HIGH-TEMPERATURE STEAM-TREATMENT OF PBI AND ITS BLENDS WITH PEEK AND PEKK: A SOLID-STATE NMR STUDY

Jacqueline C. Pope, Tim Bremner, Janet Blümel, Texas A&M University, College Station, TX, 77842, Tel. (979)845-7749, E-mail: bluemel@tamu.edu*

Abstract

Blends of polyaryletherketones (PAEK), such as polyetheretherketones (PEEK) and polyetherketone-ketones (PEKK), with polybenzimidazole (PBI) are of commercial interest especially for the oil and gas industry due to their improved high-temperature stability and wear properties. Regarding the PBI component, the origins of the properties that are generally thought to be disadvantageous in thermally or chemically aggressive environments are not well understood. The same accounts for the specifics of the interactions between the PBI and PAEK components in melt or dry blend systems. In this presentation, we focus on the molecular changes of PEEK-PBI and PEKK-PBI blends and their pure components after treating them with liquid water and steam at elevated temperatures and pressures. The pure polymer components and the PAEK-PBI (50:50 wt%) blends are steam-treated at 150 °C (302 °F) and 315 °C (599 °F), also with deuterated water (D_2O). The overall goal is to understand the chemical changes on the molecular scale that might take place upon high-temperature steam-treatment and to examine the extent and reversibility of moisture uptake. Changes of the materials, as well as interactions and reactions of the water with the functional groups of the polymer components have been studied by ^{15}N and ^{13}C CP/MAS, ^{2}H MAS, and ^{1}H wideline NMR spectroscopy, in combination with using deuterated water.

Introduction

PAEK (polyaryletherketone) polymers, and PEEK (polyetherether-ketone) polymers [1] in particular are of growing importance for the oil and gas industry. They display many advantageous properties for their use under extreme service environments, such as high pressures and temperatures [1]. They have high melting points and glass transition temperatures, and they are mechanically and chemically rather robust. In order to further improve the performance of PAEK polymers and prolong their lifetimes, blends with PBI (polybenzimidazole) have been developed. However, in contrast to the pure PAEK components, the PBI addition leads to a more complex interaction of the blend with aqueous systems, for example water and steam [2], and salt solutions. A better understanding of the interactions of water with the functional groups of the PBI component at the molecular level is necessary. Using molecular model compounds mimicking PBI, the literature discusses mainly two ways in which water could reside in PBI [3]: it can either be present in larger aqueous domains nestled between the PBI polymer strands, or it can be bound to the N-H group in the PBI backbone by hydrogen bridges. Hereby, one H_2O molecule is bound per N-H group.

In the following, solid-state NMR spectroscopy is employed to probe the interactions of H_2O and D_2O with PBI and its blends. Solid-state NMR is a powerful analytical tool that allows a multitude of diverse measurements of crystalline and amorphous materials. Polymers represent the most prominent and the classic materials for solid-state NMR investigations [4]. The basic principle of a solid-state NMR measurement consists of packing a finely ground powder densely into a ZrO_2 rotor as the sample vessel. The rotor is placed into the permanent magnetic field B_0 of the NMR spectrometer and tilted with respect to the direction of B_0 with the so-called Magic Angle of 54.7° (Figure 1).

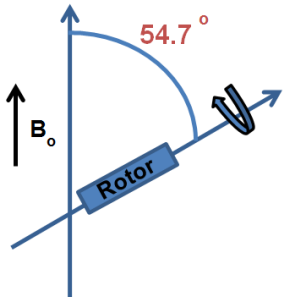

Figure 1. Principle of Solid-State Magic Angle Spinning (MAS) NMR.

Then the rotor is spun around its axis with rotational speeds ν_{rot} of up to 15 kHz, which is sufficiently fast for the polymer applications described here. This Magic Angle Spinning (**MAS**) reduces anisotropic interactions that are not averaged out like in solution, but prevail in the solid state, and would, without the rotation, lead to very broad signals. Cross polarization (**CP**) of magnetization from the abundant protons in the sample to the measured nuclei improves the obtained signal to noise (S/N) ratio [5]. An important nucleus for measurements of polymers is ^{13}C, but it will be demonstrated in the following that ^{15}N, ^{2}H, and ^{1}H NMR can give valuable complementary insights into the polymer systems on the molecular level as well.

Results and Discussion

A. Characterization of PEEK, PEKK, and their PBI Blends with ^{13}C and ^{15}N CP/MAS

First, the pure PBI and PEEK polymers have been measured with ^{13}C CP/MAS NMR spectroscopy (Figure 2a and 2b). Most of the signals are resolved and only two signal groups overlap. All resonances can be assigned unequivocally to the corresponding carbon positions in the structure, in accordance with the literature [2,6,7].

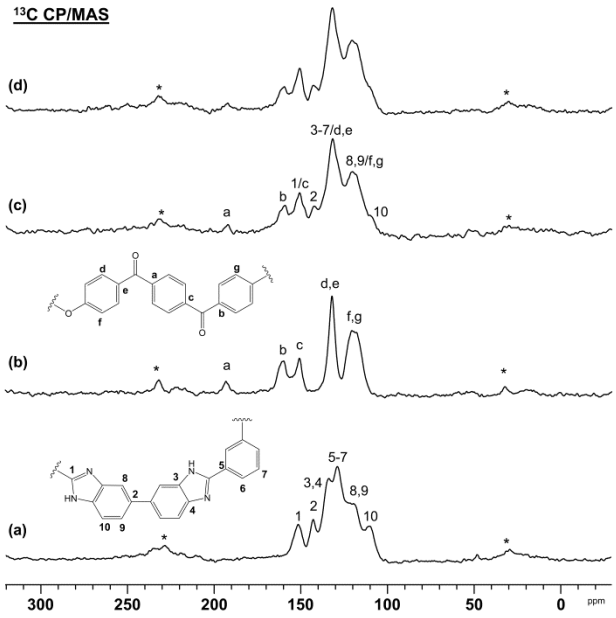

Figure 2. ^{13}C CP/MAS NMR spectra of **(a)** PBI, **(b)** PEEK, **(c)** melt-blended PEEK-PBI, and **(d)** physical mixture of powdered PEEK and PBI (50:50 wt%). Rotational speed ν_{rot} = 10 kHz. The asterisks denote rotational sidebands.

The PEEK-PBI melt-blended sample (Figure 2c) results in a ^{13}C CP/MAS spectrum that shows both components in the anticipated 50:50 wt% ratio. This is best visible in the approximate 1:1 intensity ratio of the signals b of the PEEK and 2 of the PBI component, which do not overlap.

In order to test whether melt-blending would lead to interactions of the PEEK and PBI components on a molecular level, which could potentially be seen in the ^{13}C CP/MAS spectra, a physical mixture of PEEK with PBI powder was measured (Figure 2d). However, the spectrum of this mixture is practically identical with the spectrum of the melt-blended sample (Figure 2c), and in particular the signal of the carbonyl carbon at 194 ppm retains the same chemical shift. In the case of strong N-H···O=C hydrogen bridge formation of the PBI and PEEK strands on a molecular level a low-field shift of the carbonyl carbon resonance would have been expected.

Figure 3 shows the pure components PBI and PEKK (Figure 3a and 3b), as well as the melt-blended polymer (Figure 3c) and physical mixture of PBI and PEKK powder in a 50:50 wt% ratio (Figure 3d). Again, the signal assignments for PEKK are in agreement with the literature [8] and the amounts of the components are confirmed by the approximate 1:1 intensity ratio of the signals b of the PEKK and 1 of the PBI component. Furthermore, no obvious changes can be detected in the spectra of the melt-blended versus physically mixed samples (Figures 3c, 3d). In particular, the carbonyl carbon resonance at ca. 180 ppm retains its chemical shift after the melt-blending process.

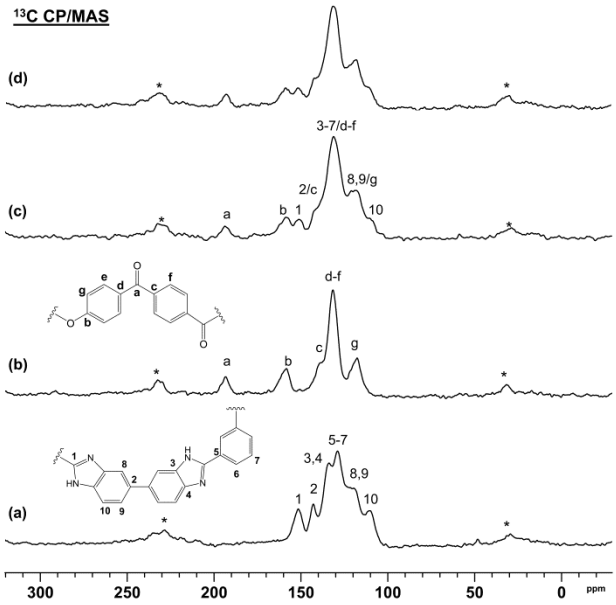

Figure 3. ^{13}C CP/MAS NMR spectra of **(a)** PBI, **(b)** PEKK, **(c)** melt-blended PEKK-PBI, and **(d)** physical mixture of powdered PEKK and PBI (50:50 wt%). Rotational speed ν_{rot} = 10 kHz. The asterisks denote rotational sidebands.

In order to probe whether hydrogen bonding interactions between PBI and PEKK strands are visible in the chemical shift of the nitrogen nucleus, ^{15}N CP/MAS spectra [7] of representative samples were recorded (Figure 4). Due to the low natural abundance and long relaxation time of ^{15}N in the solid state [9] the signal to noise ratio of the spectra obtained is comparatively low. The fact that in the blends only 50% of the sample contains nitrogen nuclei from the PBI adds to this disadvantage. Together with the large linewidths of the signals and the obvious presence of more than one ^{15}N resonance in each spectrum, this renders an unequivocal interpretation of any chemical shift trend difficult.

However, a cautious preliminary evaluation of the spectra can be made.

As it will be discussed in more detail below, the most striking change is visible in the chemical shift of the thoroughly dried PBI (113.2 ppm, Figure 4b) and PBI steam-treated with H_2O at 150 °C (not shown, 120.6 ppm). When deuterated water, D_2O, is used for the steam-treatment, the ^{15}N NMR signal appears at 118.0 ppm (Figure 4a), which might be due to the secondary isotope effect ^{2}H exerts on ^{15}N. Furthermore, there are chemical shift changes between the thoroughly dried PBI (Figure 4b) with 113.2 ppm, the melt-blended PEEK-PBI material (Figure 4c, 110.4 ppm), and the melt-blended PEKK-PBI (Figure 4d) with 116.3 ppm. One might cautiously interpret this as reflecting an increased potential for N-H···O=C hydrogen-bonding between the PEKK and PBI components, as compared to PEEK-PBI.

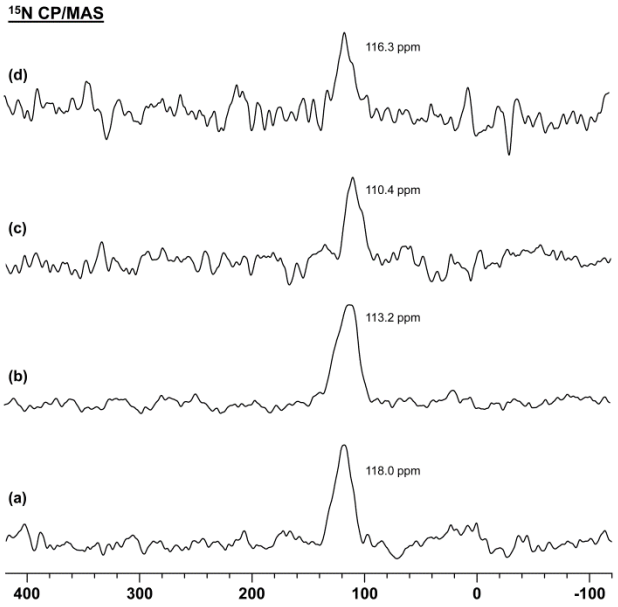

Figure 4. ^{15}N CP/MAS NMR spectra of **(a)** PBI steam-treated with D_2O at 150 °C (6 kHz), **(b)** dried PBI (6 kHz), **(c)** melt-blended PEEK-PBI (10 kHz), and **(d)** melt-blended PEKK-PBI (10 kHz).

B. Macroscopic Water Removal and Uptake for PEEK-PBI and PEKK-PBI

As described in previous work [2], PBI is a material prone to take up water readily from the atmosphere. For PBI blends with PEEK and PEKK, it is mainly the PBI component which is responsible for the water uptake. In order to quantify this effect, we sought to record the weight loss over time, when PEEK-PBI and PEKK-PBI (50:50 wt%), as received, were dried *in vacuo* at elevated temperatures, in analogy to reference [10]. The results are displayed in Figure 5. In order to test reproducibility, three dogbone-shaped samples have been submitted to the drying procedure in each case. As the curves show, there is only a minimal difference between the drying progress of the three samples, which might be attributed to a slightly different size and surface area of the dogbone pieces. The PEEK-PBI starting material contained more moisture than the PEKK-PBI blend, as after 550 hours in the first case about 14 mg of H_2O per 1 g of material are lost and in the case of PEKK-PBI only about 9 mg.

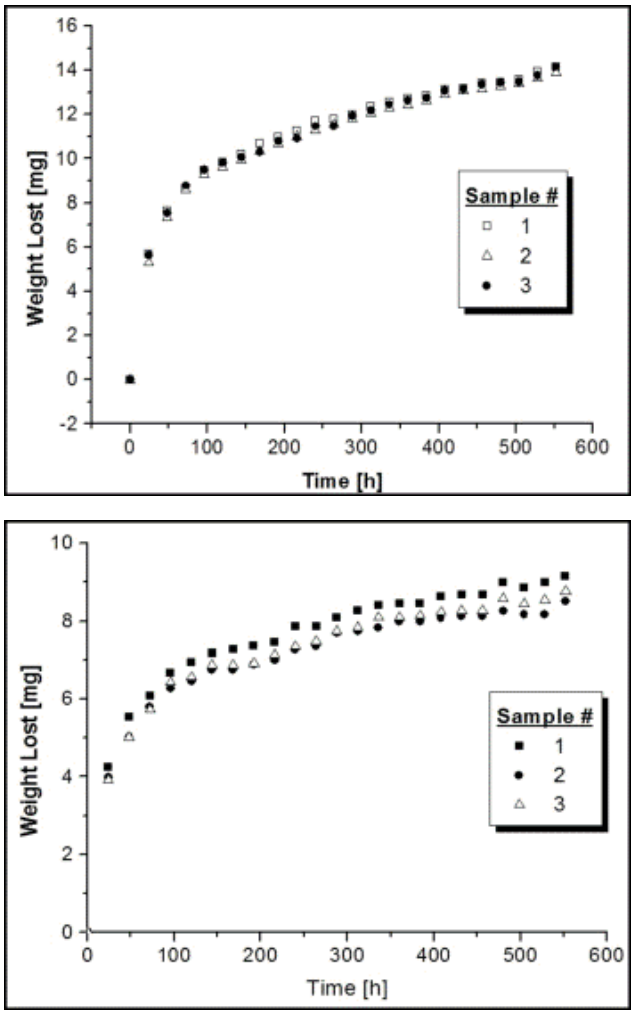

Figure 5. Weight loss of 1 g of PEEK-PBI (top) and 1 g of PEKK-PBI (bottom) when treated *in vacuo* at 110 °C. Three dogbone-shaped samples were investigated in each case.

It has been demonstrated earlier by ^{13}C T_1 relaxation time measurements that the uptake of water in PBI blends is reversible [2]. Therefore, we sought to quantify this effect and exposed the dried samples to H_2O at ambient and elevated temperatures. As Figure 6 shows, both PEEK-PBI and PEKK-PBI samples take up moisture steadily, but at room temperature only about 10 mg of H_2O have been absorbed per g of material within 220 hours. However, at 100 °C both blends take up moisture

vigorously and in excess of what the freshly received samples contained. Again, PEEK-PBI has a stronger affinity to H_2O than PEKK-PBI, as it takes up 50 mg per 1 g of material within 220 hours, versus only about 40 mg in the latter case.

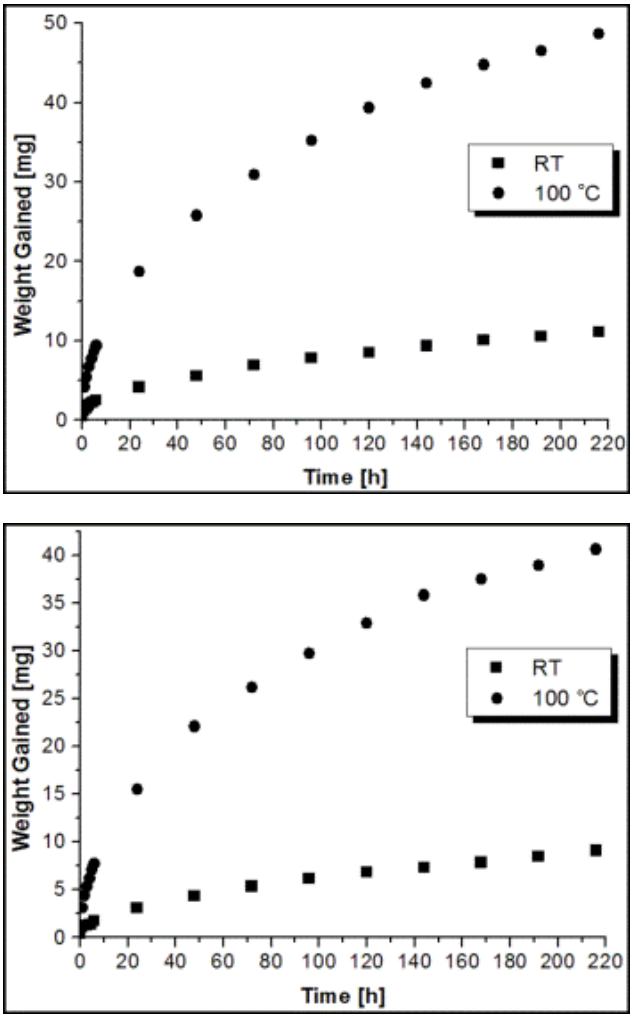

Figure 6. Weight gain of 1 g of PEEK-PBI (top) and 1 g of PEKK-PBI (bottom) when stirred in water at RT and at 100 °C.

C. ^{2}H and ^{1}H NMR Spectroscopy for Probing Different H_2O Sites in PBI and PEKK-PBI

It has been demonstrated in previous work [2,3] that ^{1}H solid-state NMR spectroscopy, when performed without sample spinning, in the "wideline mode", can be useful for distinguishing protons of the immobile polymer backbone from mobile H_2O in liquid domains. The latter leads to a relatively narrow signal sitting on the broad hump of the backbone signal in the ^{1}H wideline NMR spectra [2]. Unfortunately, this method does not allow one to probe hydrogen bridging between the water and the functional groups, for example, the N-H groups of the imidazole units. Therefore, molecular model compounds have been applied earlier [3] to probe hydrogen bridging, and it has been found that on average the N-H group of one imidazole unit forms a hydrogen bond with one water molecule.

In order to eliminate any signals from the backbone protons and to distinguish between aqueous domains and hydrogen-bonded water, we treated PBI and the PEKK-PBI blend with D_2O under various conditions, and then recorded the ^{2}H MAS spectra of the resulting materials. As an additional bonus one can obtain information about the mobilities of the ^{2}H-containing species, because ^{2}H is a quadrupolar spin-1 nucleus and the Pake Pattern [4] of its signals displays a splitting of the two maxima that allows the calculation of the quadrupolar coupling constant Q_{cc}. The latter can be correlated with the mobility of the species or functional group containing the measured ^{2}H nucleus [4,11].

Figure 7 shows the ^{2}H MAS spectra obtained starting from well-dried PBI. After stirring it in D_2O, the ^{2}H MAS signals of two species can clearly be distinguished in the MAS spectrum. One signal has a chemical shift of ca. 5 ppm, a large residual linewidth in the kHz range, and is not split into a Pake Pattern. This signal corresponds to a very mobile species according to the literature [11], and is assignable to domains of liquid D_2O nestled between the polymer chains of the PBI.

The second signal in Figure 7a is less intensive, but the Pake Pattern with its characteristic two maxima is clearly discernible. Due to the sample rotation with 6 kHz the Pake Pattern is split into a manifold of rotational sidebands. A Q_{cc} value of about 152 kHz can be estimated based on the distance of the Pake Pattern maxima. This signal corresponds to less mobile D_2O that is attached via hydrogen bonding to the N-H groups of the PBI backbone. Figure 7b displays the ^{2}H MAS spectrum of this sample after drying it thoroughly *in vacuo*. There is no longer any ^{2}H signal even after prolonged measurement times. Therefore, one can assume that in case PBI is treated with D_2O at ambient temperature, the merely adsorbed D_2O as well as D_2O residing in liquid domains can be removed again quantitatively, and there is no chemical exchange of ^{1}H versus ^{2}H.

After PBI is steam-treated with D_2O at 150 °C for 48 h, again two signals are visible in the ^{2}H MAS spectrum, as shown in Figure 7c. The only differences as compared with the spectrum in Figure 7a are that the Pake Pattern shows higher intensity in the range from -250 to +250 ppm, and that Q_{cc} assumes a larger value of about 160 kHz. When the sample is dried *in vacuo*, a Pake Pattern with a large Q_{cc} of ca. 176 kHz remains, while the broad resonance in the center is gone (Figure 7d). The latter finding corroborates our assumption that the broad center

peak belongs to domains of liquid D_2O, which is removed during the drying procedure. The persistent Pake Pattern can be assigned to N-D groups in the polymer backbone that come into existence by deuterium exchange of the N-H groups with hydrogen-bonded D_2O.

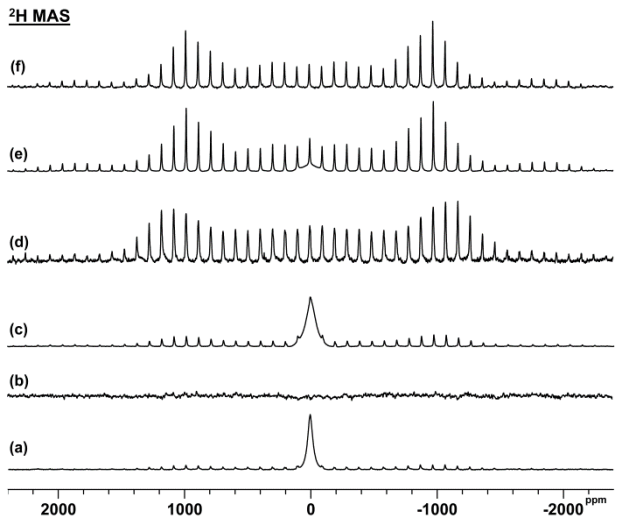

Figure 7. ^2H MAS spectra of predried PBI **(a)** stirred as a powder in D_2O at RT for 48 h and **(b)** after redrying at 100 °C *in vacuo* for 48 h. ^2H MAS spectra of predried PBI **(c)** exposed to D_2O at 150 °C for 48 h, and **(d)** after redrying at 100 °C for 48 h. ^2H MAS spectra of predried PBI **(c)** exposed to D_2O at 315 °C for 72 h, and **(d)** after redrying at 100 °C for 48 h. The Pake Patterns with approximate quadrupolar coupling constants Q_{CC} of 152 kHz **(a)**, 160 kHz **(c, e, f)** and 176 kHz **(d)** are split into rotational sidebands (spinning frequency 6 kHz for all samples).

After PBI is steam-treated with D_2O at 315 °C for 72 h, again two signals are visible in the ^2H MAS spectrum, as shown in Figure 7e. The only differences as compared with the spectra a and c in Figure 7 are that the Pake Pattern shows higher intensity in the range from -250 to +250 ppm, and that Q_{cc} assumes a value of 160 kHz. When the sample is dried *in vacuo*, the Pake Pattern with a Q_{cc} of about 160 kHz remains, while the broad resonance in the center is gone (Figure 7f).

Since deuterium has about the same chemical shift for D_2O, either in liquid domains or hydrogen-bonded, and for N-D, when taking the large residual linewidth and the huge chemical shift range of ^2H in the solid state into account, even the rotational sidebands of the MAS signals of these species overlap. This is why the rotational sidebands of the Pake Patterns which stem from the different species are not split into several sets of lines but give only one set. Another consideration is that the hydrogen-bonded D_2O molecules undergo fast exchange with the D_2O molecules in contiguous liquid domains. This means that the Q_{cc} values are variable in the presence of liquid domains. In the absence of liquid D_2O (Figure 7d and 7f) there is no longer any exchange, and only the signal for N-D groups with maximal Q_{cc} is present.

In the case of PEKK-PBI (50:50 wt%) steam-treatment at 150 °C is needed to bring substantial amounts of D_2O into the polymer (Figure 8a). Even at this elevated temperature most of the D_2O is included in the blend in the form of liquid domains, as the broad center signal implies. However, steam-treatment at 150 °C leads to the formation of less mobile ^2H-containing species (Figure 8b). After steam-treatment at 315 °C, the polymer contains more of the less mobile ^2H-containing species as indicated by the increase in intensity of the Pake Pattern. The same phenomena are observed after the treatment of PEEK-PBI (50:50 wt%) under identical conditions.

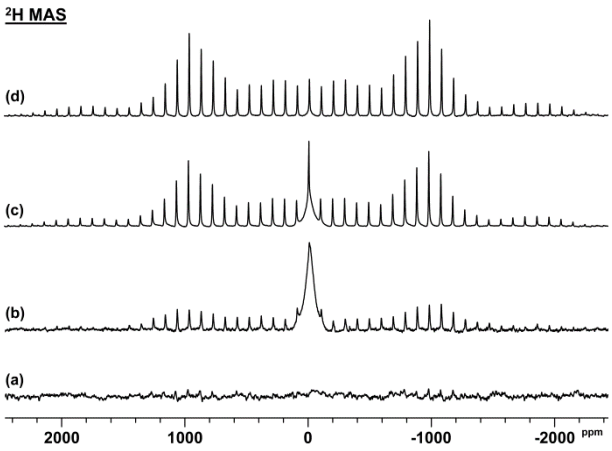

Figure 8. ^2H NMR spectra of PEKK-PBI **(a)** after treatment with D_2O at RT, **(b)** after treatment with D_2O at 150 °C, **(b)** immediately after being treated at 315 °C with D_2O, and **(d)** 1 month after this treatment. The Pake Patterns with approximate quadrupolar coupling constants Q_{cc} of 160 kHz **(b, c, d)** are split into rotational sidebands (spinning frequency 6 kHz).

Interestingly, when this material is exposed to the H_2O-containing ambient atmosphere for 1 month, the D_2O residing in liquid domains is nearly quantitatively exchanged by H_2O, a process that ultimately removes the broad center ^2H signal in the MAS spectrum (Figure 8d). In contrast to this, the Pake Pattern with a Q_{cc} of 160 kHz is fully retained, which means that the N-D groups do not undergo any D/H exchange with H_2O from the atmosphere.

The ^1H wideline NMR spectra of the PEKK-PBI blends (60:40 wt%) (Figures 9 and 10) provide complementary information and corroborate the conclusions drawn above. The PEKK-PBI sample as received contains only traces of H_2O, which is in

accordance with earlier results [2]. Therefore, only the broad signal for the backbone protons is visible in the spectrum of Figure 9a. After steam-treatment at 150 °C a narrow peak appears on top of the hump, indicating the presence of mobile H_2O (Figure 9b). When this sample is steam-treated with D_2O at 150 °C, the H_2O from the liquid domains is quantitatively exchanged by D_2O, and therefore the narrower ^1H signal is gone from the ^1H NMR spectrum in Figure 9c.

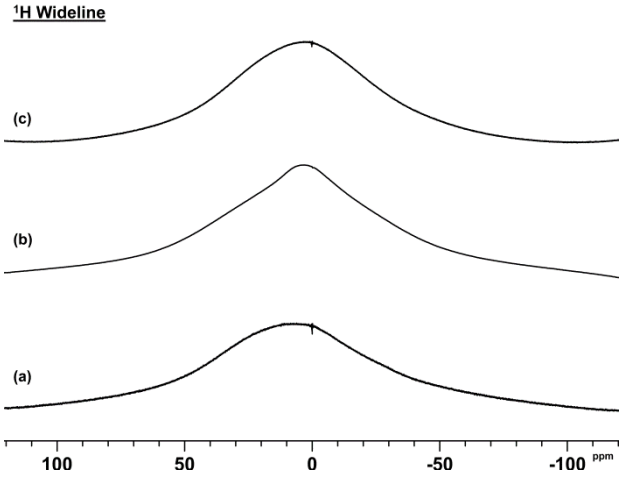

Figure 9. ^1H Wideline NMR spectra of the PEKK-PBI blend **(a)** as received, **(b)** after steam-treatment at 150 °C in H_2O for 48 h, and **(c)** steam-treated at 150 °C in D_2O for 48 h.

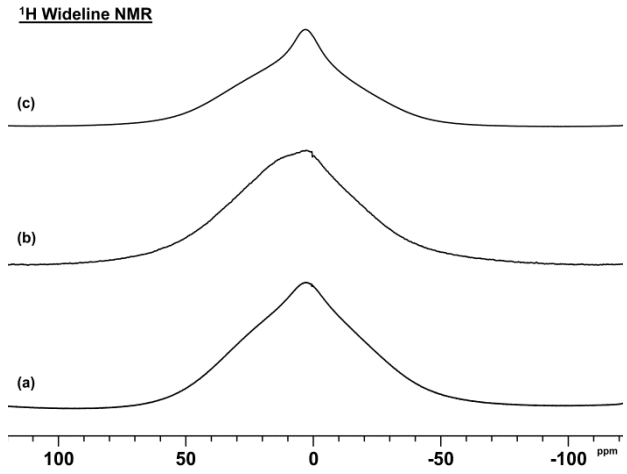

Figure 10: ^1H Wideline NMR spectra of the PEKK-PBI blend after **(a)** steam-treatment at 315 °C in H_2O for 72 h, **(b)** steam-treatment of this sample at 315 °C in D_2O for 72 h, and **(c)** after exposure to the atmosphere for 1 month.

The ^1H wideline NMR obtained after steam-treatment of PEKK-PBI (60:40 wt%) with H_2O at 315 °C shows again a broad hump and a narrower signal on top of it (Figure 10a), representing the backbone protons and the mobile H_2O in liquid domains. Steam-treating this sample with D_2O at 315 °C removes nearly all of the narrow ^1H signal, since now it is mainly D_2O residing in the liquid domains (Figure 10b). Finally, exposing the sample to the ambient atmosphere reinstates the narrow signal on top of the ^1H backbone hump, because the D_2O in the liquid domains has gradually been exchanged by atmospheric H_2O.

D. Experimental

The solid-state NMR spectra were measured on a *Bruker* AVANCE 400 spectrometer operating at 100.6 MHz for ^{13}C, 40.5 MHz for ^{15}N, 155.5 MHz for ^2H, 400.0 MHz for ^1H, and 155.5 MHz for ^7Li NMR. For the processing of the spectra line-broadening factors of 10 Hz (^1H, ^7Li), 150 Hz (^2H, ^{13}C), and 200 Hz (^2H) have been applied. All experiments were carried out using densely packed powders of the polymers in 4 mm ZrO_2 rotors. In case no signal was observed in a spectrum, block averaging measurements were performed to prove that the absence of any resonance was not merely due to a spectrometer malfunction.

The ^{13}C CP/MAS (Cross Polarization with Magic Angle Spinning) experiments were carried out at MAS rates of 10 kHz. The ^1H $\pi/2$ pulse was 2.5 µs and TPPM decoupling was used during the acquisition. The Hartmann-Hahn matching condition was optimized using the polymer Victrex 450P at a rotational speed of 10 kHz. Adamantane served as the external ^{13}C chemical shift standard (δ = 37.95, 28.76 ppm). All spectra were measured with a contact time of 1.5 ms and a relaxation delay of 5.0 s, and typically 1024 FIDs were accumulated.

The ^{15}N CP/MAS experiments were carried out at MAS rates of 6 and 10 kHz. The Hartmann-Hahn matching condition was optimized using glycine at a rotational speed of 6 kHz. Glycine also served as the external ^{15}N chemical shift standard (δ = 7.70 ppm). All spectra were measured with a contact time of 2 ms and a relaxation delay of 5 s, and typically 32800 FIDs were accumulated.

The ^2H solid-echo experiments were carried out at MAS rates of 6 kHz. The Hartmann-Hahn matching condition was optimized using deuterated PMMA (polymethyl methacrylate) at a rotational speed of 6 kHz. D_2O served as the ^2H chemical shift standard (δ = 4.79 ppm). All spectra were measured with a relaxation delay of 2 s and a quadrupolar echo τ delay of 6 µs. Typically 32800 FIDs were accumulated.

The ^1H wideline NMR spectra were recorded in the MAS probehead without sample spinning. H_2O was used as the external chemical shift standard (δ = 4.79 ppm). No background ^1H NMR signal of the probehead, loaded with an empty rotor, was obtained when a spectrum was

recorded with the measurement parameters used for the polymer samples. A π/2 pulse of 2.7 μs, a deadtime of 5.6 μs, and a pulse delay of 3 s were used and typically 32 FIDs were accumulated.

PBI and the PEKK-PBI blend were dried at 100 °C for 72 h under vacuum (0.01 torr) to obtain thoroughly dried samples. The pure components and blends were then either stirred in H_2O or D_2O at RT for 48 h, or steam-treated in Parr pressure reactors (Model 4913) at 150 °C for 48 h, and at 315 °C for 72 h. The maximal pressures in the closed vessels amounted to 5 bar (72 psi) and 110 bar (1600 psi), respectively. The redrying procedure consisted of removing the D_2O at 100 °C under vacuum for 48 h.

Conclusions

In this contribution we have successfully demonstrated that PEEK and PEKK blends with PBI (50 : 50 wt%) can be characterized by ^{13}C CP/MAS and all resonances can be assigned due to the favorable signal resolution. While physical mixtures of the components cannot be distinguished from their melt-blended versions based on their ^{13}C CP/MAS spectra, more pronounced, albeit not conclusive, differences are visible in the ^{15}N CP/MAS spectra. Interestingly, the moisture uptake of PEEK-PBI and PEKK-PBI samples is much faster than the reverse process, especially at elevated temperatures. PEEK-PBI incorporates overall more water than PEKK-PBI. With the use of ^{2}H MAS and ^{1}H wideline NMR spectroscopy for samples steam-treated with D_2O and H_2O, three different ^{2}H sites can be distinguished in the PEKK-PBI blend. Mobile D_2O can reside in liquid domains in the polymer network. Less mobile D_2O is attached to N-H (or N-D) groups via hydrogen bonds, and they are exchanging with mobile D_2O molecules in contiguous liquid D_2O domains. Finally, immobile ^{2}H nuclei, covalently bound in N-D groups are found after steam-treatment at higher temperatures.

Acknowledgements

This material is based upon work supported by The Welch Foundation (A-1706), the National Science Foundation (CHE-0911207, CHE-1358437, and CHE-0840464), the APPEAL Consortium at Texas A&M University, and Hoerbiger Corporation of America, Inc.

References

1. Kemmish, D., *Update on the Technology and Applications of Polyaryletherketones*, iSmithers, Shropshire UK: 2010.

2. Guenther, J., Wong, M., Sue, H.-J., Bremner, T., Blümel, J., *J. Appl. Polym. Sci.* **2013**, *128*, 4395-4404.

3. Brooks, N. W., Duckett, R. A., Rose, J., Clements, J., Ward, I. M., *Polymer* **1993**, *34*, 4038-4042.

4. Schmidt-Rohr, K., Spiess, H.-W., *Multidimensional Solid-State NMR and Polymers*, AP Inc., CA: 1999.

5. Reinhard, S., Blümel, J., *Magn. Reson. Chem.* **2003**, *41*, 406-416.

6. Grobelny, J., Rice, D. M., Karasz, F. E., MacKnight, W. J., *Macromolecules* **1990**, *23*, 2139-2144.

7. Clark, J. N., Jagannatan, N. R., Herring, F. G., *Polymer* **1988**, *29*, 341-345.

8. Zolotukhin, M. G., Rueda, D. R., Bruix, M., Cagiao, M. E., Balta Calleja, F. J., *Polymer* **1997**, *38*, 3441-3453.

9. Herrmann, W. A., Kratzer, R., Blümel, J., Apperley, D. C., Friedrich, H. B., Fischer, R. W., Mink, J., O. Berkesi, O., *J. Mol. Catal. A* **1997**, *120*, 197-205.

10. Chaffin, K. A., Buckalew, A. J., Schley, J. L., Chen, X., Jolly, M., Alkatout, J. A., Miller; J. P., Untereker, D. F., Hillmyer, M. A., Bates, F. S., *Macromolecules* **2012**, *45*, 9110−9120.

11. Xiong, J., Lock, H., Chuang, I.-S., Keeler, C., Maciel, G. E., *Environ. Sci. Technol.* **1999**, *33*, 224-2233.