0, 5, and 10% by volume were made for testing in 2006, a sample with 30% Pglass in 2007. Samples containing 10% Pglass, previously studied by $^{31}P$-$^1H$ NMR,[3] and 5% Pglass had been prepared in 2004. To avoid effects of grinding on the phase structure, all samples were measured as large chunks of mm dimensions, packed into the 7-mm rotors with approximate $C_n$ symmetry for balance.

### NMR Parameters

Solid-state NMR experiments were performed using a Bruker DSX400 spectrometer at 400 MHz for $^1H$ and 100 MHz for $^{13}C$. A Bruker 7-mm double-resonance magic-angle spinning (MAS) probehead was used with a spinning frequency of 6.5 kHz. $^{13}C$ and $^1H$ 90° pulse lengths of 4 μs were employed. The $^{13}C$ nuclei of the PA6 were excited either by cross or by direct polarization (CP or DP, respectively). In the CP experiments, polarization is transferred from $^1H$ to $^{13}C$ before detection, which results in strong signals but with reduced intensity of mobile segments, e.g. in the amorphous regions. The recycle delay in the CP experiments was 2 s, the cross-polarization time 0.4 ms. In the DP experiments, the $^{13}C$ were directly polarized by a 90° pulse after recycle delays of ≥ 900 s. CP/$T_1$ measurements[12] were applied to ensure that 900 s is long enough for complete equilibration of the $^{13}C$ magnetization so that the DP $^{13}C$ NMR spectra are quantitative. $T_{1C}$ filter times of 5 s were used to suppress the signal from the amorphous fraction of the PA6. The full DP spectra were recorded using the same pulse sequence with a negligible 0.001-s $T_{1C}$ filter time. The ratio of the integrated intensities gives the crystallinity, with a factor of 1.12 ± 0.08 correcting for $T_1$ relaxation during the 5-s filter time.

Direct polarization with shorter recycle delays of 2 s was used to selectively observe the signals from the amorphous phase, which have a shorter $T_{1C}$ due to their fast segmental mobility. In the CP and the DP experiments with short recycle delay, the total suppression of sidebands (TOSS)[13] scheme was used before detection to remove spinning sidebands of the NC=O signal, which is centered at 175.3 ppm. Chemical shifts were referenced to TMS, using the COO resonance of α-glycine at 176.5 ppm as a secondary external reference. Two-pulse phase modulation (TPPM) decoupling was applied during detection.

## RESULTS AND DISCUSSION

Figure 1 shows $^{13}C$ NMR spectra of neat PA6 as-received and of neat PA6 that has been run through exactly the same processing steps as the Pglass/PA6 hybrid materials. The overall spectra in Figure 1(b,e) are very similar. The DP spectra with the short recycle delay, Figure 1(c,f), which select the amorphous component, also exhibit only minor differences. The $T_{1C}$-filtered CP/TOSS spectra, Figure 1(d,g), which selectively show signals of the crystalline PA6 due to the short $T_{1C}$ of the noncrystalline polymer, are essentially the same in both neat PA6 samples. They exhibit almost exclusively peaks corresponding to the crystalline α-phase; the

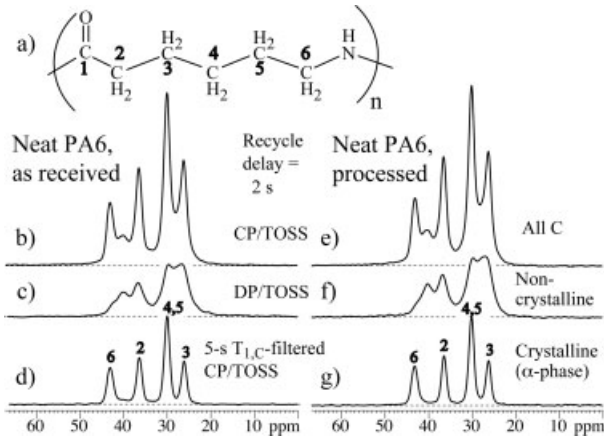


**Figure 1.** (a) Chemical structure of PA6. (b–g) CP and DP/TOSS $^{13}C$ NMR spectra of neat PA6 samples. The plots show the spectral range from 68 to 0 ppm, which contain the methylene peaks of interest. The NC=O carbon resonance at 175 ppm is not shown here. (b) and (e) are the CP/TOSS spectra of the unprocessed and processed PA6, respectively. (c) and (f) are the short-recycle-delay DP/TOSS spectra, which are selective toward the amorphous phase. (d) and (g) are the $T_{1C}$-filtered CP/TOSS spectra, which are selective toward the crystalline phase. The peaks have been assigned to the carbons using the numbering scheme shown in (a). The spectra show little effect of processing on neat PA6.

observed peak positions agree with the literature values within 0.2 ppm.

By contrast, the full and $T_{1C}$-filtered spectra of the Pglass/PA6 hybrids from 2006/2007, shown in Figure 2, exhibit strong additional peaks from a crystalline phase other than the α-phase. To show these peaks more clearly, the signals of the pure α-phase as measured in the neat PA6 [see Fig. 1(g)] were subtracted out of the crystalline-only spectrum, with the scaling factor adjusted such that the α-phase peaks at 43.2 and 26.3 ppm vanish. All three samples show the same residual peak pattern, see Figure 2(d,h,l). Comparing with previous work,[8,14] the peaks in the difference spectra are found to correspond exactly to the γ-phase.

As shown earlier,[3] there is a large-area interface between the Pglass phase and the PA6 matrix. The spectra of Figures 1 and 2 strongly suggest that the presence of the Pglass promotes growth of the γ-phase crystallites of PA6. It is worthy to note that in clay-PA6 nanocomposites, VanderHart et al. similarly showed by NMR that the γ-phase is promoted by 5 wt % clay.[8,9] Note, however, that the Pglass in our system is a liquid at the nylon crystallization temperature and therefore does not present a solid surface for nucleation, unlike the clay silicate.

The relative amounts of the γ- and α-phases can be evaluated by comparing the integrated intensities of the $T_{1C}$-filtered CP/TOSS spectra of the hybrid materials, before and after subtraction of the α-phase signal. While the 5 and 30% Pglass containing hybrids have γ-:α-phase ratios of 57:43 and 56:44 (±4), the ratio in the 10% Pglass hybrid is only 32:68. A similar, even more strongly nonmonotonic trend was observed for the 5 and 10% Pglass samples from 2004 (not shown), with γ-crystal fractions of ~55% and ~10%, respectively. At the same time, the overall crystallinity of both 10%-Pglass samples is higher than that of all other samples (39 and

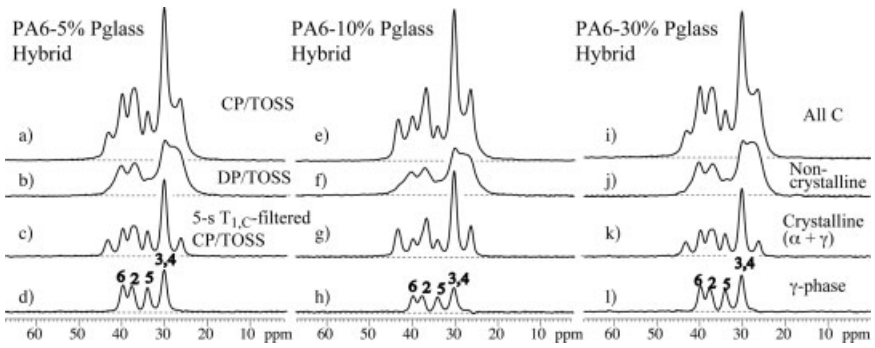


**Figure 2.** $^{13}C$ NMR spectra of chunks of PA6/Pglass hybrids from 2006/2007 with 5, 10, and 30% loading of Pglass. (a, e, i) CP/TOSS spectra at 6.5 kHz MAS. (b, f, j) DP/TOSS spectra obtained after a short, 2-s recycle delay (amorphous component). The $T_{1C}$-filtered CP/TOSS spectra (c, g, k) exhibit only peaks from the crystalline phases. The signals from the γ-phase are isolated in (d, h, l) by subtracting out the α-phase using the scaled $T_{1C}$-filtered CP/TOSS spectrum of the pure polyamide.

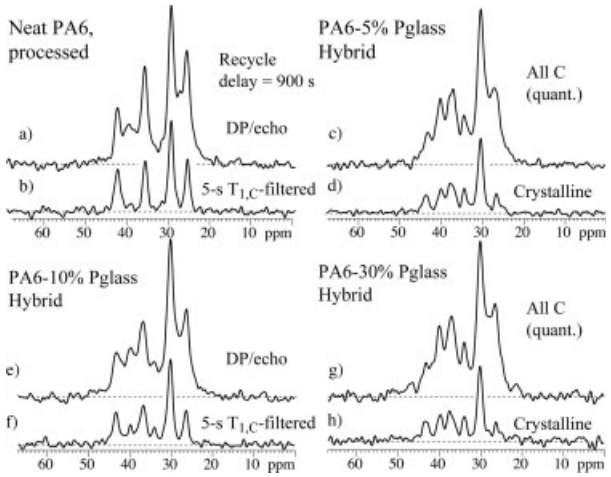


**Figure 3.** (a, c, e, g) Quantitative $^{13}C$ NMR spectra of the processed neat PA6 and the series of PA6/Pglass hybrids from 2006/2007, obtained using the DP/echo sequence with a 900-s recycle delay. (b, d, f, h) Corresponding spectra of the crystalline phases, selected by the application of a 5-s $T_{1C}$ filter before detection.

44%). In other words, not only is the $\gamma$-crystallinity reduced but also the $\alpha$-crystallinity is strongly increased. The origin of this complex behavior is not clear at this point.

Figure 3 shows the quantitative, directly polarized $^{13}C$ NMR spectra of the neat processed PA6 and the three Pglass/PA6 hybrids from 2006/2007. The ratio of the spectral areas with and without $T_{1C}$ filtering gives the weight-based crystallinity, with a correction factor of 1.12 $\pm$ 0.08 for relaxation during the 5-s filter. While the crystallinity in the neat processed PA6 is 39% $\pm$ 4%, the 5 and 30% Pglass hybrids have slightly reduced crystallinities of 34% and 31% $\pm$ 3%, respectively. The 10% Pglass has a relatively higher crystallinity of 39% $\pm$ 4%. The presence of the $\gamma$-phase and the increased amorphous content may explain the enhanced ductility observed previously in these hybrids,[1] although this may be concomitant with a plasticizing effect from the Pglass as previously reported.[2] This study points to a convenient method for tuning the morphology and properties of PA6 by adding small amounts of Pglass, and it may stimulate a better understanding of the structure/property relationships of this interesting nanostructured hybrid system.

## CONCLUSIONS

We have shown that the addition of an inorganic Phosphate glass even at relatively low concentrations has a significant effect on the crystallization behavior of PA6, producing a remarkably large fraction of $\gamma$-phase crystals. This is consistent with our previous finding of intimate mixing of the hybrid components on a 10-nm scale.

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