

## Dynamics in intercalated polymer-clay nanocomposites

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Layered-silicate based polymer nanocomposites represent an attractive set of organic-inorganic materials with great technological importance and at the same time convenient macroscopic systems for studying fundamental scientific problems. Mixing polymers with inorganic materials may result in three different nanostructures, the *phase separated* composites where the polymer and inorganic material are immiscible, the *intercalated* where the polymer chain is intercalated between the inorganic layers and the *exfoliated* where the silicate layers are dispersed in the polymer matrix [1]. More specifically, in the case of intercalated hybrids, a 1.5-2.0 nm polymer film resides between parallel inorganic layers resulting in a well ordered multilayer with a repeat distance of a few nanometers offering a unique avenue to study the behavior of macromolecules in nanoscopic confinement (1-3 nm thick films) by utilizing conventional analytical techniques on macroscopic samples. The study of the dynamics of small- and macro-molecules in thin films or in pores has been of high scientific interest [2] and the specific system of intercalated polymer silicate hybrid offers the opportunity of investigating confined systems in the nanometer scale. In this work we study the effect of this severe confinement on the segmental dynamics, the overall motion of a polymer chain, as well as of the different side groups attached on the backbone of the chain. The systems studied are poly(methyl-phenyl-siloxane) (PMPS,  $M_w = 2600$ ,  $M_w / M_n = 1.20$ ,  $T_g = 223\text{K}$ ) homopolymers and poly(styrene-b-isoprene) (SI,  $M_w = 15700$ ,  $w_{PS} = 0.55$ ,  $T_{g,PI} = -60\text{ }^\circ\text{C}$ ,  $T_{ODT} = 100\text{ }^\circ\text{C}$ ) diblock copolymers mixed from the melt with organophilic montmorillonite hectorite. X-ray diffraction measurements were used to verify intercalation: the increase of the  $d_{001}$  spacing of the nanohybrid with respect to that of the parent silicate by approximately 10-13Å establish the intercalation.

Dielectric spectroscopy is used to probe the segmental motion of confined PMPS [3] as well as the segmental and overall motion in the SI/M system. The segmental dynamics in confinement was significantly faster than the respective in the bulk and with a much weaker temperature dependence. In order to continue this investigation, extend the time scale of the dielectric studies, add a length scale component, and also study how the side groups motion is affected by the confinement, elastic and quasielastic neutron scattering measurements were performed (in the IN16 backscattering spectrometer, at ILL Grenoble). For the elastic measurements the total scattered intensity from the samples is measured as a function of temperature covering the range  $1.5 < T < 360\text{K}$ . Figure 1 shows the elastic scans for the silicate matrix, the PMPS homopolymer, and the composite at a series of wavevectors. The data for PMPS and the composite exhibit two distinct relaxation processes which correspond to the rotation of the methyl group (the one at low temperatures) and to the  $\alpha$ -relaxation (at higher temperatures) whereas there is only a very broad decrease of the scattered intensity for the silicate.

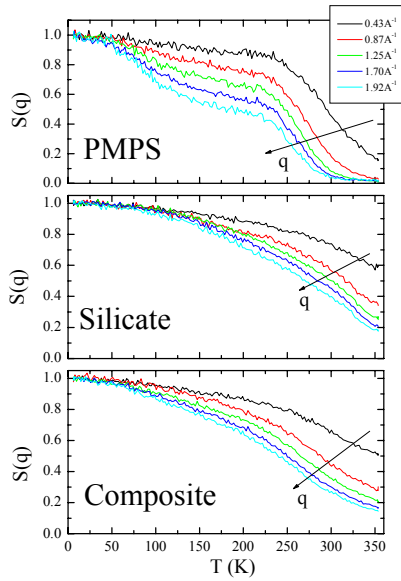


Figure 1: Elastic scans for the bulk and the confined PMPS as well as the silicate matrix.

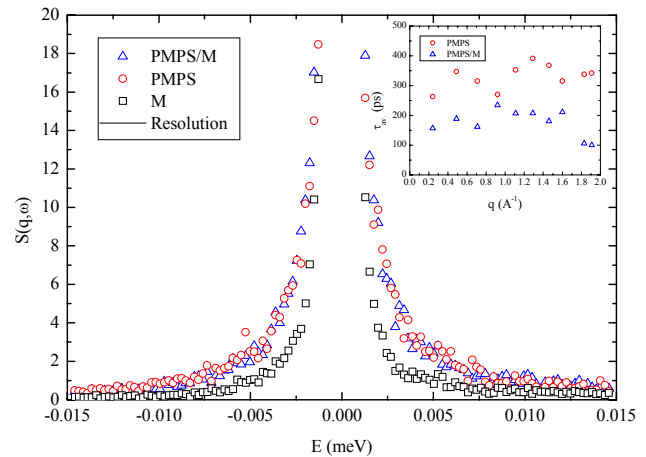


Figure 2: Quasielastic spectra of the silicate, the PMPS and the PMPS/M at  $q=1.46\text{\AA}^{-1}$  and  $T=100\text{K}$  with the line corresponding to the instrumental resolution. The average relaxation times are shown in the inset

Figure 2 shows the incoherent structure factor for the inorganic matrix M, the PMPS homopolymer, and the PMPS/M nanocomposite for a wavevector  $q=1.46\text{\AA}^{-1}$  and for  $T=100\text{K}$ , i.e., in the range of the methyl rotation. The instrumental resolution function which is also included in the plot assures the absence of any dynamics in the silicate at this temperature. The average relaxation time of the methyl group rotation which is included in the inset shows that there is no wavenumber dependence in any of the systems and becomes slightly faster under confinement.

In conclusion, our study results in much faster dynamics of the segmental motion for the confined system with respect to the bulk. The methyl group seems to be only slightly affected by the severe confinement whereas more sophisticated studies are needed in order to reveal the effect on the overall motion of the chains.

### References:

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