SAND2015-XXXXR
LDRD PROJECT NUMBER: 188719
LDRD PROJECT TITLE: Resolving and Measuring Diffusion in Complex Interfaces: Exploring New Capabilities
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ABSTRACT:

This exploratory LDRD targeted the use of a new high resolution spectroscopic diffusion capabilities developed at Sandia to resolve transport processes at interfaces in heterogeneous polymer materials. In particular, the combination of high resolution magic angle spinning (HRMAS) nuclear magnetic resonance (NMR) spectroscopy with pulsed field gradient (PFG) diffusion experiments were used to directly explore interface diffusion within heterogeneous polymer composites, including measuring diffusion for individual chemical species in multi-component mixtures. Several different types of heterogeneous polymer systems were studied using these HRMAS NMR diffusion capabilities to probe the resolution limitations, determine the spatial length scales involved, and explore the general applicability to specific heterogeneous systems. The investigations pursued included a) the direct measurement of the diffusion for poly(dimethyl siloxane) polymer (PDMS) on nano-porous materials, b) measurement of penetrant diffusion in additive manufactures (3D printed) processed PDMS composites, and c) the measurement of diffusion in swollen polymers/penetrant mixtures within nano-confined aluminum oxide membranes. The NMR diffusion results obtained were encouraging and allowed for an improved understanding of diffusion and transport processes at the molecular level, while at the same time demonstrating that the spatial heterogeneity that can be resolved using HRMAS NMR PFG diffusion experiment must be larger than ~µm length scales, expect for polymer transport within nano-porous carbons where additional chemical resolution improves the resolvable heterogeneous length scale to hundreds of nm.

INTRODUCTION:

Transport of different chemical species through polymer materials is critical for a wide range of applications including separation membranes, conductive layers in battery and fuel cells, polymer coatings and polymer composites. Understanding the transport process at material interfaces is crucial for the accurate modeling and prediction of polymer curing, adhesion, aging and composite performance. The ability to directly measure polymer interface diffusion separately from diffusion within the "bulk" polymer is difficult and for multi-component chemical mixtures dissolved into polymers has proven to be very difficult. The interplay of transport through polymer networks versus interfaces is encountered in many applications and ultimately controls the material performance for systems ranging from separation membranes, conductive layers in battery and fuel cell, along with understanding polymer aging and composite performance. From a scientific point of view the challenge is to develop an understanding of the physics/chemistry at the molecular level. Current permeability measurements provide only an "average" diffusion rate over of relative volume fraction and individual diffusion rates for the bulk and interface environments. Changes in diffusion due to variation of polymer phase and interface free volumes are not well understood or characterized.

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In addition, current modeling parametrizes the role of interfaces, and cannot distinguish between differences in tortuosity, relative interface volume fraction or the impact of changing physics/chemistry on the overall transport process. For example, composites materials involve multiple different diffusion environments due to the presence of interfaces, but there has not been a direct resolution of diffusion at interface versus constrained polymer layers, or the role of confinement of diffusion in multi-component polymer mixtures.

As part of this LDRD, we investigated small-molecule diffusion in polymer composites. The molecular transport (diffusion) of penetrants (chemicals, plasticizers, impurities etc.) in polymer networks is a key process in determining the overall material performance, and is a parameter that should be evaluated. Even in this "simple" case, and following decades of research, there is still no model that correctly identifies the transport of penetrants over large ranges of polymer concentrations. It is this concentration dependent (degree of swelling) diffusion that can be used reflected in the presence of polymer heterogeneities. One of theories to describe diffusion in polymer systems as a function of local component concentration was originally forwarded by Vrentus-Duda, and then recast in a simpler form by Fujita

$$\frac{D}{D_0} = \exp\left\{ \frac{-B\left(f_s - f_p\right)}{(Q-1)f_s^2 + f_s f_p} \right\} \tag{1.1}$$

where D is the diffusion coefficient of the penetrant within the polymer, relative to the diffusion of the pure solvent (penetrant) D_0, with the molecular free volumes of the polymer and solvent represented by f_p and f_s, respectively, with the displacement volume of the penetrant incorporated into the parameter B_d. The concentration dependence enter the relationship through the volume swelling fraction Q via

$$Q = \frac{1}{\varphi_p} = \frac{V}{V_0} = \frac{\left(V_s + V_p\right)}{V_p} \tag{1.2}$$

with V_s and V_p being the volume of the swelling solvent and polymer. While this approach has been successful in describing swelling effects, the introduction of molecular level descriptions including the impact of polymer entanglement or cross-link mesh size is introduced as a scaling factor to B_d, for which a functional form has not been determined. A question that we attempted to address in the current LDRD was the impact (and how to describe it) of nanoporous confinement of a hydrodynamic description (Eqn 1.1) given that the volume swelling of the inter-pore polymer remains essentially the same.

An alternative way to describe the penetrant diffusion is from a hydrodynamic theory where the reduced diffusion is described by

$$\frac{D}{D_0} = \exp\left\{ -\alpha Q^{-\nu} \right\} \tag{1.3}$$

where α is related to the size of the penetrant, and the stretch parameter v is some function of the polymer system. While this stretch parameterization describes many diffusional processes well, it is really an empirical formulation with no direct relationship to a molecular level description. An alternative model was forwarded by Petit, in which the local friction coefficient ζ is additive with respect to the contribution from polymer concentration and effect due to polymer mesh size (related to cross-link density) ζ_m with $\zeta_{net} = \zeta_{soln} + \zeta_m$ This model uses the connection between diffusion and viscosity via the Stokes-Einstein equation

$$D = \frac{kT}{\zeta} \tag{1.4}$$

This impact can be reformulated through the de Gennes' scaling theory to give

$$\frac{D}{D_0} = \frac{1}{1 + \alpha Q^{-2v'}} \tag{1.5}$$

We argue that diffusion near surfaces can be treated in a similar manner with the frictional contribution from the surface (or polymer at the surface) is also additive, with $\zeta_{net} = \zeta_{soln} + \zeta_m + \zeta_{surf}$. The ability to distinguish between these different will be one of the items we hope the specific diffusion experiments pursued in this LDRD could address in the future.

DETAILED DESCRIPTION OF EXPERIMENT/METHOD:

For solid materials, including swollen polymers and polymer melts, the NMR signal is often broadened due to homo- and hetero-nuclear dipolar coupling, chemical shift anisotropy (CSA), and magnetic susceptibility or quadrupolar interactions. This broadening can be reduced or eliminated either by multi-pulse NMR experiments or a technique called magic angle spinning (MAS). For samples that are in the liquid/solid classification, motional averaging will partially reduce or remove many of these broadening interactions. It is also possible to swell or plasticize polymers to increase the local mobility, thereby reducing the magnitude of these interactions. Even for liquid environments in a heterogeneous sample, differences in the magnetic susceptibility within the material can drastically reduce the observed resolution. For these types of dynamically averaged or susceptibility broadened systems, MAS even at moderate speeds will produce high resolution NMR spectra: this is the niche of HRMAS NMR, and is the focus of this exploratory LDRD effort.

This improved resolution due to MAS arises because the Hamiltonians describing the dipolar, CSA and magnetic susceptibility interactions all contain an orientational component that scales as $(3\cos^2\theta-1)$, where θ is the angle between the rotor spinning axis and the magnetic field (Figure 1). When a sample is spun about an axis that is at the "magic angle" ($\theta = 54.7^o$) these interactions vanish. A simplistic schematic of a HRMAS stator is pictured in Figure 1. The main difference between a standard MAS stator and an HRMAS stator is the magic angle gradient coil that can produce a gradient along the rotor spinning axis. It is this gradient that will be crucial for the measurement of diffusion for the studies detailed below. For samples where residual dipolar

interactions or differences in magnetic susceptibility are small, HRMAS NMR reduces the observed line widths to be similar to those observed in solution high resolution NMR spectroscopy. For liquids adsorbed into/onto materials MAS speeds between 1 and 2 kHz may result in high resolution, while for plasticized/swollen materials MAS speeds between 4 and 10 kHz may be necessary to obtain the desired resolution.
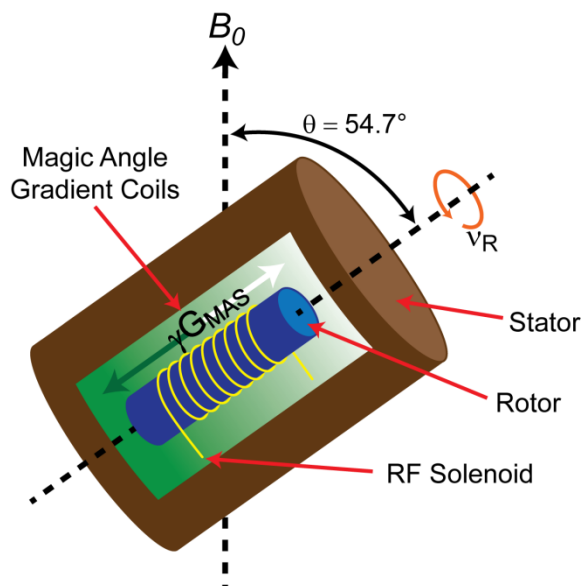
Figure 1: Schematic of a HRMAS NMR stator with a magic angle gradient along the rotor spinning axis. This gradient is used to spectroscopically "tag" spins to measure diffusion.

All of the NMR spectroscopy data presented in this report was collected on a Bruker Avance-III 600 MHz spectrometer using a commercial 4 mm single magic-angle gradient triple resonance ^{1}H/^{13}C/^{31}P HRMAS probe operating at an observe frequency of 600.13 MHz for proton (^{1}H). The ^{1}H HRMAS NMR experiments were performed at 4 kHz spinning speed with a ± 0.1 K temperature regulation. During the pulsed field gradient (PFG) diffusion experiments, the application of a gradient "tags" a spin with a controlled phase that is related to its spatial position. Figure 2 provides a pictorial representation of the dephasing of spins around the magic angle caused by the magic angle gradient. If the position of the spin does not change during the diffusion period (Δ), this dephasing is refocused and the original signal intensity (E_0) is recovered. If on the other hand the spin changes spatial position (diffuses) during Δ, the dephasing for that spin is not refocused, and the signal intensity decreases. The loss in signal intensity with increasing gradient strength is related to the self-diffusion rate with the classic Stejskal-Tanner equation (Eqn. 1.6).

A)

B)
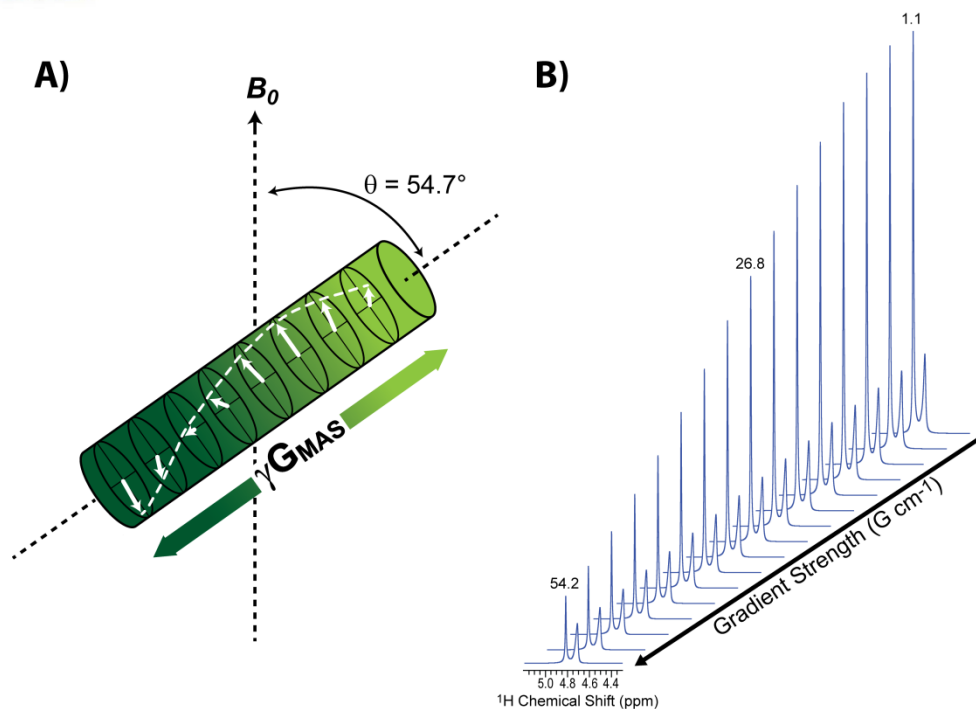
Figure 2: A) Pictorial representation of the gradient produced along the magic angle of the rotor, with the resulting phase encoding of the different spin packets. B) The decay of two different water signals found in a 1N methanol solution in a polymer membrane with increasing gradient strength. Gradient strength values (G/cm) are shown above the stack plot.

The ^{1}H HRMAS PFG diffusion experiments used a stimulated echo (STE) sequence with bipolar gradient pulses and a spoil gradient pulse, a fixed gradient pulse length of δ= 1 ms, and 16 gradient steps between 1.14 to 54.2 G/cm, with , with an inter-pulse delay ranging from $\Delta = 50$ ms to $\Delta = 500$ ms, The gradient strength was calibrated using the self-diffusion coefficient (D) of water at 298 K (2.3×10^{-9} m^2/s) with the echo decay $E(q,\Delta)$ fit using the standard Stejskal-Tanner formula

$$\frac{E(q,\Delta)}{E(0,\Delta)} = \exp\left[-q^2 D\left(\Delta - \frac{\overline{\delta}}{3}\right)\right] \qquad (1.6)$$

where D is the self-diffusion coefficient (m^2 s^{-1}), Δ is the diffusion period, and q which is the product of γ the gyromagnetic ratio of the observed nuclei, g the gradient strength, and δthe length of the gradient pulse.

RESULTS:

The targeted milestones for this project included the investigation of different heterogeneous polymer environments to evaluate the developed HRMAS NMR PFG diffusional capabilities. In particular, we wanted to address signal-to-noise limitations, time-scale and length-scale resolution. The investigations included diffusional studies of swollen siloxane composites, polymer diffusion on surfaces, and diffusion of confined polymer mixtures.

1. Penetrant Diffusion in PDMS Polymers and PDMS 3D-Printed Composites

As a demonstration of the types of HRMAS NMR PFG diffusion experiments that are possible, the diffusion of octane (a good θ solvent) in linear PDMS as a function of the degree of swelling (Q) was measured (Figure 3). While this is not a heterogeneous polymer system, this initial experiment allowed the theoretical modeling frame work to be evaluated and could be compared to the results from later diffusion studies in the composite polymer systems. The reduction of the diffusion constant (D/D_0) as a function of octane concentration was clearly evident and increased at lower Q values (higher polymer volume fractions). There was also an increase in the measured diffusional reduction with increasing molecular weight and PDMS fluid viscosity. Fits of the three different models described by Eqn. 1.1 – 1.3 are provided in Figure 3.
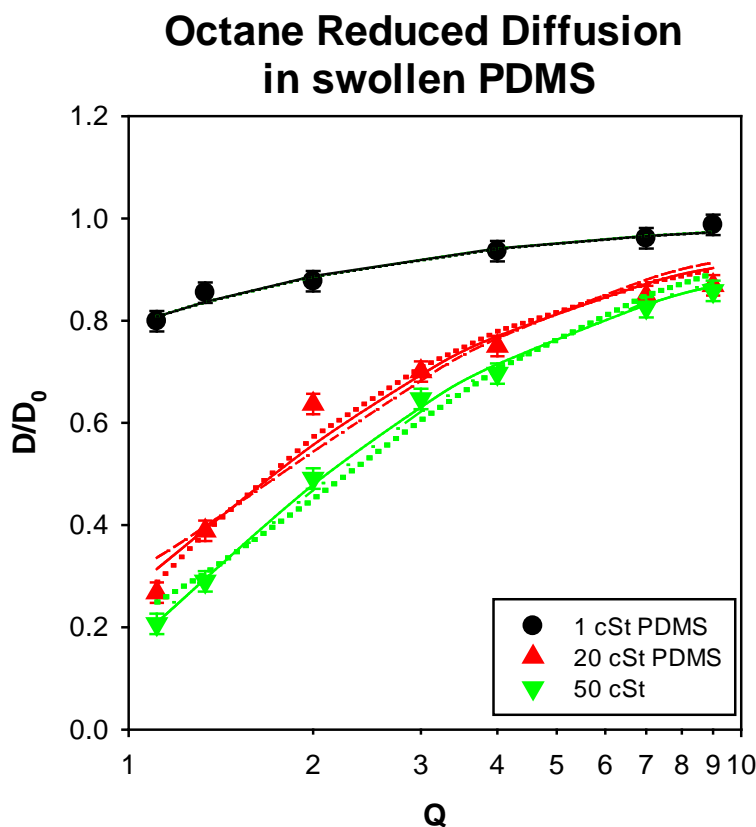

Figure 3: Diffusion rate variation for octane in linear PDMS fluids as a function of swelling.

The local viscosity can be determined directly from the diffusion reduction using the Stokes-Einstein relationship (Eqn. 1.4) via

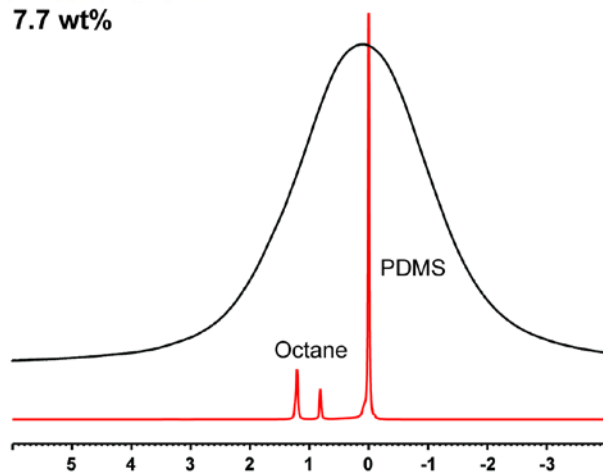$$\frac{D}{D_0} = \frac{kT/\zeta}{kT/\zeta_0} = \frac{\zeta_0}{\zeta} \tag{1.7}$$

where ζ_0 is the viscosity in the pure octane (solvent). The local viscosity as a function of polymer volume fraction for the octane/50 cSt PDMS mixture is shown in Figure 4.
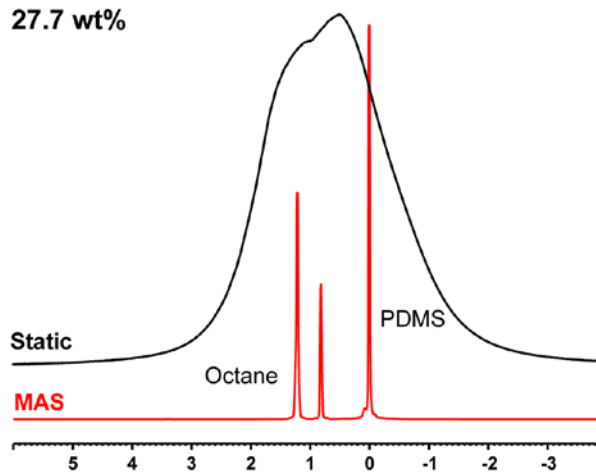
Effective Viscosity
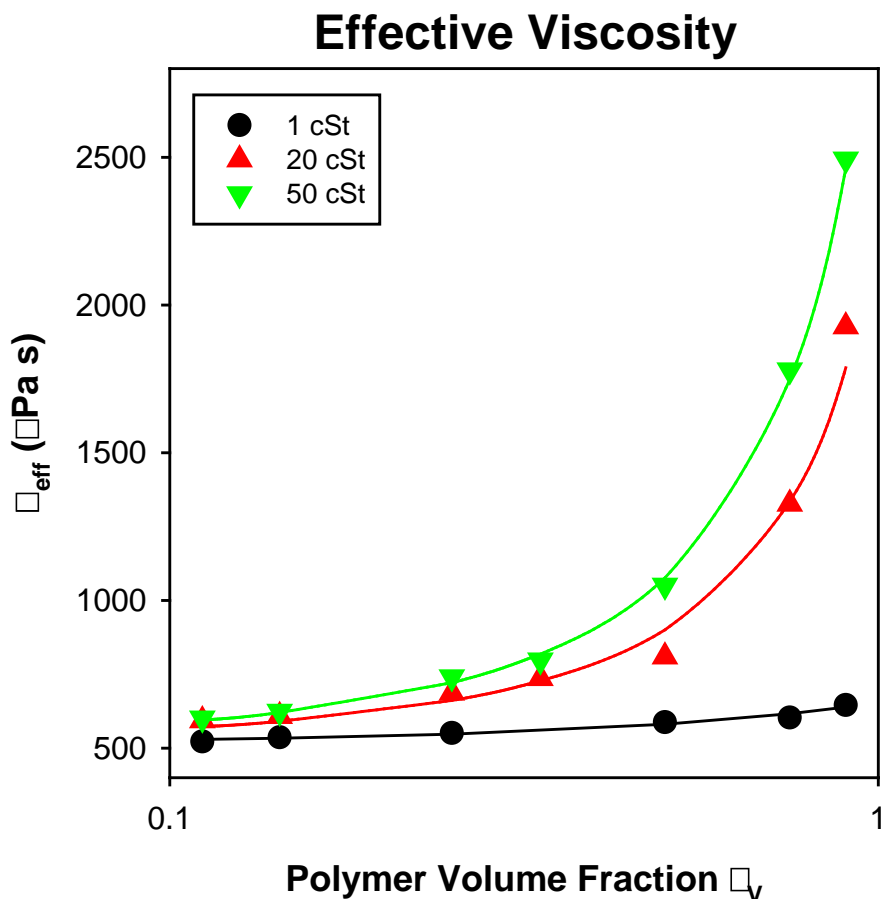
Figure 4: The local viscosity experienced by octane in different linear PDMS fluids as a function of polymer concentration.

Figure 5 shows the ^{1}H HRMAS NMR spectra for an octane swollen 3D-printed PDMS composite as a function of solvent concentration. These materials are composed of a layered mesh of PDMS filaments of controlled size, spacing and number of layers (see inset figure). Note the dramatic improvement in spectral resolution between HRMAS NMR and the static NMR conditions, thus allowing the measurement of diffusion for each chemical species present.
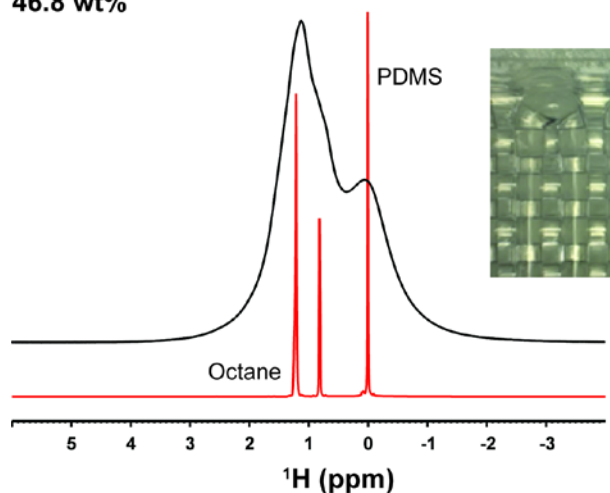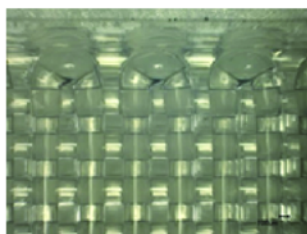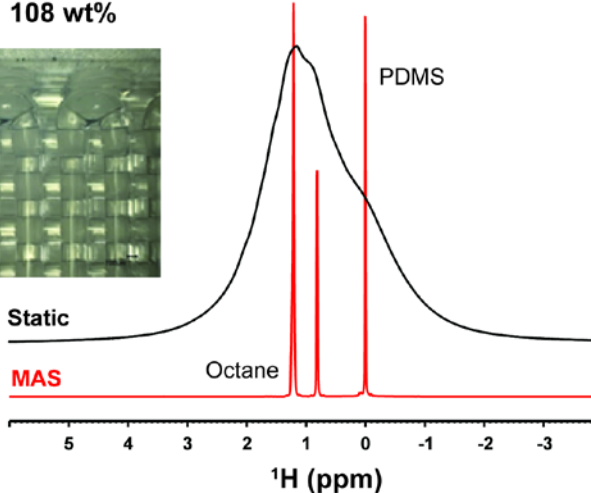
Figure 5: The ^{1}H HRMAS NMR spectra for 3D-printed PDMS composites swollen at different octane concentrations. Inset photo is of an 8-layers 3D printed mesh.

The measured reduced octane diffusion rate ratios are presented in Figure 6, along with diffusion ratios observed for swollen linear PDMS systems (solid line). Results for different 3D-printed composites based on number of layers and the cure conditions are also included in Figure 6.
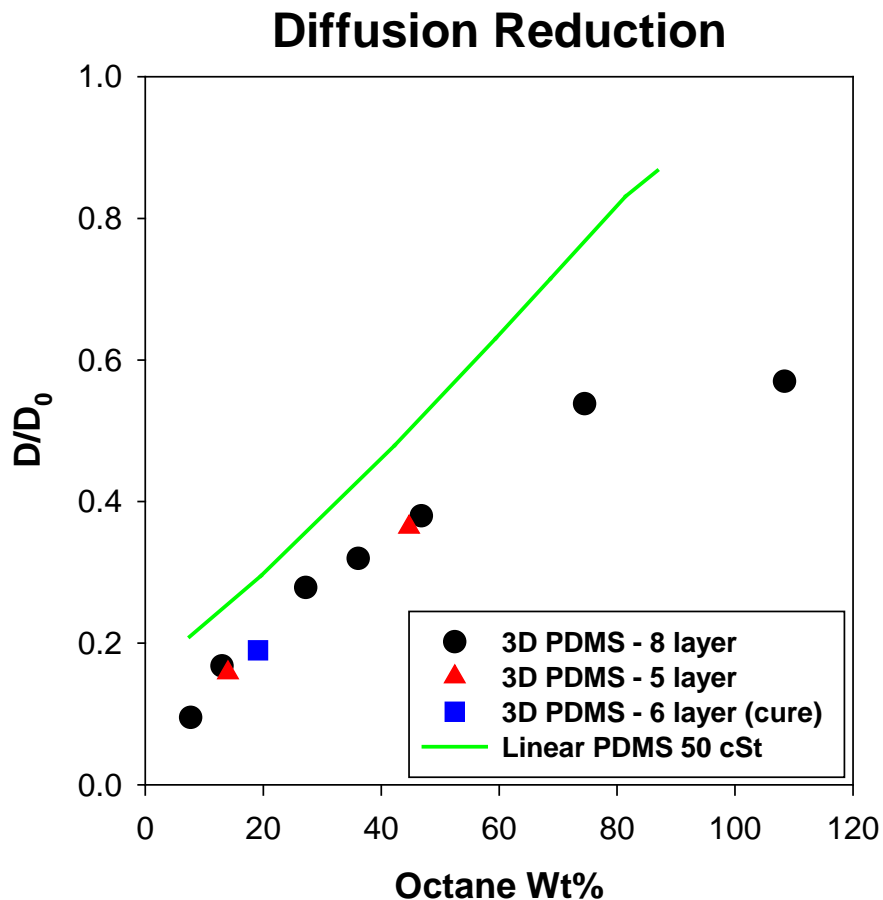
Figure 6: The reduced diffusion ratios for octane swollen 3D print PDMS composites.

Because the 3D-printed PDMS composite materials have layers and write lines on the order of 100's μm the HRMAS NMR PFG diffusion studies were also performed as a function of the diffusion period (Δ) in the experiment as this allows one to address a length scale and the possibility of local barriers to diffusion. For PFG experiments the mean squared displacement for a given diffusion period (Δ) is given by

$$\left\langle z_m^2\left(\Delta\right)\right\rangle = 2D\Delta \tag{1.8}$$

Figure 7 shows the measure diffusion rates as a function of the Δ delay, and revealed no large changes or heterogeneity in these composites over the corresponding length scales. The importance of this is presented in the discussion section.
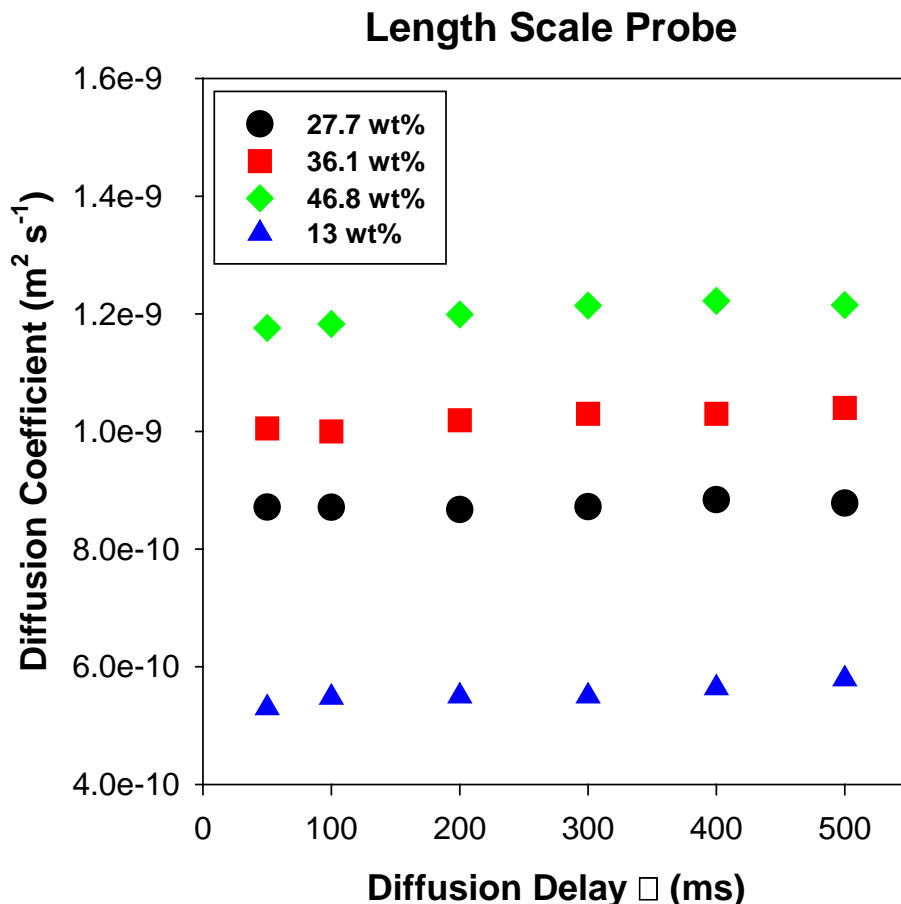
Figure 7: Variation of measure diffusion in octane swollen 3D printed PDMS composites.

2. Linear PDMS Polymer Adsorbed on Nano-Porous Carbon

The influence of surface interaction with PDMS polymer infiltrated into nano-porous carbon materials was also addressed by obtaining the ^{1}H HRMAS NMR spectra for different PDMS concentrations, as shown in Figure 8. Due to aromatic ring current of the structured carbon the signal for PDMS shifts from approximately +0.1 ppm for the pure sample, to approximately -2.7 ppm when the PDMS polymer resides in the nano-pore, and at approximately -0.2 ppm when it is surface adsorbed on the carbon material. It is possible to measure the diffusion rate of these inner-pore species using the HRMAS NMR PFG diffusion capacities, with the experimentally determined reduced ratios provided in Figure 8.
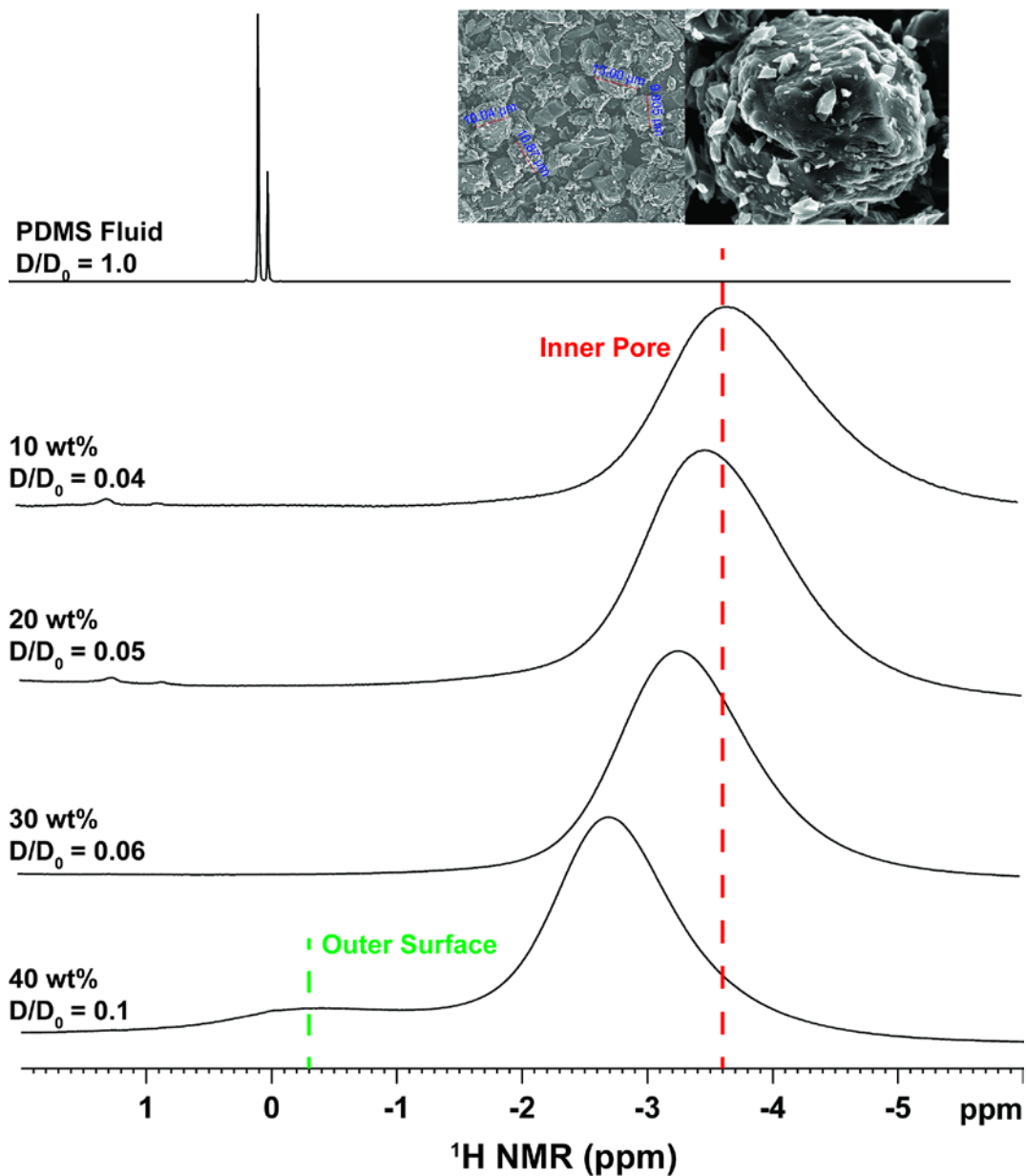
Figure 8: [1]H HRMAS of PDMS adsorbed in nano-porous carbon.

The two-dimensional (2D) NOESY NMR spectrum is shown in Figure 9 for the PDMS adsorbed on nano-porous carbon, and allow the identification of the heterogeneous pore structure present in these materials. Additional discussion provide in later sections.
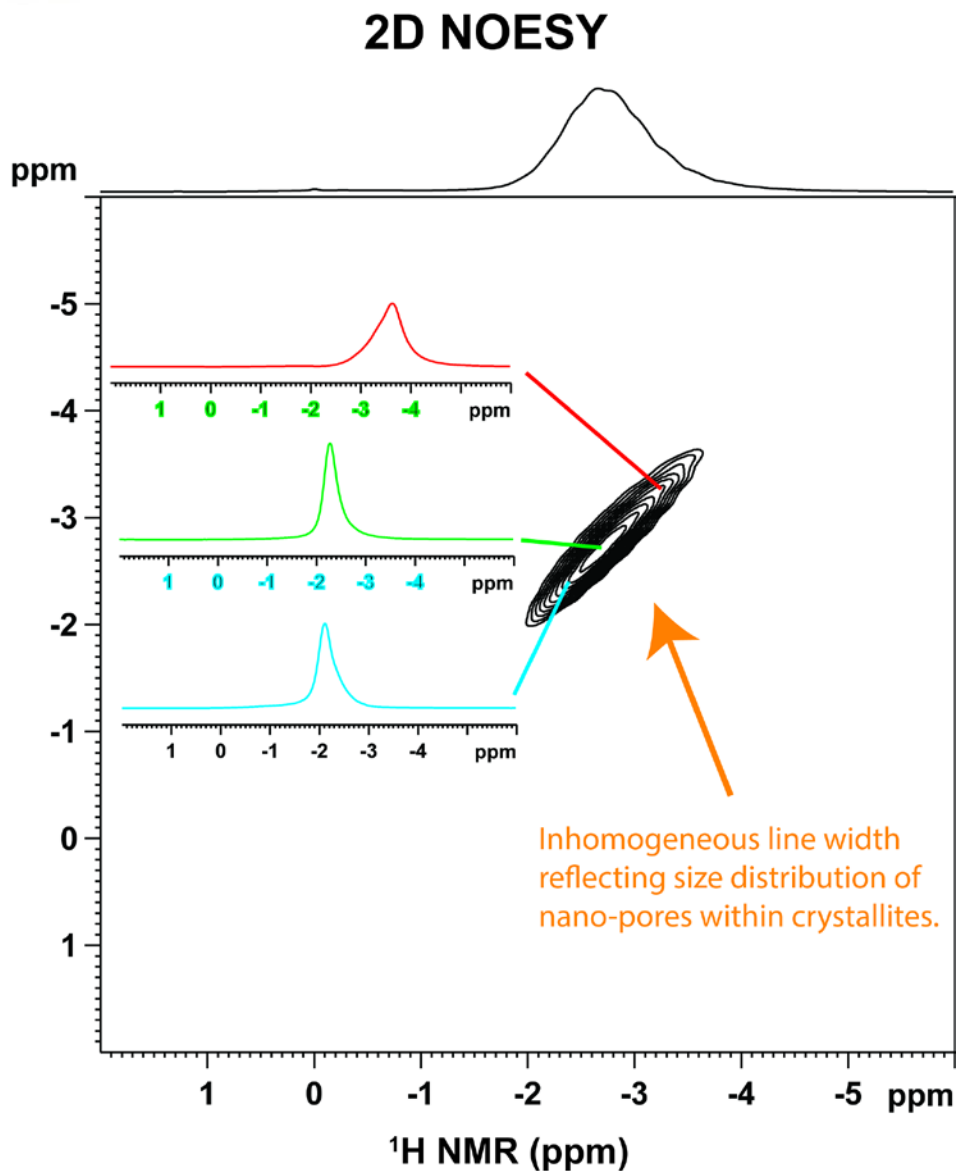
Figure 9: 2D ^{1}H NOESY NMR spectrum of the 40 wt% PDMS nano-carbon mixture.

3. PDMS/Penetrant Diffusion in Confined Dimensions

The developed ^{1}H HRMAS NMR technique also allowed for the measurement of diffusion for swollen polymers inside of confined environments, in this case 200 nm aluminum oxide membranes. Note the improved resolution of both the octane and PDMS signal resulting from HRMAS NMR in comparison to the static conditions. See below for specific discussion.
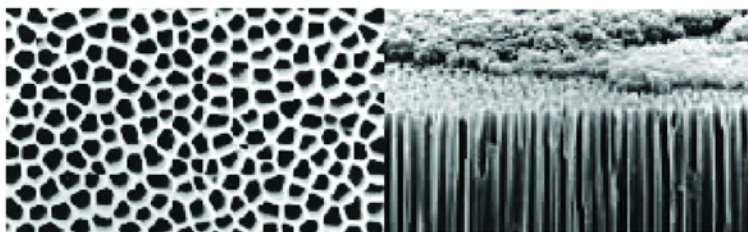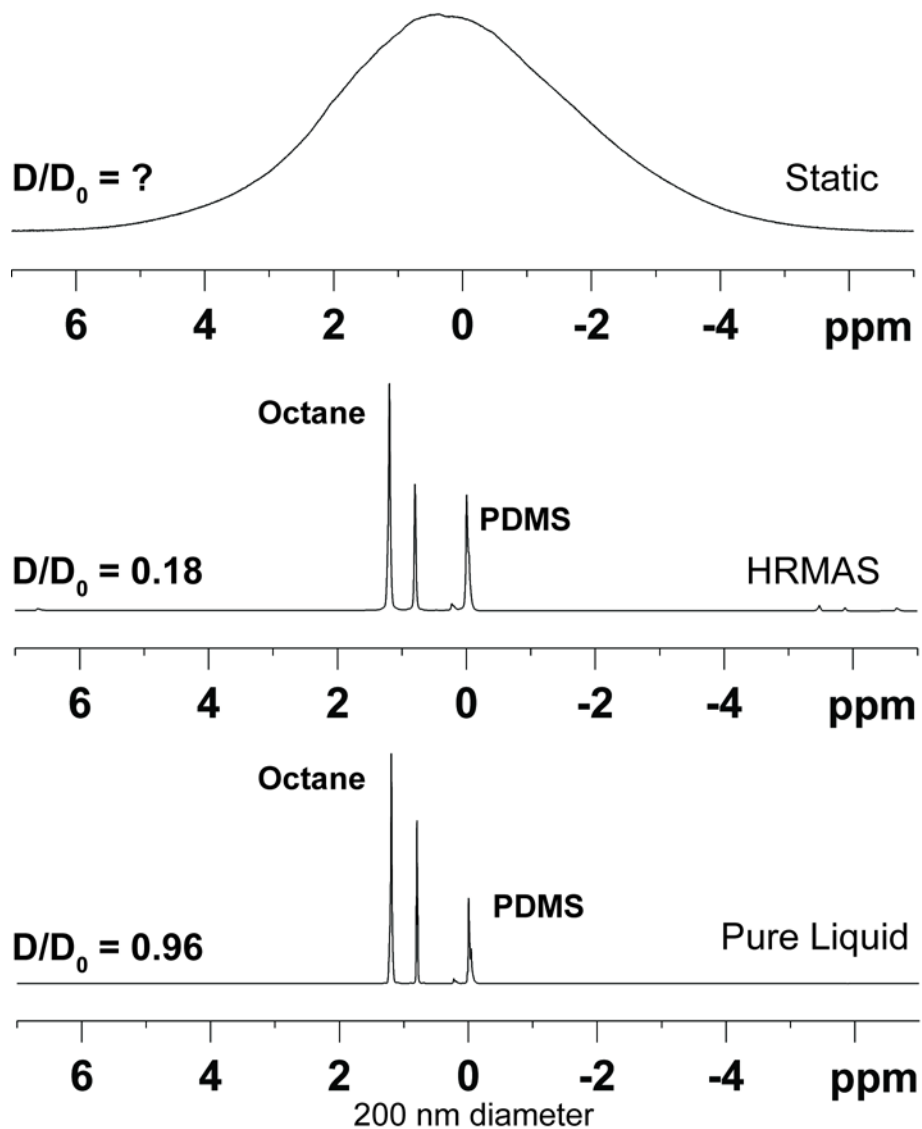
Figure 10: ^{1}H HRMAS NMR spectra of a 1:3 octane/PDMS mixture inside of 200 nm aluminum oxide membranes.

DISCUSSION:

The diffusion results for the swollen linear PDMS polymers (Figure 3) demonstrates the ability to measure diffusion for systems that are in equilibrium, but are not in the fully swollen state. One common misconception is that penetrant diffusion in polymers is described by a single diffusion rate, while in reality the diffusion depends on the penetrant (or polymer) concentrations. While not expected for the linear PDMS evaluated here, there will be situations where heterogeneities in the degree of swelling may impact the local diffusion and subsequently the material performance. The similarity of the fits for the different models in Figure 3 [solid line, free volume (Eqn. 1,1) dashed line, using hydrodynamic theory (Eqn 1.3) or the Petit local friction model (Eqn. 1.6)] demonstrates for the current materials studies that all of the proposed models can describe the diffusional process. For these swollen systems it is also possible to determine the local viscosity at the molecular level from the diffusion rates obtained using the HRMAS NMR capabilities (Figure 4). This capability could prove very useful when looking at mixtures of chemical species or for different surface loadings and wanting to determine what the local molecular level friction coefficient is. Future measurement of diffusion in a wide range of polymers and polymer composites may allow a more critical test of these different diffusional models.

The HRMAS NMR spectra of the swollen 3D printed PDMS material (Figure 5) is an excellent example of the improved resolution afforded by this technique. Note, that at especially low penetrant concentration is would not be possible to clearly identify the octane from the back ground PDMS under static conditions making the measurement of the separate diffusion rates very difficult. While not demonstrated here, the HRMAS technique would allow for independent diffusion measurements where there were multiple chemical species present. The spectra in Figure 5 are no able to distinguish between polymer (or penetrant solvent) near the silica filler surface versus the polymer removed from this filler. In this situation there is no chemical resolution, and the observed spectral lines and corresponding measured diffusion rates are a weighted average over the surface polymer fraction and the remaining polymer component. The measured reduction in the diffusion rates (Figure 6) shows that penetrants in the composite material does experience a significant reduction in the diffusion rate in comparison to swollen linear PDMS. Additional experiments as a function of filler loading would help determine the relative contributions, and would be a proposed future experiment. The length scale studies shown in Figure 7 reveal that there are no heterogeneities in these 3D printed materials between the 3 to 300 μm length-scale. The lower resolution limit for our current gradient configuration with the HRMAS NMR instrumentation is ~ 1 μm.

The HRMAS NMR studies of PDMS adsorbed on the nano-porous carbon (Figure 8) demonstrates that for certain materials there is a chemical resolution based on the properties of the materials and the local environment for surface adsorbed materials. The HRMAS NMR PFG experiments revealed that there is a 25-fold reduction in the polymer diffusion rate for PDMS within these carbon pores, and that the measured diffusion changes with the degree of loading. Similar to the 3D composite, while a variation of the chemical shift with loading was observed, it was not possible to resolve an immediate surface adsorbed signal, but instead the NMR experiments provides a weighted average of all PDMS species present within the first few hundreds of nm of the surface. Because the HRMAS NMR technique allows us to perform

additional spectroscopic correlation experiment, different details about the local polymer environment can be obtained. For example, the 2D NOESY NMR spectrum in Figure 9 demonstrates that the broad resonance observed is inhomogeneous in nature, and is composed of different chemical environments whose signals are overlapping. In this case, a distribution in the local pore size gives rise to this inhomogeneous broadening. The measured diffusion rate for these different pore environments are equivalent within experimental error. The 2D NOESY experiments also showed that there is inter-pore diffusion of the PDMS between the different pore environments on the order of ms for pores that are within the same nano-porous carbon grain.

Finally, the HRMAS NMR spectra of an octane-swollen PDMS polymer confined inside nano-pore cylinders of an aluminum oxide membrane are shown in Figure 10. This is an excellent example of a truly heterogeneous material, containing a solid support, polymer and a small-chemical penetrant. It was possible to resolve and measure the diffusion for the octane (and PDMS) in these systems revealing an almost 5-fold decrease in the diffusion rate of the octane inside of the pore. The free volume theory does not predict this, as the degree of polymer swelling is essentially the same inside and outside of the aluminum oxide membrane. These results suggest that local viscosity (i.e. a contribution from the membrane surface) must be included in the development of models to describe this process. HRMAS NMR appears to be an excellent choice for these types of experiments. Future efforts in this area are proposed.

ANTICIPATED IMPACT:

This work demonstrates the utility of HRMAS NMR PFG as a novel characterization technique to measure interface diffusion in mixed component systems. These results could directly impact a wide range of existing and future-developed DOE materials including polymers, polymer composites, MOFS and biologically based gels. These capabilities will impact the national security mission either through a discovery-focused understanding of the role interfaces play in transport and will leading to improvements in performance and aging of DOE energy related materials (e.g. battery and fuel cell membranes, high strength composites), materials in NNSA components (e.g. coatings and encapsulants), as well as an improved understanding chemical transport as related to DOD chemical agent dispersal and mitigation objectives.

Next Steps:

While this exploratory LDRD provided a demonstration that the idea works, it greatest impact would result following further development and expansion of the characterization technique. Specific avenues to seek funding for further advances include:

1) *Increasing the chemical speciation range:* The present LDRD concentrated on measurement of diffusion on proton (^{1}H) containing chemical species. There are many diffusional problems at Sandia that could utilize diffusional capabilities of different NMR active nuclei (i.e. transport of lithium (^{7}Li), sodium (^{23}Na), Fluorine (^{19}F), carbon (^{13}C), etc. To further develop these diffusional capacities for this arsenal of nuclei would allow the transport properties for a wider range of chemical species to be measured.

2) *Increase the transport rate range:* One of the limitations of the current hardware (commercial) is the lower gradient strengths which limit the size of the molecules that the technique is able to obtain diffusional data for. For the present case, we concentrated on diffusion of small molecules (penetrants) or highly swollen polymer systems to maintain the targeted diffusion rates on the order of 10^{-9} to 10^{-10} m^2/s. To study the diffusion of larger molecules such as cross-linked polymers or ionic liquids (10^{-12} to 10^{-14} m^2/s) would require the design and construction of a stronger gradient component in these probes. This could be pursued either at Sandia using improved micro-fabrication capabilities, or exploring the possibility of working closer with the instrument companies to help direct this improvement.

3) *Coupling to Imaging Capabilities:* The impact of the novel diffusional measurement capability would be even further enhanced by coupling the PFG NMR with imaging capabilities. Simple 1D imaging (for example across a very small electrochemical cell) should be possible in the current configuration, but is would be the most beneficial to couple with 3D imaging techniques and larger sample configurations.

This work provided the technical basis to these submitted white pages/proposals.

1) FY16 Enhanced Non-Nuclear Materials Technical Proposal, "Aging in 3D-printed silicone polymer materials: Impact on diffusion properties", Todd M. Alam (PI), submitted 8/2016.
2) DOE BES White Page, "Resolving Multi Scale Dynamics within Heterogeneous Polymers", Team: Todd M. Alam (PI), Gary Grest, Mike S. Kent and Brad Jones. Submitted to Sandia BES program management submitted 7/2015.

CONCLUSION:

The initial results obtained under this exploratory LDRD clearly demonstrate that the improved resolution obtained using this new HRMAS NMR spectroscopy capability allows the measurement of diffusion of different chemical species in heterogeneous environments and surfaces. The greatest impact will be for heterogeneous polymer systems where the diffusion of multiple chemical species needs to be individually measured at the same time. These types of diffusion experimental measurements can be used to directly access and test proposed models to describe transport in complex system. As an example, the role of confinement on diffusion is not explained by simple free-volume theory, and instead must incorporate a hydro-dynamic argument to correctly predict the experimental results obtained using this technique.

There were limitations to the HRMAS NMR diffusion capabilities identified during this LDRD study. The current hardware places a lower limit on the magnitude of diffusion rates that can be measured, with the current study concentrating on penetrants and low molecular weight PDMS at surfaces which have relatively rapid diffusion rates. Diffusion experiments of rigid (highly cross-linked) polymer materials would not be possible until probes with higher gradient strengths could be manufactured. For materials that produced enhanced chemical resolution due to the material properties (i.e. nano-porous carbon) it was possible to resolve distribution of pores/surfaces on the order of hundreds on nm. On the other hand, for the silica filled PDMS composites studies this type of chemical spectral resolution was not realized, such that the

measured diffusion was a weighted average of all the local polymer environments, and thus unable to resolve heterogeneities smaller that a μm.

In conclusion, this new characterization capability does provide the ability to measure diffusion in a wide range of heterogeneous materials, and gives a novel tool to look at diffusion/transport properties in complex multi-component systems.