Segmental diffusion in attractive polymer nanocomposites: A quasi-elastic neutron scattering study

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The addition of nanoparticles (NPs) to a polymer matrix, forming a polymer nanocomposite (PNC), can significantly enhance the thermal, mechanical, and functional properties of the host matrix. As a result, PNCs are appealing materials for a variety of fields, industries, and applications [1]. The dynamics of polymer segments are particularly important because they significantly influence or dictate the processability, applications, glass transition temperature (T_g), and various macroscopic properties (such as creep, toughness, and transport) of the PNC. Despite decades of research on various PNC systems, additional fundamental studies are needed to explore the complex parameter space and understand the underlying physics of interfacial and confined polymer dynamics. In this work, we use quasi-elastic neutron scattering (QENS) and temperature modulated differential scanning calorimetry to present a systematic and detailed study of segmental dynamics in highly attractive polymer nanocomposites comprised of poly(2-vinyl pyridine) (P2VP) and colloidal silica (SiO_2) NPs as a function of temperature, NP concentration, and P2VP molecular weight.

There are several methods that can be used to analyze segmental dynamics including nuclear magnetic resonance (NMR), dynamic mechanical analysis (DMA), broadband dielectric spectroscopy (BDS), temperature-modulated differential scanning calorimetry (TMDSC), neutron spin echo (NSE), and quasi-elastic neutron scattering (QENS) [2]. The approximate timescales associated with many of these measurement techniques, as they pertain to segmental dynamics, are schematically represented in Figure 1 with measurements of neat P2VP and a global fit to Vogel-Fulcher-Tammann (VFT) temperature dependence. QENS, the focus of this paper, has the advantage of spanning short time scales (≈ 1 ns), providing simultaneous temporal and spatial information to capture the timescales and geometries of measured segmental motions, and measuring the fraction of relaxing segments through the elastic incoherent structure factor.

First, by monitoring the elastic scattering intensity in a fixed window scan (FWS) as a function of temperature, the mean-squared displacement ($\langle x^2 \rangle$) of P2VP segments was found to decrease for all $T > T_g$ as a function of NP concentration (Figure 2a). Similar results were observed by analysis of the QENS spectra for $T >> T_g$. Specifically, we observe the full-width at half max (FWHM) of quasi-elastic broadening increases linearly as a function of q^2 for all NP concentrations, which is indicative of translational diffusive motion over these length and time scales (≈ 1 nm and ≈ 1 ns). The extracted diffusion coefficient of the alpha process (D_α) obtained from this simple model (FWHM ~ $D_\alpha q^2$) is plotted as a function of inverse temperature in Figure 2b, and the relaxation time for neat P2VP aligns with extrapolations from BDS and TMDSC measurements (Figure 1). However, as attractive SiO_2 NPs are added to the polymer matrix, D_α is slower than bulk by as much 80% at NP concentrations of ≈ 50 vol%, and despite the slowed timescale, the temperature dependence remains largely unchanged (Figure 2b). A similar q-dependence of FWHM with a simultaneous slowing of mobility indicates that segmental dynamics in PNCs are perturbed much more temporally than spatially, i.e. the segmental relaxation process is slowed but segments relax in a similar manner. Interestingly, all polymer segments in the 50 vol% PNC are in close proximity to a NP surface because the interparticle distance is ≈ 2.5 nm. Thus, our measurement of segmental relaxations shows that interfacial segments are dynamically active, albeit slowed, at these high temperatures.

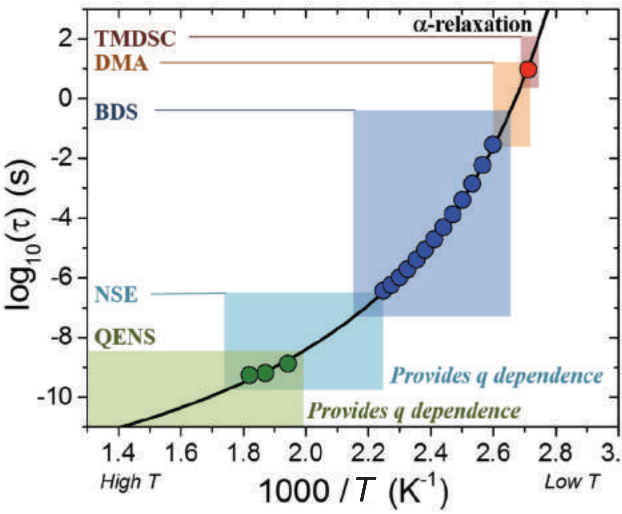

FIGURE 1: Primary segmental relaxation times (α-process) of bulk P2VP measured via TMDSC (red circle), BDS (blue circle), and QENS (green circle). Approximate time scales for five techniques, and their corresponding temperatures, are depicted by shaded regions along the relaxation curve.

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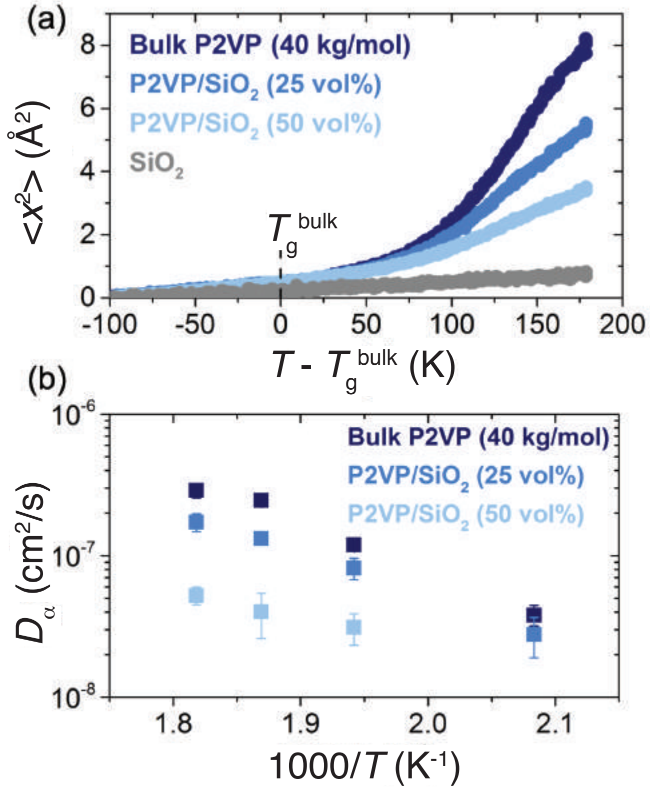

FIGURE 2: (a) Average segmental mean-squared displacement ($<x^2>$) obtained from FWS of bulk 40 kg/mol P2VP and P2VP/SiO_2 PNCs with concentrations of 25 vol% and 50 vol%. (b) Extracted segmental diffusion coefficient (D_a) as a function of inverse temperature for neat polymer and PNCs.

We next probe the effect of P2VP molecular weight on segmental dynamics in PNCs by studying P2VP/SiO_2 (25 vol% SiO_2) with unentangled to well entangled P2VP (10 kg/mol, 40 kg.mol, 190 kg/mol). All bulk and PNC materials exhibit classic characteristics of translational segmental diffusion (FWHM ~ $D_\alpha q^2$) that differ only in the associated timescale. In Figure 3, the extracted diffusion coefficient of the PNC is normalized to that of bulk to highlight the impact of molecular weight on segmental diffusion in PNCs. For all P2VP molecular weight, D_α in the PNC is reduced relative to neat P2VP by a factor of ≈ 2, although a slight trend can be observed where NPs are more impactful in lower molecular weight P2VP. In contrast, a strong molecular weight dependence on segmental dynamics has been observed in P2VP/SiO_2 PNCs using BDS and TMDSC [3]. However, not only do these techniques probe and sample segmental dynamics differently, QENS measurements are at much higher temperatures which may indicate that the interfacial structure and dynamics have a strong temperature dependence or may indicate an existence of an equilibrium structure that other techniques do not access [2].

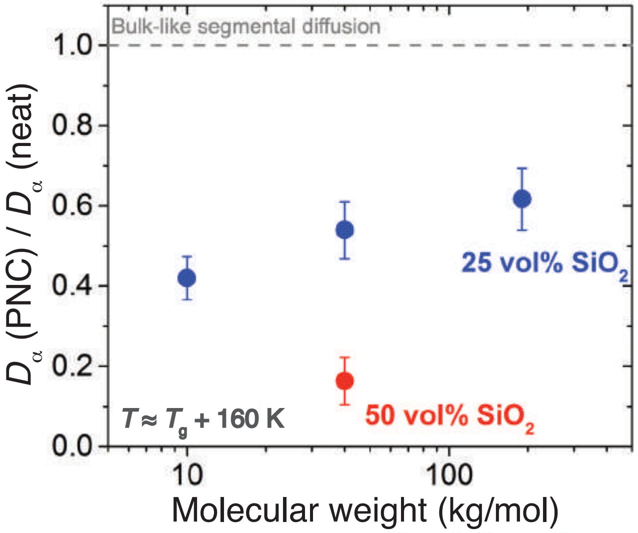

FIGURE 3: Diffusion coefficient of P2VP segments (D_α) in PNC normalized to D_α in neat P2VP as a function of polymer molecular weight for 25 vol% SiO_2 (blue) and 50 vol% SiO_2 (red).

In summary, we systematically study P2VP/SiO_2 PNCs using QENS as a function of NP concentration, temperature, and P2VP molecular weight and compare to measurements from other techniques (e.g. TMDSC and BDS). We show that motions of P2VP segments on ≈ 1 nm length scales and ≈ 1 ns time scales are well described by classic translational diffusion, even at NP concentrations of ≈ 50 vol% where the average interparticle spacing is ≈ 2.5 nm. The average segmental diffusion coefficient decreases with increasing NP concentration by up to a factor of ≈ 5 and is nearly independent of temperature over the studied temperature range. In contrast to the well-documented molecular weight dependence of segmental diffusion in the deeply supercooled regime, our measurements of the same dynamic process at higher temperatures show slowed segmental dynamics that are largely independent of matrix molecular weight [3]. Finally, by comparing TMDSC, BDS, and QENS, our results suggest that temperature has a significant impact on the NP-induced perturbation to segmental dynamics in PNCs and highlight the unique and complementary insights that can be provided by QENS.

References

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