Experimental report

09/02/2017

Proposal: **9-12-443** **Council:** 4/2016

Title: Slow dynamics in self-organised silica rubber nanocomposites

Research area: Materials

This proposal is a resubmission of 9-12-368

Main proposer: **Richard THOMPSON**

Experimental team: James HART
Richard THOMPSON

Local contacts: Bernhard FRICK

Samples: Silica in polybutadiene nanocomposite

Instrument	Requested days	Allocated days	From	To
IN16B	3	3	20/06/2016	23/06/2016

Abstract:

The dynamics of filled rubbery polymers remain poorly understood, yet underpin macroscopic phenomena of energy dissipation, which accounts for 80% of C-footprint of vehicle tyres. QENS experiments on IRIS (ISIS) aided by detailed structural analysis by SANS at ILL&ISIS show that polymer chain motion is suppressed near silica nanoparticle interfaces. We have achieved this by H-labelling end-functional polymer chains which segregate to silica nanoparticle interfaces. However, the maximum time scale on IRIS (~150 ps) was too short to determine any difference in relaxation times, and our results so far are based on the immobile background fraction. By selecting 3 samples for which IRIS could show a difference in background behaviour, will offer the best possible opportunity to quantify the slowing of PBd dynamics relative to the base polymer (i) in the presence of nanoparticles and (ii) when localised near the surface of nanoparticles. This experiment requires 3 days beamtime on IN16b to conclude this part of the study.

Slow Dynamics in Self-Organised Silica-Rubber Nanocomposites – EXPERIMENTAL REPORT

Experimental setup

As stated in the experimental proposal, 3 samples,

i. "PBOH dPB blend" isolates the impact of the functional group on dynamics,
ii. "pure hPB composite" shows the effect of silica on bulk PB dynamics, and
iii. "15k PBOH composite" isolates the impact of the silica on PBOH chains at the silica interface.

were examined on IN16b to study the effects of filler materials on the polymer dynamics. A 5k resolution scan was performed on the 4OH dPB blend, and QENS measurements were done at 220K, 250K, 280K, 310K, and 363K for all samples.

Results

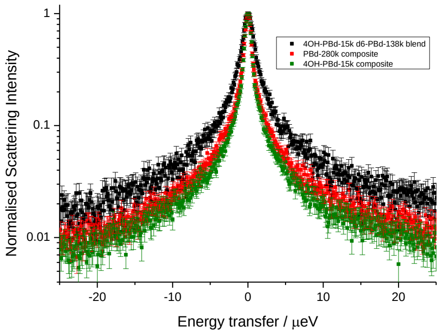

Figure 1: Normalised IN16b energy transfer peaks for selected samples, 280K $Q = 1.23$ Å^{-1}

Quasi-elastic data gathered from the experiment was reduced and analysed with several methods. Simple qualitative analysis of the peaks finds the same trend observed on the IRIS instrument. The dynamics of composite samples show a clear decrease, seen in figure 1, compared with the blend baseline sample. The peaks were Fast Fourier transformed to produce autocorrelation functions *I(q, t)*, and a stretched exponential decay curve, equation 1, was fitted to each function.

$$I(q,t) = A + (1 - A)e^{(-t/\tau)^{\beta}} \quad (1)$$

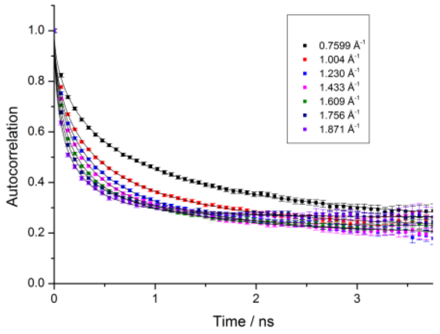

Figure 2: IN16b autocorrelation functions, lines are fitted stretched exponential functions, 4OH-PBd-15k composite at 280k

The fitted curves where found to model the decay accurately out to a range of 3ns, an example set is shown in figure 2. After this timescale the data was too noisy to be used with certainty. The beta parameter was found to vary between 0.4-0.6, a typical range for polymers, and no correlation with *Q* was noted. Representative sets of the background value, *A*, and relaxation time, tau, are shown in Figures 3 and 4 respectively.

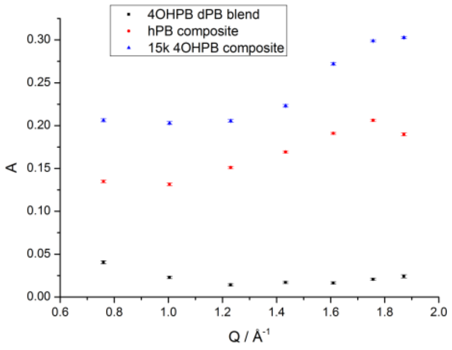

Figure 3: KWW equation background over

measured Q range for all samples at 310K on IN16b

As with our previous results on IRIS, there is a clear difference in background between the samples, related to the presence of a glassy polymer layer about the filler material. The relative scattering proportion of this layer is highest in the 15k 4OHPB composite, resulting in the higher recorded background. The increase in the background values of the composites with increasing *Q* is likely due to limits in the reduction, as only a 5K baseline of the blend was run due to time constraints and had to be used for all the samples.

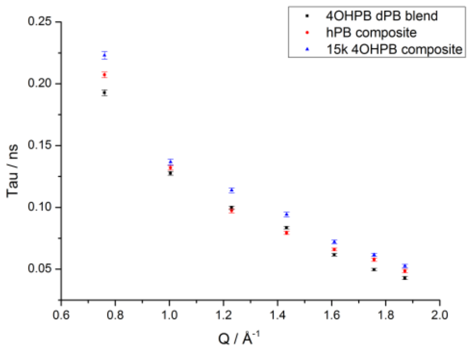

Figure 4: KWW equation decay constant, tau, over measured Q range for all samples at 310K on IN16b

There is a small but notable increase in tau in the 15k OHPB composite compared with the blend and fully hydrogenous composite, and was unseen on the IRIS data. This increase in relaxation time is from the glassy dynamics of the polymer near the silica interface, which due to IN16b greater resolution is observable. Given the presence of the increased background it is unlikely that IN16b observed the entirely of the slowed dynamics. However the shift demonstrates that the increased background is from slowed dynamics rather than coherent scattering, and that the slowing of the polymer near these surfaces is severe.

Conclusions

The experiment was successful in achieving the goal of examining polymer dynamics near silica interfaces at greater timescales than previous work on IRIS. The polymer dynamics were found to be greatly hindered by the surface and mostly beyond the range of the instrument; however some change in the relaxation time was noted. Analysis is ongoing and these results are to be included in a paper soon to be submitted for review.