Experimental report

02/09/2022

Proposal: **9-12-628**

Council: 10/2020

Title: Polymer dynamics in one component nanocomposites (OCNC)

Research area: Soft condensed matter

This proposal is a resubmission of 9-12-609

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Samples: (C4H6)n(C4D6)n
(C4H6)n(C4D6)nSiO2

Instrument	Requested days	Allocated days	From	To
D22	1	0		
D33	1	1	18/05/2021	19/05/2021
IN15	8	6	08/07/2021	14/07/2021

Abstract:

Polymer nanocomposites display superior viscoelastic and mechanical properties compared to the corresponding pure melt. One component nano composites (OCNC) consisting of polymer grafted nano particles only, overcome the dispersion problem of conventional polymer nano composites (PNC) and promise among others superior mechanical properties. We follow up an experiment by Mark et al., who has shown that grafting leads to chain confinement even in the Rouse regime where entanglements between chains are not formed. In the proposed experiment we want to go one step further and find out, how grafting caused chain confinement interplays with the tube confinement that in long chain polymer melts leads to reptation. We conjecture that the combined action of both confinement types is at the origin of the excellent mechanical properties of OCNC.

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Samples: We aimed to study the structure and dynamics of polyethylene oxide grafted on nanoparticles. The polymer molecular weight was 10000 g/mole. The nanoparticles were made of crosslinked polybutadiene with a core radius of 12.8 nm confirmed via small angle X ray scattering studies. In the polymer grafted nanoparticles (OCNCs) the core was matched with the shell to avoid interference from the core scattering. Two different labelling schemes were used in the one component nanocomposites: 1) Half of the grafted chain near the particle core was labelled by protonation (dhd). 2) The entire grafted chain was protonated (dh). These schemes were used to study the conformation and dynamics of polymer segments near the particle core compared to the averaged dynamics across the chain. This labelling allows us to probe the effect of grafting in the different zones along the grafted polymer chain. Neat polyethylene oxide (10 % protonated and 90 % deuterated) of 8000 g/mole molecular weight was measured as the reference sample.

Experiments and results:

Small angle neutron scattering:

The neat polymer and one component nanocomposites were studied using small angle neutron scattering (SANS) on D33 for confirming the matching condition. The data is shown in Figure 1. The black shows the calculated intensities for neat polymer using Gaussian form factor.

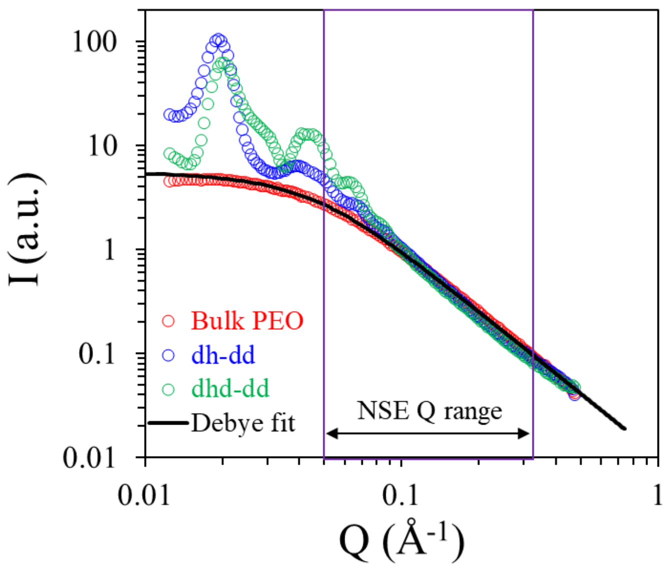

Figure 1. Small angle neutron scattering data from pure polyethylene oxide and polyethylene oxide grafted nanoparticles with two different labelling schemes (see text).

The pure PEO SANS intensities match with the predicted intensities for our sample. In case of the grafted samples, we notice some contribution from the particle structure factor peaks at low Q. However, in the NSE Q range, this contribution is not significant.

Neutron spin echo:

The NSE experiments were performed at the spectrometer IN15. We studied the neat melt, i.e. blend of h-PEO (10%) with d-PEO (90%) at different temperatures in the range from 350 K to 450 K covering the time range 0.1 < t < 550 ns at momentum transfers of Q = 0.05, 0.078, 0.096, 0.13 and 0.15 $Å^{-1}$. The OCNC experiments were carried out at 415 K. Due to instrumental problems the time range was limited to 0.1 < t < 150 ns. The accessed Q values were Q = 0.049, 0.077, 0.097, 0.114 and 0.131 $Å^{-1}$. The dhd-dd sample was measured only at the first four Q values.

The data obtained on the pure PEO sample at 413 K is shown in Figure 2. As could be seen, the data for pure samples decays throughout the accessible time range. This is according to our expectations. The data could be described using a modified Rouse model with varying amplitudes.

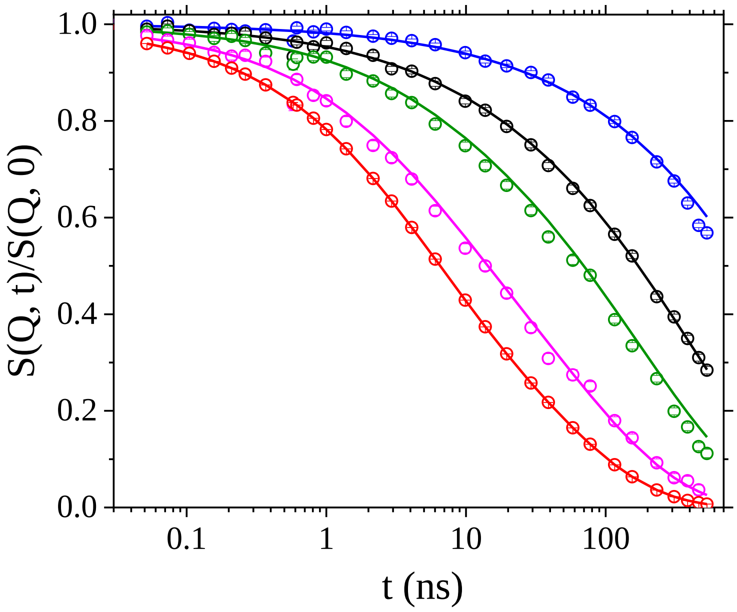

Figure 2. NSE data from blend of h-PEO (10%) and d-PEO (90%) at 413K. The lines are fitted Rouse modes analysis.

On the other hand, data from the one component nanocomposites contained significant artifacts. We show the data from dh as well as dhd samples in Figure 3.

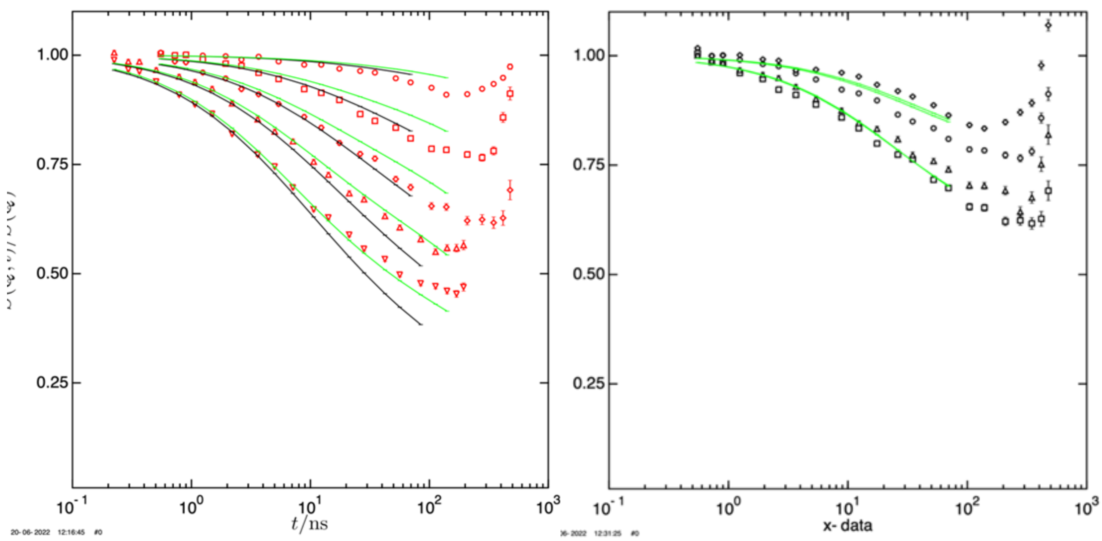

Figure 3. (a) NSE data from dh (fully labelled samples) and (b) from dhd (half chain labelled samples). The lines are different attempts to fit the data using Rouse mode analysis with constant and varying friction.

As could be seen in the Figure 3, both dh and dhd one component nanocomposites show a decay in the echo at lower times but then the echo starts increasing with time at longer times. The increase in the echo signal with time is unphysical and hence must be arising from some artifact.

The oven used to heat the samples was a new one and our samples were the first official samples which used this oven. Most probably, the upturning of NSE data is caused by instrumental failure, the reason of which is unknown to us.

The solid lines in the Figure 3 are attempts to describe the data using modified Rouse mode analysis. We introduce the varying friction along the grafted polymer chain to capture the dh as well dhd data using same set of parameters. Our initial analysis indicates that the friction decreases along the grafted chain as one moves from the grafting point towards the chain end. Figure 4 shows the friction profile along the grafted chain.

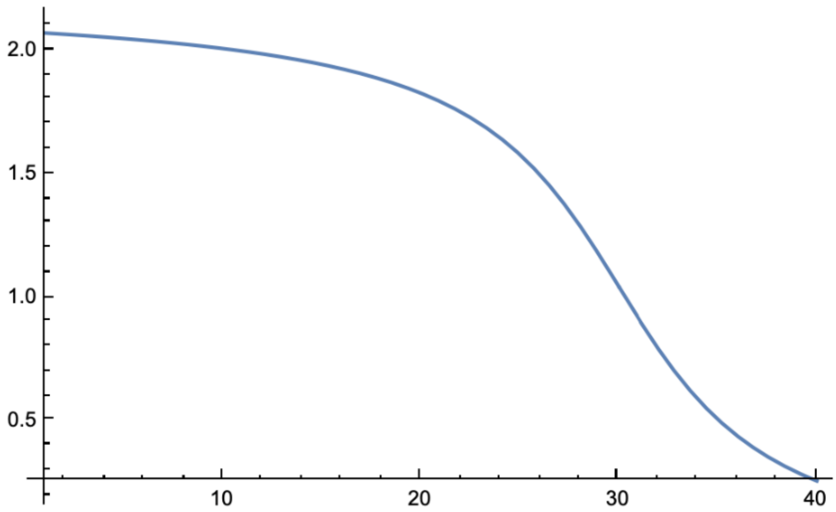

Fig 4. Friction profile for the grafted chain.

However, due to the artifacts in the NSE data, we cannot trust the quantitative results. There is no possible way to decide the time range in which the NSE data sets could be trusted. We do not notice any strong trend of these artifacts in Q. Therefore, the current results obtained from one component nanocomposites cannot be published. A repetition of the experiment on one component nanocomposites is must after the problems with the operation of IN15 are eliminated.

Conclusion:

The experiments performed on the neat polymer samples of polyethylene oxide were successful and the data obtained is analysed using Rouse mode analysis. On the other hand, the one component nanocomposites showed artificial upturn in the spin echo data which is an artifact generated due to malfunctioning of the IN15 instrument. Due to the uncertainty of the Fourier time at which this artifact is generated, we cannot analyse OCNC data with full confidence. Qualitatively, the data appears to advocate the presence of site dependent friction in the polymer brushes which could be introduced phenomenologically in the Rouse mode analysis model. Repetition of experiment is must to resolve the artifacts.