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Enhancement of Diffusion in a High-Permeability Polymer by the Addition of Nanoparticles

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ABSTRACT: A nanocomposite was formed by adding fumed silica to the high-permeability random copolymer of tetrafluoroethylene (TFE) and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (PDD). The self-diffusion constant of pentane in cast films of the pure polymer and nanocomposites containing 10, 20, 25, and 30 wt % fumed silica was measured. The addition of 30 wt % fumed silica increased the self-diffusion constant by an order of magnitude. For the pure polymer and all four nanocomposite compositions, the apparent self-diffusion constants are a function of the time over which diffusion is observed, Δ, in the pulse field gradient experiment. At a given level of fumed silica, diffusion appears to be faster when observed over shorter times and decreases toward a plateau value at long times. This result is qualitatively indicative of tortuous diffusion. The addition of fumed silica not only increases the apparent self-diffusion constants but also changes the dependence of the apparent self-diffusion constants on Δ. The self-diffusion constants decrease more slowly as a function of Δ, indicating better connectivity of the more permeable domains. The apparent diffusion constants also increase as a function of time after the introduction of pentane. This phenomenon is observed in the pure polymer as well and is described as conditioning of the membrane. Conditioning of the membrane increases diffusion constants initially; but after a few months, aging of the membrane leads to a decrease in translational mobility.

Diffusion of small molecules through high-permeability polymers is rapid because these polymers have bulky backbone units which form poorly packed glasses with large fractional free volumes.[1−5] Positron annihilation lifetime spectroscopy indicates free volume elements with a radius in the range of 0.6 nm, which is about twice the size observed in conventional polymeric glasses. Some high-permeability polymers have reverse selectivity where the permeability of larger molecules is higher than that of smaller molecules. In these systems, there is only weak sieving by molecular size and the solubility of larger molecules is greater, leading to the reverse selectivity.

Recently nanocomposites of such high-permeability polymers with fumed silica were shown to have significantly increased permeability relative to the pure polymer while retaining selectivity.[6−8] In this report, the nature of the diffusion of pentane in a nanocomposite will be characterized using pulse field gradient (PFG) NMR for comparison with the diffusion process observed in the pure polymer.

One of these high-permeability polymers is the random copolymer of tetrafluoroethylene (TFE) and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (PDD), and diffusion of small molecules in this polymer has been reported using PFG NMR,[9,10] which determines the self-diffusion constant. In the TFE/PDD copolymer which is 35% TFE, the apparent diffusion constant in the PFG NMR experiments on this polymer depends on the time over which diffusion is allowed to occur. This behavior is indicative of a barrier to the random walk a penetrant would undergo in a homogeneous system. The barrier arises from regions that are less peremable where penetrant diffusion and/or penetrant solubility is lower. Two classes of diffusion in heterogeneous systems involving barriers are tortuous diffusion and restricted diffusion.[9,10] In tortuous diffusion the material can be considered to have pores that support rapid penetrant diffusion surrounded by walls that are impenetrable or much less penetrable. In tortuous diffusion there is a pathway for long-range diffusion associated with an interconnected pore space. In restricted diffusion, the pores are isolated so long-range diffusion is absent if the walls are impenetrable or very slow if the barriers support only very slow diffusion. In the 35% TFE copolymer, tortuous diffusion has been observed for low molecular weight penetrants such as propane and pentane. Thus, the self-diffusion constant for these penetrants appears larger if one observes diffusion over a short time or length scale in the PFG NMR experiment since diffusion within a pore is being monitored. As time increases, the penetrant encounters the pore wall restricting its path, and the self-diffusion constant apparently decreases. At very long times in an interconnected pore space a plateau value of the self-diffusion constant is reached. TFE/PDD does not have pores in the sense of large unoccupied volumes but has regions with higher free volume bounded by regions of lower free volume. This leads to diffusion which has the characteristics of a truly porous system such as limestone. This behavior observed in pure TFE/PDD will be compared to the characteristics of diffusion in the nanocomposite.

The nanocomposite is prepared by combining a dilute solution, ∼2 wt %, of the copolymer (AF 1600 supplied by DuPont) in perfluoroheptane with the fumed silica (CAB-O-SIL TS-530 purchased from Cabot) to form a slurry.[6] A film of the slurry is cast and then dried leading to a clear material. About 8 wt % pentane is added to 0.5 g of film in an 8 mm NMR tube, which is then sealed. The diffusion measurements were made on a 400 MHz Varian Inova using the proton signal from pentane with the pulse sequence shown in Figure 1. The duration, δ, of the gradient pulse is 1 ms, and the recycle time is 15 s. The spin−lattice relaxation time of the protons in pentane sorbed in the film is about 1 s.

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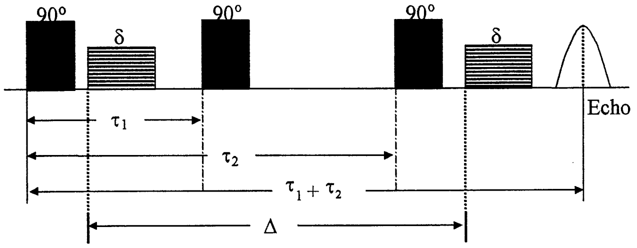

Figure 1. Pulse sequence used for the measurement of proton translational diffusion. The gradient pulse width δ is typically 1 ms, and the time over which diffusion occurs, Δ, can be varied from 3 to 1000 ms.

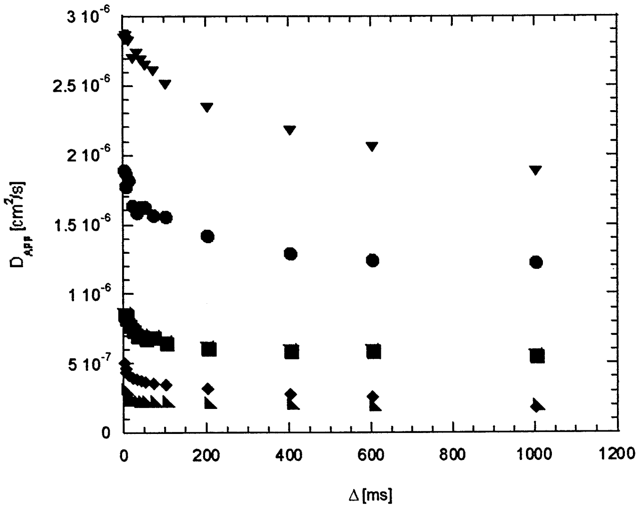

Figure 2. D_{app} vs Δ for different concentrations of fumed silica in the TFE/PDD copolymer. Pure polymer data are the half squares, 10 wt % silica are the diamonds, 20 wt % silica are the squares, 25 wt % are the circles, and 30 wt % are the inverted triangles. All measurements in this figure were made 1 day after sample preparation. The error in an individual point is ±5%.

The time over which diffusion is varied, Δ, ranges from about 3 to 1000 ms. At each value of Δ, the diffusion constant is calculated from the slope of the echo intensity as a function of the strength of the gradient squared. Only the initial decay of the intensity is used. Figure 2 contains a plot of the apparent diffusion constant as a function of Δ for films containing 0,10, 20, 25, and 30 wt % of fumed silica.

The increase in translational diffusion with addition of silica to the polymer is striking with an order of magnitude change between 0 and 30 wt % silica. The silica particles are regarded as impenetrable,[6] so the effect of the nanoparticles is the opposite of what is observed with conventional sized particles which reduce apparent diffusion constants. Figure 3 is a plot of the apparent diffusion constant at 600 ms as a function of silica concentration.

The increase in diffusion with silica content is roughly exponential. The silica particles are considered to disrupt polymer packing, leading to an increase in free volume in the polymer at the polymer−silica interface.[6] For the diffusion to have a greater than linear dependence on number of particles as is observed, there must also be improved connectivity of the high free volume regions. The increases in the apparent diffusion constant occur at all diffusion measurement times, Δ. This corresponds to an increase at all length scales in the diffusion measurements.

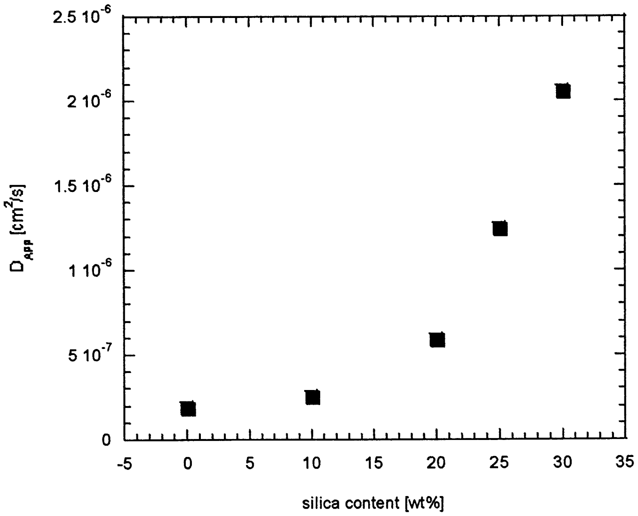

Figure 3. D_{app} at a Δ of 600 ms vs silica content.

At each concentration of silica, the apparent diffusion constant decreases with diffusion time toward a plateau value. This indicates the diffusion of pentane in the composites is qualitatively tortuous at all compositions as it is in the pure copolymer. At 30 wt % silica, the apparent diffusion constants are still decreasing. However, a plot of D_{app} vs Δ which is proportional to the mean-square displacement of penetrant molecules is continually increasing, which is indicative of tortuous rather than restricted diffusion. The slower approach to a plateau value of D_{app} as Δ increases at higher silica content reflects an increase in the length scale heterogeneities of the system which are influencing diffusion. Plots of the mean-square displacement vs Δ can be used to estimate the length scale of the heterogeneities influencing diffusion. In these plots there is a change in slope at about the mean-square displacement corresponding to the mean-square size of the heterogeneities. This approach indicates a size of the heterogeneites in the micron range, which increases by about a factor of 10 as the concentration of fumed silica increases to 30 wt %. This is a long length scale relative to the size of the fumed silica particles or to the size of individual free volume elements. This structure will be considered further in subsequent, more complete reports.

Films of high-permeability polymers are subject to two effects associated with the history of the sample. They are referred to as conditioning and aging.[1−5] Conditioning is associated with an increase of permeability produced by adding a nonsolvent to the high-permeability polymer film. Aging of these disordered glasses manifests itself as a decrease in permeability with time after the membrane has been prepared. For samples prepared for the PFG NMR experiment, the two processes are competitive with conditioning, leading to an increase in diffusion over shorter periods of time, and aging, leading to slower diffusion over longer periods of time. This behavior has been characterized in the case of the pure polymer.[10] Figure 4 is a plot of the apparent diffusion constant at $\Delta = 600$ ms for a film containing 20 wt % silica for measurements performed after sample preparation ranging from a few hours to a few months.

The data shown in Figure 4 for $\Delta = 600$ ms are representative of the results at all long values of Δ. There is a rapid increase in the diffusion constants shortly after the pentane is added to the film, which is

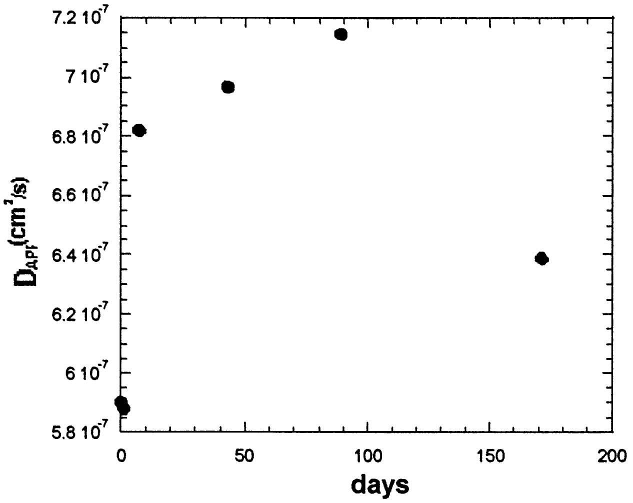

Figure 4. D_{app} vs time after sample preparation.

similar to the conditioning behavior noted for the pure polymer. After several months diffusion slows, which is also similar to results on the pure polymer. The similarity of these data to the results on the pure polymer supports the idea that the penetrant in the nanocomposite is still diffusing through polymer involving free volume elements and regions that are related to those present in the pure polymer. The nanoparticles greatly enhance the diffusion by increasing the free volume elements and by improving connections between free volume regions.

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