

LOCAL DYNAMICS OF BULK AND NANOPARTICLE FILLED POLY(VINYL ACETATE) OBSERVED BY QUASIELASTIC NEUTRON SCATTERING

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The addition of nanoparticles to polymers leads to changes in the physical and mechanical properties of the matrix. This effect depends on parameters such as particle size, shape and distribution, state of dispersion in the matrix, particle-particle as well as particle-matrix interactions.

One of the major consequences of adding particulate fillers to a polymer is the formation of an "interphase", *e.g.* the bound rubber in rubber/filler composite. Changes in chain dynamics at the polymer-filler interface play an important role in the reinforcement effect [1-2] but aggregation of filler particles arising from filler-filler interactions probably also contributes to the reinforcement [3].

While many studies of filled polymers have focused on the mechanical and rheological behaviour, there have been fewer measurements attempting to investigate the changes in chain dynamics, at the microscopic level. Our aim has been to characterize the local polymer dynamics in filled systems, using quasielastic neutron scattering (QENS) [4,5], hoping to combine microscopic information with macroscopic behaviour.

Polymer motion is per se a complex issue. The large size of any polymeric chain means that molecular motion occurs over a wide range of distances and frequencies. It is therefore crucial, in dynamic studies, to use a combination of experimental methods in order to probe a wide dynamic range. This is particularly true for quasielastic neutron scattering and much can be gained in this case by using a range of instruments differing in energy resolution and energy window.

The aim of the measurements carried out on MIBEMOL was to complement existing data collected on the backscattering spectrometers IN10 (ILL) and IRIS (ISIS) (Table 1). The system chosen for the study is poly(vinyl acetate) (PVAc, $M_w = 237,100$ g/mol, $M_w/M_n = 2.64$). Fumed silica particles with specific surface area equal to 90 (A90) and 300 (A300) m^2/g were used as filler.

At temperatures below the glass transition ($T_g = 314$ K), rotational motion of the methyl groups dominates the PVAc dynamics. Previous measurements carried out on IRIS with the PG004 analyser had shown that the motion of the CH_3 groups can be modeled by the rotational rate distribution model (RRDM). However, a Q and temperature dependent background was observed,

which suggested the existence of a fast process. This was confirmed by the time-of-flight data collected on MIBEMOL. As shown in Figure 1, at $T < T_g$, the MIBEMOL data consist of three components: (a) a fast process which has a Lorentzian shape, (b) a slower process due to the CH_3 motion and (c) an elastic component.

Table 1. Characteristics of neutron spectrometers.

Instrument	Energy resolution (FWHH)	Energy range	Q range
IN10	1 μ eV	-13 ~ 13 μ eV	0.5 \AA^{-1} ~ 1.96 \AA^{-1}
IRIS	PG004: 54.5 μ eV ($< T_g$)	-4 ~ 4 meV	0.3 \AA^{-1} ~ 3.7 \AA^{-1}
	PG002: 15 μ eV ($> T_g$)	-0.2 ~ 1.2 meV	0.25 ~ 1.9 \AA^{-1}
MIBEMOL	$\lambda_i = 6$ \AA : 107 μ eV	-1 ~ 10 meV	0.72 \AA^{-1} ~ 1.95 \AA^{-1}
	$\lambda_i = 3$ \AA : 850 μ eV	-5 ~ 50 meV	0.92 \AA^{-1} ~ 3.90 \AA^{-1}

FWHH= full width at half height, $Q = 4\pi/\lambda \sin(\theta/2)$, λ =neutron wavelength, θ = scattering angle.

The intermediate scattering function, $I(Q,t)$, obtained via inverse Fourier transform, shows that there is good overlap between data obtained from IRIS and MIBEMOL (Figure 2). A CONTIN analysis of the overlapped $I(Q,t)$ data indicates that the distribution of relaxation times is made up of two distinct processes.

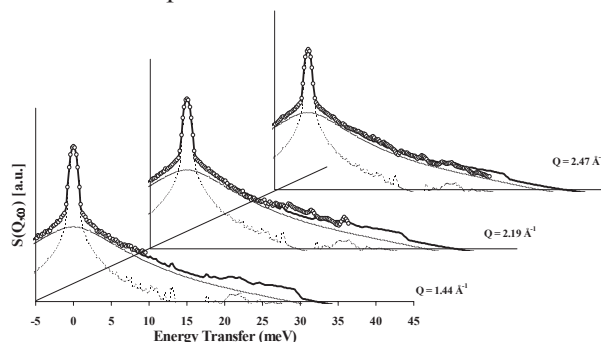


Figure 1. QENS spectra of PVAc (FWHH=850 μ eV) at 150 K: data points (\circ) and fits (continuous line). The dotted line is the contribution from CH_3 motion and the dashed line shows the fast process.

Above the glass transition, measurements carried out on IN10 and IRIS (PG002), enabled us to probe the segmental motion of the PVAc chains and its temperature dependence. The QENS spectra were fitted using a Kohlrausch-Williams-Watts (KWW) function, convoluted with the instrumental resolution plus a flat background. This procedure leads to two parameters: the shape parameter β ($\beta=0.58$, independent of temperature) and the characteristic time τ_{KWW} . The latter was

found to vary as Q^{-n} , with n close to 2, independent of temperature, as expected for a diffusive process. The temperature dependence of τ_{KWW} is expressed by the Vogel-Fulcher-Tammann (VFT) equation, in agreement with results from other techniques such as dielectric spectroscopy.

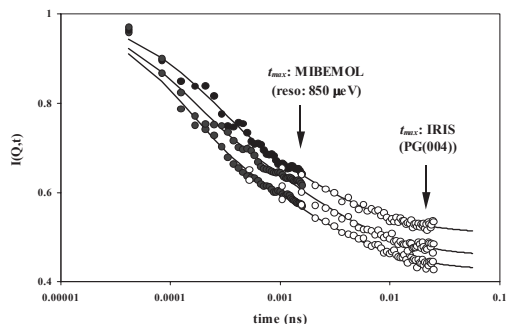


Figure 2. $I(Q,t)$ data of PVAc at 150 K and $Q = 1.68, 1.91$ and 2.13 \AA^{-1} (top to bottom) from MIBEMOL (\bullet) and IRIS (PG004) (\circ). The lines are fits to the experimental data using a two-process model.

Similarly to the QENS data at $T < T_g$, the higher temperature QENS spectra from the IRIS spectrometer had revealed the existence of a Q and temperature dependent background. By combining results from the analyses below and above T_g , the fast process observable on MIBEMOL was found to follow an Arrhenius temperature dependence with an activation energy of 1.9 kJ/mol.

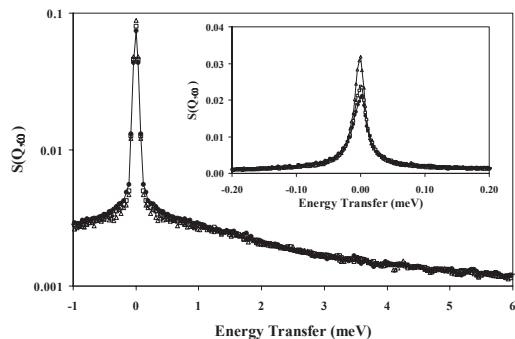


Figure 3. Normalized QENS spectra from MIBEMOL (FWHH: $107 \mu\text{eV}$) of PVAc (\bullet) and PVAc containing 40 wt% A90 (\square) and A300 (Δ) at 1.68 \AA^{-1} and 400 K. Inset: normalized QENS spectra of the same samples from IRIS (PG002) at 1.58 \AA^{-1} and 478 K.

The QENS measurements carried out on PVAc samples containing A300 and A90 indicated that the addition of the filler particles has a negligible effect on the sub- T_g dynamics. However, at $T > T_g$,

there exists a portion of chains with reduced mobility compared to the pure polymer and it increases with increasing the particle surface area and filler content. The dynamic restriction is evident at all resolutions (Figure 3). The QENS spectra of the filled samples show bimodal dynamics *i.e.* a portion of the chains has unperturbed dynamics while a smaller fraction seems to be “immobile” within the timescale of the experiment. This immobile fraction is believed to be related to the “bound” polymer layer that is chains strongly interacting with the surface.

The density of states spectra obtained on MIBEMOL indicate some interesting features. As shown in Figure 4 two distinct peaks can be observed, centered at ca. 18 and 32 meV for both bulk and filled PVAc at $T < T_g$. The position of the latter peak is close to the value calculated from the attempt frequency of the fast process ($\Gamma_\infty = 30.2 \text{ meV}$) obtained from the analysis of the MIBEMOL QENS spectra. The intensity of the two peaks decreases with increasing the filler surface area. At 400 K ($T > T_g$), the density of states of pure and filled polymers show significant differences. For pure PVAc, an additional broad peak, probably ascribed to the vibrational modes associated with the backbone, appears at higher energy but it is almost unnoticeable in the filled PVAc samples (Figure 4).

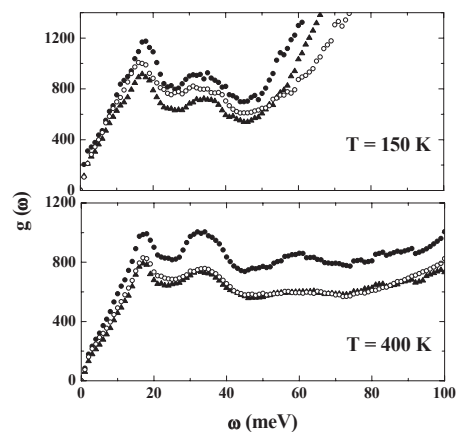


Figure 4. Hydrogen-weighted vibrational density of states for PVAc (\bullet) and PVAc filled with 40% (w/w) A90 (\circ) and A300 (\blacktriangle) at 150 K and 400 K (MIBEMOL, FWHH: $107 \mu\text{eV}$)

References

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