

Nanoscope-Confinement Effects on Local Dynamics

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(Received 19 February 1999)

The segmental dynamics of 1.5–2.0 nm polymer films confined between parallel solid surfaces is investigated with dielectric spectroscopy in polymer/silicate intercalated nanocomposites. The confinement effect is evident by the observation of a mode, much faster than the bulk-polymer α relaxation and exhibiting much weaker temperature dependence. This is discussed in relation to either the interlayer spacing restricting the cooperative volume of the α relaxation or to the dominance of the more mobile interphase regions as predicted by simulations; the data qualitatively support the former.

PACS numbers: 61.41.+e, 68.15.+e, 77.22.Gm

Intercalation of polymers in layered-silicate inorganic hosts is a way to synthesize polymer nanocomposites, an attractive set of organic-inorganic hybrids because of their high technological potential [1]. Beyond the conventional phase separated polymer/silicate nanocomposites, two types of hybrids are possible: *intercalated*, in which a 1.5–2.0 nm polymer film resides between parallel inorganic layers resulting in a well-ordered multilayer with a periodicity of a few nm's; *exfoliated* (the silicate layers are dispersed in a continuous polymer matrix). The intercalated hybrids offer a unique avenue to study the static/dynamic behavior of macromolecules in nanoconfinement; one can utilize conventional analytical techniques on macroscopic samples and, nevertheless, study the properties of 1–3 nm films [2].

The dynamics of small and macromolecules in thin films or in porous media has been attracting the scientific interest [3–15]. For supported films, the effective glass transition temperature (T_g) decreases [3] with decreasing film thickness (h) except for strongly attractive substrates which lead to T_g increases [4]. For freely standing films, the effects are strong [5]: for $h < 2R_g$, T_g decreases linearly with decreasing h (R_g is the bulk gyration radius) with as much as 70 °C reduction for $h \cong R_g$. Although it was suggested [6] that the effects are due to density modifications near the interfaces (lower at free surfaces and higher near attractive walls), experiments in both supported and freely standing films do not show measurable density changes for h as low as $0.37R_g$ [7]. Alternatively, 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 [3,8]. 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 [5]. For small molecules confined within pores, the calorimetric T_g decreases with de-

creasing pore size [9], whereas their spin-lattice NMR relaxation times are shorter than in the bulk [10]. Slightly slower [11,12] or slightly faster [8,13,14] local dynamics in the pores is observed as well as an extra broadening of the relaxation function [11,14,15], whereas the issue of a cooperativity length determining the T_g has been raised [8,11–15]. Recently, very fast dynamics is observed under severe confinement [15]. Finally, coating the pore surface influences the dynamics [10,12,13].

In this Letter, a dielectric spectroscopy investigation is presented aiming to probe the role of nanoconfinement on local dynamics utilizing intercalated polymer/silicate nanocomposites. Polymethylphenylsiloxane (PMPS) forms an intercalated hybrid when mixed with organically modified layered silicates resulting in 1.5–2.0 nm thin PMPS films confined between parallel layers; the PMPS segmental motion is dielectrically active. A relaxation mode much faster than the bulk α relaxation is observed with a weak T dependence. This should be attributed to either 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.

Organically modified layered silicates were prepared by a cation exchange reaction between the Na^+ in the silicate hosts and dioctadecyl-dimethyl-ammonium bromide at exchange capacity [16], in order to render the originally hydrophilic silicate surface organophilic. Hybrids were prepared by mixing dry organosilicate and PMPS ($M_w = 2600$, $M_w/M_n = 1.20$, $T_g = 223$ K) with various PMPS concentrations (Table I) in order to span the range from starved to just-over-full galleries. Sufficient time was allowed at ~ 60 °C under ultrasonication for the chains to diffuse into the silicates. The hybrids as well as the silicates were characterized by x-ray diffraction (Scintag θ - θ diffractometer with a Ge detector using Cu $K\alpha$ radiation) in order to determine the interlayer spacing (Table I).

Dielectric spectroscopy was used to investigate the collective segmental dynamics of PMPS in the frequency

TABLE I. Characteristics of the samples.

Code	Silicate	Polymer	wt% Polymer	d_{100} Spacing
H^a	2C18-HT	23 Å
M^b	2C18-MMT	25 Å
15%	2C18-HT	PMPS	15	33 Å ^c
20%	2C18-MMT	PMPS	20	32 Å
25%	2C18-MMT	PMPS	25	36 Å
30%	2C18-HT	PMPS	30	34 Å

^a H : Dimethyl-dioctadecyl-ammonium modified hectorite.

^b M : Dimethyl-dioctadecyl-ammonium modified montmorillonite.

^cA weak diffraction peak at 23-Å d spacing indicates the existence of nonintercalated silicates (polymer-starved system).

range 10^{-2} to 10^7 Hz (Solatron-Schlumberger frequency response analyzer FRA 1260). The measured complex dielectric permittivity $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ is given by the one-sided Fourier transform of the time derivative of the dipole-dipole correlation function $C(t)$; for a nonzero dipole moment perpendicular to the chain contour, $C(t)$ probes local motions. The sample, pressed in the form of a pellet, was residing between two gold-plated stainless steel electrodes (diameter 20 mm) in a cryostat with its T controlled via a nitrogen gas jet heating system with a Novocontrol Quatro controller (sample T of ± 0.1 °C in the range -160 to $+300$ °C). The experimental $\epsilon''(\omega)$ data were inverted [17] in order to determine the distribution of relaxation times $\tilde{F}(\ln\tau)$ assuming only a superposition of Debye processes: $\epsilon''(\omega) = \int_{-\infty}^{\infty} \tilde{F}(\ln\tau) \{\omega\tau/[1 + (\omega\tau)^2]\} d(\ln\tau)$; integration of $\tilde{F}(\ln\tau)$ yields the relaxation strength $\Delta\epsilon$.

Figure 1 shows the dielectric loss, $\epsilon''(\omega)$, versus frequency for the 20% PMPS/ M together with that for the organosilicate M at 193 K (below the bulk-PMPS T_g). The silicate spectra are quite broad and complicated over the whole T range but their contribution can be subtracted

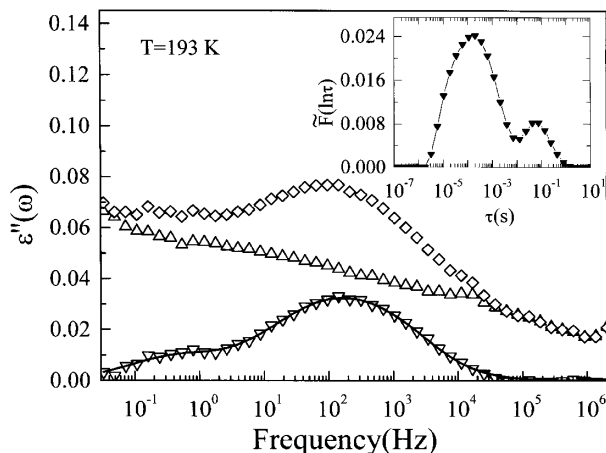


FIG. 1. Dielectric loss $\epsilon''(\omega)$ vs frequency for the organically modified silicate M (Δ), for the 20% PMPS/ M composite (\diamond), and the difference spectrum (∇) at 193 K. Inset: Distribution of relaxation times $\tilde{F}(\ln\tau)$ from the inversion of the net-loss spectrum. Error bars are smaller than the size of the symbols ($\sim 1\%$).

from the data of the composites (Fig. 1). The resulting “net-loss” data correspond to the motion of PMPS confined within the galleries and are shown in Fig. 2(a). 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 a process is not observed in neat PMPS or in neat silicates. The lines in Figs. 1 and 2(a) are the fits to the net-loss data in order to determine the distribution spectra $\tilde{F}(\ln\tau)$ (inset of Fig. 1); 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. At even higher T 's [18], a process with very weak amplitude which superimposes on the neat-PMPS α relaxation is also observed (not shown), which corresponds to not intercalated minute PMPS amounts.

Figure 3 shows an Arrhenius plot of the most probable relaxation times of the processes associated with PMPS.

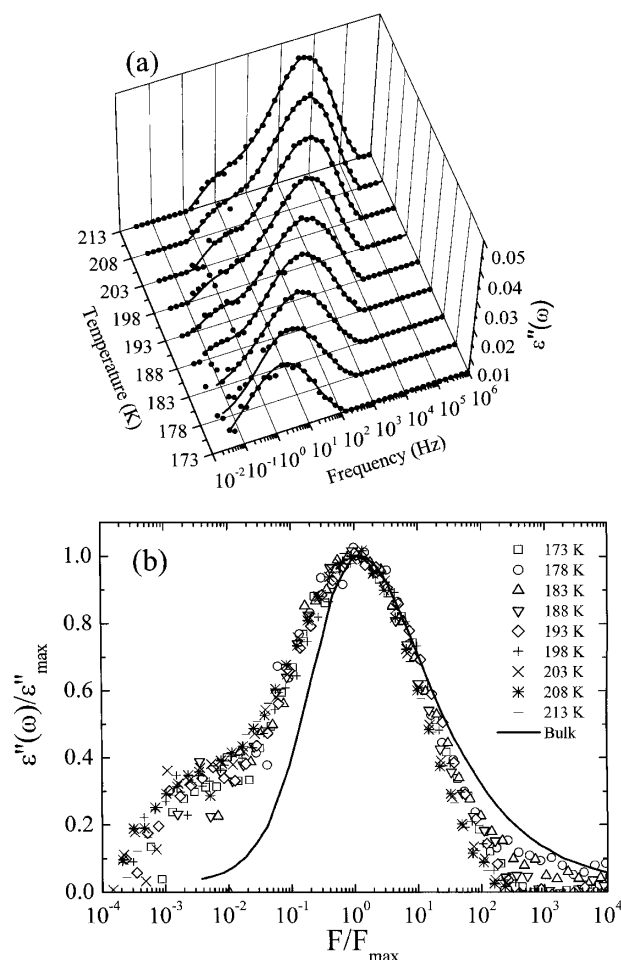


FIG. 2. (a) Frequency and temperature dependence of the net loss $\epsilon''(\omega)$ for 20% PMPS/ M intercalated silicate for temperatures 173–213 K. (b) Normalized net dielectric loss $\epsilon''(\omega)/\epsilon''_{\max}$ for the 20% PMPS/ M vs reduced frequency F/F_{\max} for the main process of (a) together with the bulk-PMPS α relaxation at 233 K (line). Individual error bars are smaller than the size of the symbols ($\sim 1\%$).

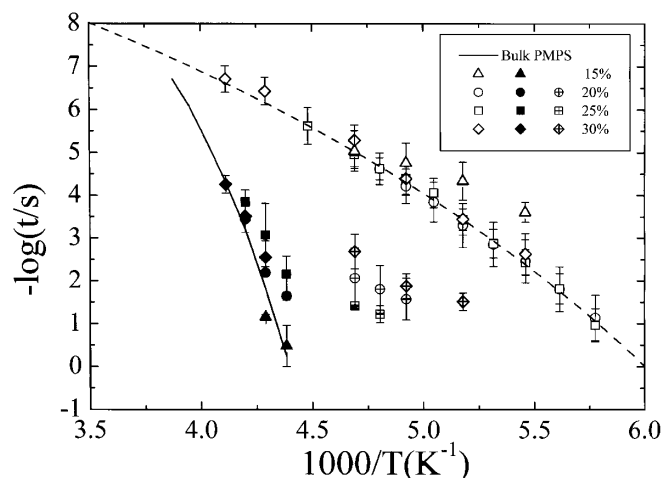


FIG. 3. Arrhenius plot of the relaxation times associated with bulklike PMPS (slow), the confined PMPS (fast), and the intermediate process (shoulder in Fig. 2) for all specimens; (—) bulk PMPS; (---) VFT fit to the data.

The error bars shown are estimated from the uncertainty of the spectra subtraction [18] and the inversion procedure. The slow process (bulk-PMPS-like) is evident for all compositions; its dielectric strength is very small in the 15% PMPS/*H*, which is apparently starved. The intermediate process appears in the same range of τ values with one of the two processes observed for the bare *M* organosilicate (possibly related to orientational motions of the surfactant); this possesses higher $\Delta\epsilon$ in the composite than in the pure *M* since the silicate contribution has already been subtracted (Fig. 1). The fast process due to the confined PMPS shows the very weak T dependence in all cases (it is weakest for the 15% PMPS/*H*). 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 six decades faster. At high T 's, it is impossible to clearly separate the bulklike and the fast processes due to their close temporal proximity and to the low amplitude of the bulklike one. The data for the fast process, if analyzed with the Vogel-Fulcher-Tamman (VFT) equation, $-\log\tau = -\log\tau_0 - B/(T - T_0)$, with τ_0 the microscopic time and T_0 the Vogel temperature, lead to $T_0 = 93 \pm 2$ 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) [19]. Moreover, $\tau_0 = 10^{-13}$ s similar to $\tau_{0,\text{bulk}} = 1.7 \times 10^{-13}$ s. The fragility parameters, $D = B/T_0$, of 10.3 (confined) and 2.3 (bulk) indicate that the confined PMPS behaves as a stronger glass (more Arrhenius-like), i.e., the confinement influences the landscape of the potential for conformational rearrangement. The data in Fig. 3 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 [5]. Note that no clear calorimetric T_g was observed (only a T_g corresponding to the excess PMPS was clearly identified in all but the 15% specimen).

The shape of the relaxation function is an important characteristic of the glass former. Figure 2(b) shows the normalized net loss $\epsilon''(\omega)/\epsilon''_{\text{max}}$ for the fast process of Fig. 2(a) vs reduced frequency together with that of bulk-PMPS α relaxation. 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 [19] and slightly broader at high frequencies; the high-frequency slopes in a log-log plot are -0.50 (confined) and -0.37 (bulk); note that the shoulder at low frequencies complicates the comparison of the slopes. The shape similarity agrees with the behavior of freely standing films [5] but disagrees with that of small molecules confined within pores [11,14,15].

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 leads to an estimation of $\xi \cong 7$ nm near the calorimetric T_g [13]. 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 [15] for ethylene glycol (EG) confined to zeolitic hosts. It was revealed that, when at least six EG molecules were able to rearrange cooperatively in the pores, bulklike 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 [20]. In the bulk, ξ increases unhindered as [20] $\xi \approx \xi_0 [T_0/(T - T_0)]^{2/3}$ (ξ_0 is a material specific constant), whereas within the galleries the increase of ξ is limited by d ; for $\xi_0 \approx 1.5$ nm (a few segment lengths), ξ exceeds 2.5 nm below 285 K. Thus, bulk dynamics can be increasingly retarded compared to that within the galleries. The effect of the interplay between ξ and d on the α dynamics has been considered [8]; for d less than the nominal ξ , faster dynamics is expected as d decreases. The data can, therefore, support the cooperativity idea with reasonable values of ξ_0 .

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 R_g ; fitting the mobilities to a VFT equation results in the same T_0 (equal to $T_{0,\text{bulk}}$)

but different B 's [6(d)]. Under severe confinement this interphase is anticipated to extend over the whole film thus leading to fast relaxation; note that the dielectric experiments cannot discern between parallel and perpendicular relaxations due to the random orientation of the silicates within the specimen. However, fitting the experimental data to a VFT leads to significant differences in both T_0 and B in apparent disagreement with the simulation, which, however, covered only three decades in mobility. Variation of the effective relaxation times across a thin film has been proposed to explain the fast dynamics in thin films and porous media [3,5,8].

The observation of fast dynamics is consistent with positron-annihilation-lifetime spectroscopy studies on the same hybrids [21] which showed no transition near the bulk T_g ; existence of fast dynamics in the confines was suggested by the slope of the positron lifetime with T . Moreover, spin-echo NMR on similar hybrids showed a very wide distribution of relaxation times including times much faster than in the bulk over a wide range of T 's above and below the bulk T_g ; concurrent Si-H cross-polarization NMR attributed the fast relaxations to segments located near the middle of the 2 nm layer [22].

A question one may pose is on the effect of the organic modifier on the PMPS motion, e.g., whether a mixing may occur between PMPS and the alkyl surfactant chains leading to faster dynamics. To address this, mixtures of PMPS with the amine derivative of the surfactant modifier were studied. For a polymer:amine weight ratio 62:38 (polymer to surfactant ratio within the gallery) two processes are observed: one corresponding to neat PMPS, and one even faster than the fast process in Fig. 3. The $\Delta\epsilon$ (scaling with the PMPS wt %) and the superimposition of the shape of the slower process indicate that it is due to PMPS-rich regions in a phase separated system, and, thus, direct comparison with the hybrids cannot be made, since the PMPS and the surfactant are in molecular proximity within the gallery. Besides, experiments on hybrids with a dielectrically transparent polystyrene did not indicate any fast process. Estimating the plasticization effect on the kinetics of intercalation showed that it is very minor relative to the effects observed [23].

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.

This research was sponsored by NATO's Scientific Affairs Division (Science for Stability Programme), by the

Greek General Secretariat for Research and Technology, by ONR, and the CCMR (funded by NSF).

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