

LOCAL DYNAMICS UNDER SEVERE CONFINEMENT IN NANOCOMPOSITES

S. H. Anastasiadis,[†] K. Karatasos,[‡] and G. Vlachos
 Foundation for Research and Technology-Hellas
 Institute of Electronic Structure and Laser
 P. O. Box 1527, 71110 Heraklion, Crete, Greece

E. Manias,[§] and E. P. Giannelis
 Cornell University

Department of Materials Science and Engineering
 Ithaca, NY 14853, U.S.A.

Introduction

Intercalation of polymers in layered silicate hosts is a promising way to synthesize polymer nanocomposites, an attractive set of organic-inorganic hybrid materials because of their high technological potential [1]. Of special interest to this work are the *intercalated* nanocomposites, in which in which a 1.5-2.0 nm polymer film is intercalated between parallel inorganic layers resulting in a well ordered multilayer with a repeat distance of a few nanometers. The intercalated polymer/silicate nanocomposites offer a unique avenue for studying the static and dynamic behavior of small molecules and macromolecules in nanoscopic confinements: one can utilize conventional analytical techniques (e.g., thermal analysis, NMR, dielectric spectroscopy, inelastic neutron scattering, rheology) on macroscopic samples and, nevertheless, study the properties of 1-3 nm thick polymer films [2]

The dynamics of small- and macromolecules in thin films or in pores has been attracting the scientific interest. For supported films, the effective glass transition temperature (T_g) decreases [6] with decreasing film thickness h except for strongly attractive substrates [7c]. For freely standing films, the effects are strong [8]: for $h < R_g$, T_g decreases linearly with decreasing h (R_g is the bulk gyration radius) with as much as 70°C reduction for $h \approx R_g$. The existence of a thin (a few nm) "interphase" layer (more mobile for neutral or free surfaces and less mobile near an attractive wall) affecting the T_g and the segmental dynamics has been proposed [6,7]. The shape of the relaxation function for freely standing films is found similar to that in the bulk and the temperature (T) dependence of the relaxation times is accounted for by a simple T_g -shift [5c]. For small molecules confined within pores, T_g decreases with decreasing pore size [8], whereas slightly slower [9] or slightly faster [10,6] local dynamics in the pores is observed as well as extra broadening of the relaxation function [11]; the issue of a cooperativity-length determining the dynamic glass transition has been raised [6,9-11]. Recently, very fast dynamics is observed under severe confinement [11].

In this report, a dielectric spectroscopy investigation is presented aiming to probe the role of nano-confinement on the segmental motion of poly(methyl phenyl siloxane) (PMPS) utilizing intercalated polymer/silicate nanocomposites with 1.5-2.0 nm thin PMPS films confined between with organically-modified parallel silicate layers. A relaxation mode much faster than the bulk α -relaxation is consistently observed with a weak T dependence. This should be attributed either to the restrictions placed by the interlayer spacing on the cooperative volume of the α -relaxation or to the dominant contribution of more mobile interphase regions.

Experimental

Organically modified layered silicates were prepared by a cation exchange reaction between the layered silicate hosts and excess dioctadecyl-dimethyl-ammonium bromide (to render the originally hydrophilic silicate surface organophilic). Hybrids were prepared by mixing at $\sim 60^\circ\text{C}$ under ultrasonication dry organosilicate and PMPS ($M_w=2600$, $M_w/M_n=1.20$, $T_g=223\text{K}$) of various concentrations in order to span the range from starved to just over full galleries. The hybrids as well as the silicates were characterized by x-ray diffraction in order to determine the interlayer spacing (Table 1).

[†] Also at University of Crete, Physics Dept., 710 03 Heraklion Crete, Greece
[‡] Present Address: University of Leeds, Department of Physics and Astronomy, Leeds LS2 9JT, U. K.
[§] Present Address: Pennsylvania State University, Department of Materials Science and Engineering, University Park, PA 16802, U.S.A.

Table 1. Sample Characteristics

Code	Silicate	Polymer	wt% Polymer	d_{100} spacing
H ¹	2C18-HT	-	-	23 ¹
M ²	2C18-MMT	-	-	25 ¹
15%	2C18-HT	PMPS	15	33 ^{1,3}
25%	2C18-MMT	PMPS	25	36 ¹

1 H: dimethyl-dioctadecyl-ammonium modified hectorite; 2 M: dimethyl-dioctadecyl-ammonium modified montmorillonite; 3 A weak diffraction peak at 23¹ d-spacing indicates the existence of non-intercalated silicates (polymer-starved system)

Dielectric spectroscopy, DS, was used to investigate the collective segmental dynamics of PMPS in the frequency range 10^{-2} to 10^7 Hz (Solatron-Schlumberger frequency response analyzer FRA 1260). The measured complex dielectric permittivity $\tilde{\epsilon}^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ is given by the one-sided Fourier transform of the time derivative of the dipole-dipole correlation function $C(t)$; for non-zero dipole moment perpendicular to the chain backbone, $C(t)$ probes local motions. The sample was pressed in form of a pellet and was residing between two gold-plated stainless steel electrodes (diameter 20 mm) in a cryostat with its T controlled ($\pm 0.1^\circ\text{C}$) via a nitrogen gas jet heating system with a Novocontrol Quatro controller. The experimental $\tilde{\epsilon}^*(\omega)$ were inverted [12] in order to determine the distribution of relaxation times $\tilde{F}(\ln\tau)$ without any *a priori* assumption of the form of the relaxation function but only of a superposition of Debye processes.

Results and Discussion

Fig. 1 shows the dielectric loss, $\epsilon''(\omega)$, versus frequency for the 25% PMPS/M together with that for the organosilicate M at 193 K (below the bulk T_g). The silicate spectra are quite broad and complicated over the whole T -range but their contribution can be subtracted from the data of the composites (Fig. 1). The resulting "net-loss" data correspond to the reorientational motion of PMPS confined within the galleries. A very fast process dominates the spectra, it is observed at T 's much lower than bulk-PMPS T_g and exhibits a weaker T -dependence than that of the bulk-PMPS α -relaxation; such process is not observed in neat PMPS or in neat silicates. The line in Fig. 1 is the fit to the net-loss data in order to determine the distribution spectra $\tilde{F}(\ln\tau)$ (inset); the most probable relaxation times correspond to the maxima of $\tilde{F}(\ln\tau)$. Besides the fast process, a weak slower one (exhibiting a weak T -dependence, too) is also evident as a shoulder in the net-loss data. This behavior is observed for the 25% PMPS/M for $173 < T < 213\text{K}$. At higher T 's, a process with very weak amplitude which superimposes on the neat-PMPS α -relaxation is also observed (not shown), which corresponds to minute PMPS amounts not intercalated within the galleries.

Fig. 2 shows an Arrhenius plot of the most probable relaxation times of the processes associated with PMPS for the 25% PMPS/M. The slow process (bulk-PMPS like) is similarly evident for all compositions investigated with its dielectric strength very small for the apparently starved 15% PMPS/H.

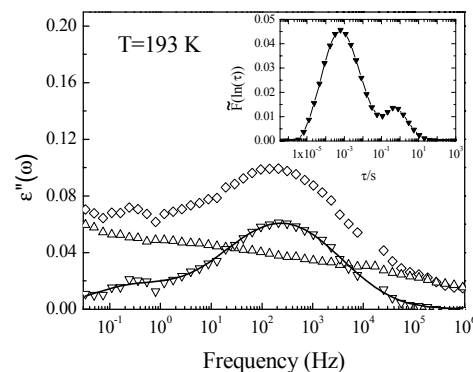


Figure 1. $\epsilon''(\omega)$ vs. frequency for silicate M (Δ), the 25% PMPS/M composite (\diamond), and the difference spectrum (∇) at 193K. Inset: $\tilde{F}(\ln\tau)$ from the inversion of the net loss spectrum.

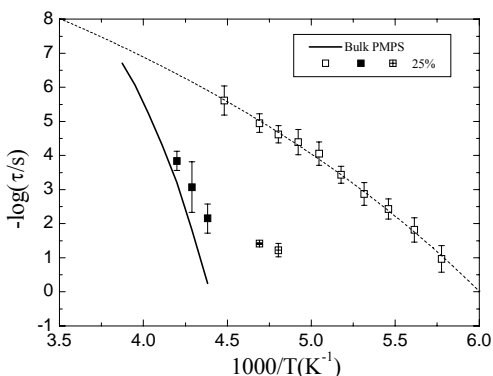


Figure 2. Arrhenius plot of the relaxation times associated with bulk-like PMPS (slow), confined PMPS (fast), and the intermediate process (shoulder in Fig. 2) for the 25% PMPS/M. (□): bulk PMPS. (---): VFT fit to the data.

The intermediate process appears in the same range of times with one of the two processes observed for the bare M organosilicate (possibly related to orientational motions of the surfactant). The fast process due to the confined PMPS shows the very weak T -dependence in all cases. The dynamics appears to eventually merge with that for bulk PMPS at high T 's, whereas at 228 K (near the bulk T_g) it is by 6 decades faster. Analysis of the temperature dependence of the fast process with the Vogel-Fulcher-Tamman (VFT) equation, $-\log \tau = -\log \tau_0 - B/(T - T_0)$, leads to the Vogel temperature $T_0 = 93 \pm 2$ K, which is ~ 100 K lower than $T_{0,\text{bulk}} = 195 \pm 2$ K, and to $B = 962 \pm 20$ K (all data but the 15%), much different from that for bulk PMPS ($B_{\text{bulk}} = 440 \pm 30$ K). The fragility parameters, $D = B/T_0$, of 10.3 (confined) and 2.3 (bulk) indicate that the confinement influences the landscape of the potential for conformational rearrangement. The data in Fig. 2 cannot be superimposed when plotted vs. $1/(T - T_0)$, i.e., a simple T_0 -shift is not sufficient to account for the behavior, in disagreement with the freely standing films data [5c].

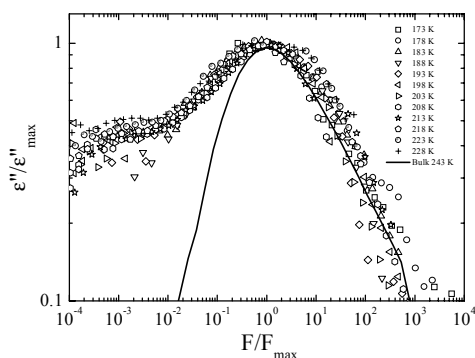


Figure 3. Normalized net dielectric loss $\varepsilon''(\omega)/\varepsilon''_{\text{max}}$ for the 25% PMPS/M vs. reduced frequency F/F_{max} for the fast process of Fig. 1 together with the bulk-PMPS α -relaxation at 233K (line).

The shape of the relaxation function is an important characteristic. Fig. 3 shows the normalized net loss $\varepsilon''(\omega)/\varepsilon''_{\text{max}}$ for the fast process of the 25% PMPS/M vs. reduced frequency together with that of bulk-PMPS α -process. The shape of the loss data is only a weak function of T and apparently not very different from that in bulk, which is insensitive to T and slightly broader at high frequencies; the high-frequency slopes are -0.50 (confined) and -0.37 (bulk); the shoulder at low frequencies complicates the slope comparison. The shape-similarity agrees with the behavior of freely standing films [5c] but not with that of small molecules within pores [11].

The existence of such fast dynamics within the galleries should be discussed. The argument of a characteristic length scale ξ of cooperatively rearranging regions has been invoked in studies of low-molecular-weight glass-formers. For salol confined in nanopores (2.5, 5.0, and 7.5 nm), the slightly faster dynamics within the pores lead to an estimation of $\xi \approx 7$ nm near the calorimetric T_g [10]. The effective confinement in that case was much less than the one herein; here the interlayer spacing d available to the polymer chain is about 1.5-2.0 nm, which is of the order of a few statistical segment lengths of PMPS. Such severe confinement was recently investigated [11] for ethylene glycol (EG) confined to zeolitic hosts. DS together with computer simulations revealed that, when at least six EG molecules were able to rearrange cooperatively in the pores, bulk-like behavior was obtained; however, when the confinement was even stronger, the dynamics of the EG molecules was dramatically faster and exhibited an Arrhenius T -dependence. Within the cooperativity argument one may think that at very high temperatures, ξ is smaller than d ; thus, no difference can be expected between bulk and confined PMPS. As T decreases, the dynamics deviate from an Arrhenius T -dependence at the onset of cooperativity. In the bulk, ξ increases unhindered whereas within the galleries the increase of ξ is limited by d . Thus, bulk dynamics can be increasingly retarded compared to that within the galleries. The effects of the interplay between ξ and d on the α -dynamics has recently been considered [6b]; for d smaller than the nominal ξ , faster dynamics is expected as d decreases.

The effects on dynamics of the perturbation in the chain structure / orientation within an "interphase" next to a wall may alternatively be considered. Simulations show that chains adopt a preferentially parallel configuration near a wall with oscillations in the monomer density profile. These lead to a dynamic anisotropy with enhanced parallel and reduced perpendicular monomeric-mobilities extending over distances which increase with supercooling in excess of the chain end-to-end distance; fitting the mobilities to a VFT equation results in the same T_0 but different B 's [7]. Under severe confinement, this interphase is anticipated to extend over the whole film thus leading to a fast relaxation. Variation of the effective relaxation times across a thin film has also been proposed in order to explain the fast dynamics in both thin films and porous media [6b,8,11].

Concluding Remarks

Dielectric Relaxation Spectroscopy has been utilized to probe local dynamics in a series of nanocomposites consisting of PMPS intercalated in organically modified silicates. X-ray diffraction showed that PMPS is confined within 1.5-2.0 nm. The effect of confinement is directly reflected on the local reorientational dynamics, as evidenced by the observation of a new mode much faster than the segmental α -relaxation of the bulk polymer and characterized by a much weaker temperature dependence. Interpretation of the observed behavior in terms of the current views on local dynamics in confinement is discussed; the data qualitatively support the cooperativity arguments without, however, being able to exclude the layering idea.

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