Physical aging in PMMA/silica nanocomposites: Enthalpy and dielectric relaxation

Virginie M. Boucher [a], Daniele Cangialosi [b,*], Angel Alegrìa [b,c], Juan Colmenero [a,b,c],
Juan González-Irun [d], Luis M. Liz-Marzan [d]

[a] Donostia International Physics Center, Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain
[b] Centro de Física de Materiales Centro Mixto (CSIC-UPV/EHU), Pº Manuel de Lardizabal 5, 20080 San Sebastián, Spain
[c] Departamento de Física de Materiales, Universidad del País Vasco (UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain
[d] Universidad de Vigo, Deptartamento de Química Física Unidad Asociada CSIC, 36310 Vigo, Spain

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ABSTRACT

We have investigated the physical aging below the glass transition temperature, namely the slow evolution occurring in non-equilibrium glasses, of poly(methyl methacrylate)/silica (PMMA/silica) nanocomposites. To do so we have followed the time evolution of the enthalpy and that of the dielectric strength of PMMA β process during isothermal annealing. The results indicate that physical aging is generally accelerated in all nanocomposites in comparison to pure PMMA, despite the lack of effect of the nanoparticles on PMMA molecular dynamics. Furthermore, the shorter is the interparticle distance, and hence the higher is the area/volume of silica in PMMA, the more pronounced is such acceleration. The acceleration of the physical aging together with the invariance of PMMA dynamics in the nanocomposites in comparison to pure PMMA poses serious questions on the idea that the molecular mobility is the only responsible parameter for the rapidity of physical aging. Thus, an interpretation based on the free volume holes diffusion towards the external surface, in this case represented by the polymer/silica interface, is provided.

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1. Introduction

Physical aging in glass-forming systems, namely the slow evolution of properties towards the equilibrium occurring below the glass transition temperature (T_g), has been the subject of extensive investigation during the last decades [1,2]. Nowadays, general consensus has been attained that physical aging in "bulk" glass-forming systems depends on both the temperature and the structure, which determine the molecular mobility responsible for the time evolution of the properties of the glass former [3,4].

More recently, increasing interest has been devoted to the study of the physical aging process in polymer nanocomposites and other nanostructured glass-forming systems such as thin films and glass formers confined in nanopores [5]. In this case, the main challenge is the elucidation of the effect of confinement, induced by the presence of nanoparticles in nanocomposites, the matrix in nanoporous systems and the external surface in thin films, on the rate of physical aging. How the presence of a confining surface interferes on this process in comparison to the corresponding bulk system is a matter of open debate. As far as the molecular mobility is concerned, two opposing effects can result from the presence of such a surface: i) the length scale imposed by the confinement is comparable to that characteristic of the glass transition and this results in an acceleration of the associated mobility, the so-called finite size effects that speed up physical aging; ii) the dynamics close to the external surface, depending on the nature of such a surface, either speeds up or slows down and this, in turns, accelerates or slows down the physical aging process. It is noteworthy that both effects are relevant at length scales of the order of several nanometres. In particular, the length scale of the glass transition has been generally found to lie between 1 and 3 nm by means of different approaches [6–10], whereas recent molecular dynamics simulation reveals that the effect of the external surface on the dynamics of a typical glass former vanishes at several nanometres from the external surface [11,12].

According to the previous considerations, surface and finite size effects are of importance in affecting the rate of physical aging for glassy systems possessing typical length scale of the order of nanometres. Despite this, a number of experiments in polymer films with thickness in the micron range clearly display accelerated physical aging in comparison to the bulk counterpart [13–17]. The typical length scale of these systems is therefore far too large to justify any argument invoking the role of surface or finite size effects. Thus an alternative explanation has to be sought to explain the accelerated physical aging in such systems.

In this work, we monitored the physical aging process of poly(methyl methacrylate)/silica (PMMA/silica) nanocomposites possessing an interparticle distance in the micrometre range. To do so, we followed the evolution with time of the enthalpy – measured by

* Corresponding author. Tel.: +34 943 015389; fax: +34 943 015600.
E-mail address: swxcacad@sw.ehu.es (D. Cangialosi).

differential scanning calorimetry (DSC) – and the dielectric strength of PMMA secondary relaxation process – that dominates the dielectric response below the T_g – obtained by broadband dielectric spectroscopy (BDS). The latter technique was also employed to assess the effect of silica particles on PMMA molecular mobility. Similarly to polymer thin films [13–17], physical aging in PMMA/silica nanocomposites speeds up in comparison to pure PMMA and such acceleration is more pronounced for nanocomposites with larger ratio area of silica/volume of polymer. Furthermore no effect on mobility due to the presence of silica particles was found. An interpretation based on the diffusion of free volume holes towards the interface between the polymer and the nanoparticles has been provided.

2. Experimental

PMMA/silica nanocomposites were prepared via in-situ polymerization of methyl methacrylate in the presence of silica nanoparticles conveniently modified to improve the particles dispersion in the polymer matrix. The surface of the silica particles was modified by grafting 3-(trimethoxysilyl) propyl methacrylate (TPM) (samples labelled as A10 and V10) and octadecyltrimethoxy silane (OTMS) (sample labelled as V10) on the surface. Details about the preparation of the nanocomposites are reported elsewhere [18]. All nanocomposites had about 9% wt. silica content as determined by thermogravimetric analysis. The samples labelled as A10 and R10 possess silica particles with a diameter of 350 nm, whereas the silica particles present a diameter of 200 nm in the nanocomposite labelled as V10. Details of all investigated samples are reported in Table 1 including PMMA molecular weight and its distribution. TEM micrographs, displayed in Fig. 1, testify the good dispersion of silica particle in the PMMA matrix.

Thermal analyses of the samples were carried out by means of the differential scanning calorimeter (DSC) (DSC-Q2000 from TA-Instruments). The temperature was calibrated with melting indium. All DSC measurements were performed under nitrogen atmosphere on samples of about 10 mg. Hermetic aluminium pans were used for all the materials. In order to erase their previous thermal history, all samples were first heated to 423 K, and subsequently cooled down to room temperature at a cooling rate of 10 K min^{-1} for data collection.

DSC has been also employed to monitor physical aging. After erasing the thermal history above T_g, the samples were then cooled in liquid nitrogen and stabilized at 353 K for isothermal aging for a predetermined time ranging from 5 min to 35 days. The amount of enthalpy relaxed during aging for a period of time t_a at a given temperature T_a is evaluated by integration of the difference between the thermogram of the aged sample and the one of the unaged sample (recorded immediately after) according to the relation [20]:

$$\Delta H(T_a, t_a) = \int_{T_x}^{T_y} \left(C_p^a(T) - C_p^u(T) \right) dT. \tag{1}$$

In this equation, $C_p^a(T)$ and $C_p^u(T)$ are the heat capacity measured after annealing and that of the unannealed sample, respectively, whereas T_x and T_y are arbitrary temperatures ($T_x \ll T_g < T_y$). Eq (1)

actually provides the expression of the experimental enthalpy difference produced by the thermal treatments with and without annealing at a temperature set at $T_g - 43$ K in this work.

A broadband dielectric spectrometer, Novocontrol Alpha analyzer, was used to measure the complex dielectric function, $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, in the frequency ($f = \frac{\omega}{2\pi}$) range from $f = 10^{-2}$ Hz to $f = 10^7$ Hz. The samples, having a thickness of around 0.2 mm, were placed between parallel gold electrodes. The capacitor assembly was kept in a cell equipped with a nitrogen cooling/heating system, with temperature stability better than ± 0.1 K over the duration of the experiments. Broadband dielectric spectroscopy was employed to characterize the dynamics of PMMA both pure and in the nanocomposites and to probe physical aging. As far as the characterization of the dynamics is concerned, samples were measured after quenching in liquid nitrogen in isothermal frequency scans recording $\varepsilon^*(\omega)$ every 5 K over the temperature range of 273–423 K. No effect of the thermal history was found on the typical relaxation times of PMMA, identified with the time corresponding to the maximum of the loss peak of the permittivity.

The physical aging of the samples was monitored by following the time evolution of the complex dielectric function $\varepsilon^*(\omega)$, which was measured continuously at the annealing temperature T_a. Prior to any measurement, the samples were firstly "rejuvenated" at a temperature corresponding to $T_g + 30$ K, for 5 min, and subsequently quenched in liquid nitrogen. Then, the temperature of the samples was increased to the selected annealing temperature. A time of about 10 min was required for accurate temperature stabilization. The selected aging temperatures ranged from 303 to 353 K with an interval of 10 K. In order to quantify the extent of physical aging, the complex dielectric function associated to PMMA secondary relaxation process was fitted by the Havriliak–Negami (HN) function [19]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left[1 + \left(i\omega\tau_{HN} \right)^{\alpha_{HN}} \right]^{\gamma_{HN}}}. \tag{2}$$

where ε_∞ is the high frequency limit value of the dielectric permittivity, $\Delta\varepsilon$ is the dielectric strength of the relaxation process, τ_{HN} is the HN relaxation time, and α_{HN} and γ_{HN} are the shape parameters of the HN function describing respectively the symmetric and asymmetric broadening of the complex dielectric permittivity. During the course of physical aging, a decrease of the $\Delta\varepsilon$ was observed, whereas τ_{HN}, α_{HN} and γ_{HN} remained constant. Thus $\Delta\varepsilon$ associated to PMMA β process represents a robust parameter to monitor physical aging in glassy PMMA.

3. Results and discussion

In the first part of this section, we report the characterization of the dynamics of PMMA/silica nanocomposites with particular emphasis on the comparison with the dynamics of the pure polymer. Figs. 2 and 3 display respectively the calorimetric and dielectric response of all nanocomposites and pure PMMA. In particular, the specific heat vs. temperature plots are reported in Fig. 2, whereas Fig. 3 presents the loss part of the permittivity (ε'') as a function of the frequency at 393 K as an example. The inset of Fig. 3 reports the temperature dependence of the relaxation time obtained from the frequency of the maximum of ε''. The following observations can be done from the inspection of the figures: i) the calorimetric glass transition, determined as the temperature corresponding to half of the heat capacity change, is not affected by the presence of silica nanoparticles ($T_g = 396$K); ii) the dynamics of nanocomposites is identical to that of pure PMMA. The latter statement arises from the invariance of the shape and the typical frequency of the relaxation (that corresponding to the maximum, see Fig. 3) and is valid in the whole investigated temperature range as testified by the superposition of the relaxation time vs. the temperature plots of the nanocomposites and pure PMMA displayed in the inset of Fig. 3. Thus, the first
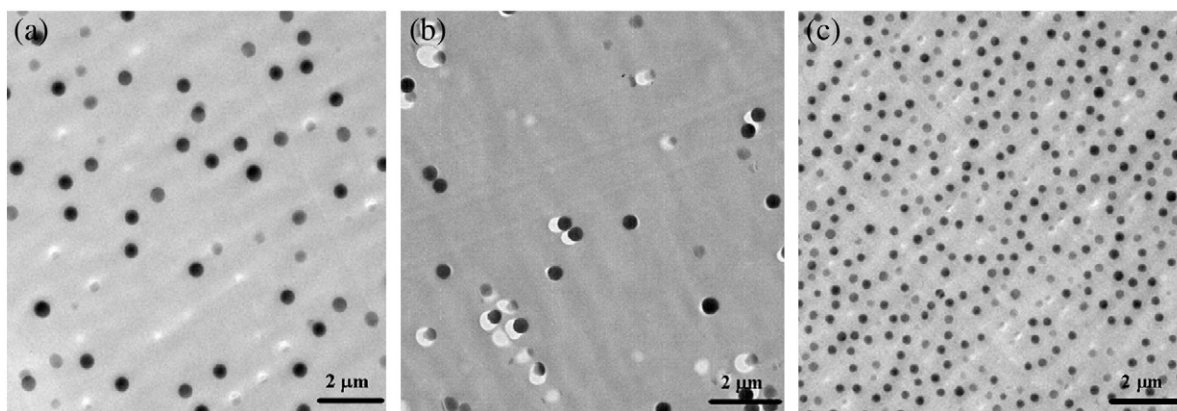
Table 1
Summary of PMMA and PMMA nanocomposites characteristics.

Sample	Silica weight fraction, W_f (%)	Surface treatment	Particle diameter (nm)	Interparticle distance (nm)	PMMA M_w (kg mol^{-1})	M_w/M_n
PMMA	–	–	–	–	880	4
A10	8.9	TPM	350	1410	877	4
R10	8.9	OTMS	350	1410	760	4
V10	8.9	TPM	200	806	830	4

Fig. 1. TEM micrographs of PMMA/silica nanocomposites: a) A10; b) R10; c) V10.

conclusion of our investigation is that the dynamics of PMMA/silica nanocomposites is essentially unaffected by the presence of nanoparticles.

Figs. 4 and 5 respectively display the effect of physical aging on the dielectric and calorimetric response of PMMA/silica nanocomposites and pure PMMA. In particular, in Fig. 4 the loss part of the permittivity is presented as a function of the frequency at the beginning of the aging process and after aging during 1.1×10^4 s for the nanocomposite labelled as V10, as an example, and pure PMMA. The dielectric strength of PMMA β process, showing up in the available frequency window, clearly decreases during the course of aging for both the nancomposites and PMMA as a consequence of reduced orientation polarization due to relaxed molecular dipoles [16,17]. Furthermore, the decrease of the dielectric strength of PMMA β process is more marked in the nanocomposites than in pure PMMA. This implies that physical aging in nanocomposites proceeds faster than in pure PMMA. A similar conclusion can be drawn observing the evolution of the temperature dependence of the specific heat with aging time. This allows the evaluation of the recovered enthalpy during physical aging via Eq. (1). In Fig. 5, the evolution of the enthalpy during physical aging is clearly identified through the endothermic peak appearing below T_g [20]. As can be observed, despite the smaller specific heat overshoot in comparison to pure PMMA, the enthalpy of the nanocomposite V10 stops evolving at aging times shorter than bulk PMMA. A similar result has been recently obtained by Simon et al. [21] investigating the enthalpy relaxation of o-terphenyl (OTP) confined in nanopores.

The results on the physical aging of all nanocomposites and pure PMMA are summarized in Figs. 6 and 7. These figures respectively
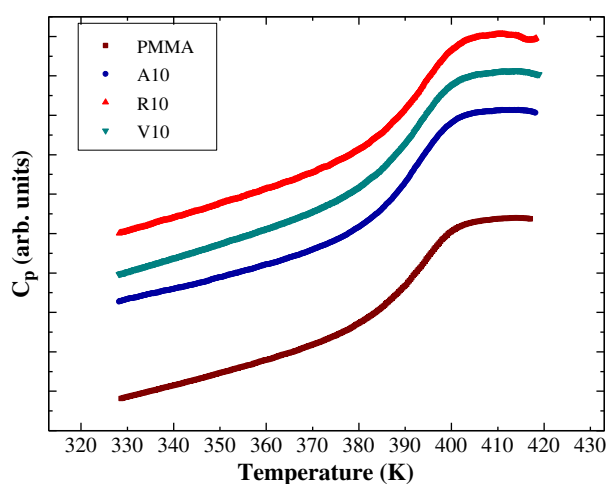
display the time evolution of the dielectric strength of PMMA β process, normalized to the one at the beginning of the aging process, and the relaxation function associated to the enthalpy relaxation. The latter is defined as: $\varphi(t) = (H(t) - H(\infty))/(H(0) - H(\infty))$. Both figures display results obtained at 353 K. Observing Figs. 6 and 7, the increase of the rate of physical aging in nanocomposites in comparison to bulk PMMA is evident. Thus, enthalpy relaxation measurements are in general agreement with the results obtained through dielectric spectroscopy.

The most relevant results of our investigation can be summarized as follows: despite the lack of effect of silica nanoparticles on the segmental dynamics of PMMA, the rate of physical aging, probed by monitoring the enthalpy relaxation and the evolution of the strength of the dielectric strength of PMMA β process, is generally accelerated in PMMA/nancomposites in comparison to pure PMMA. The latter observation is the result of the analysis of two observables and, therefore, can be considered independent of the technique employed to monitor physical aging. Thus, our results pose serious concerns on the idea that physical aging is exclusively controlled by the molecular mobility and the distance from equilibrium of the glass [3,4]. One possible explanation could reside on enhanced mobility close to the interface. Such a hypothesis has been suggested by Rowe et al. [22], measuring the physical aging of glassy polysulfone through variable energy positron annihilation lifetime spectroscopy measurements.
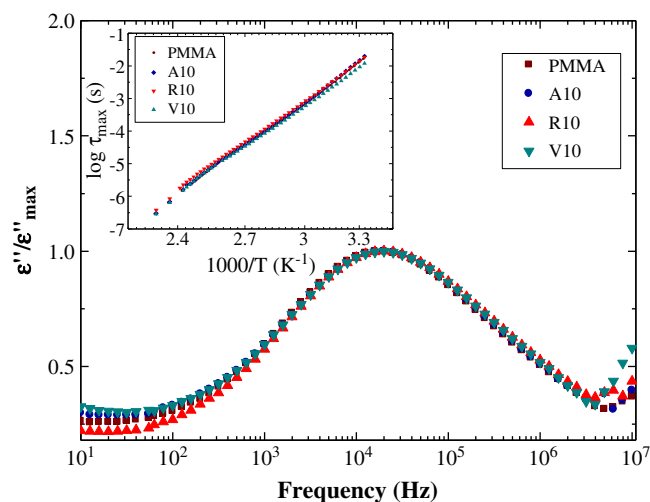

Fig. 2. Calorimetric response of all PMMA/silica nanocomposites and pure PMMA.

Fig. 3. Loss part of the dielectric permittivity, normalized to the value at the maximum of the displayed relaxational process, vs. the frequency for PMMA/silica nanocomposites and pure PMMA at 393 K. The inset displays the corresponding temperature dependence, for the same systems, of the relaxation time taken as the inverse of the frequency corresponding to the maximum of the loss part of the permittivity.
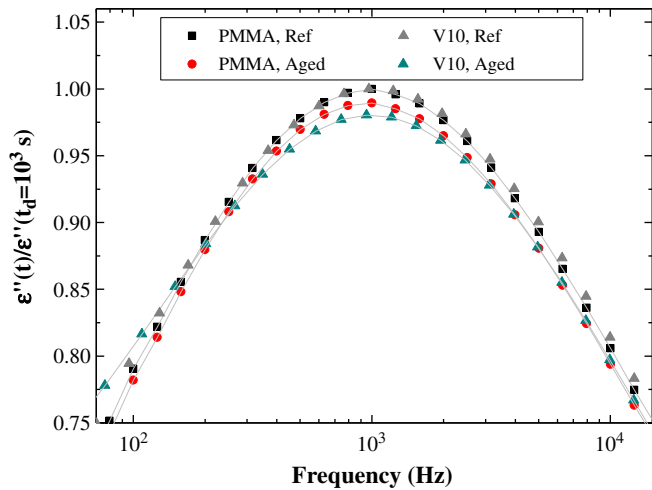
Fig. 4. Loss part of the dielectric permittivity, normalized to the value at the maximum of the displayed relaxational process, vs. the frequency at different aging times for V10 and pure PMMA at 353 K.

Rowe et al. [22] proposed that physical aging proceeds faster in polymer thin film as a consequence of enhanced mobility at distances from the interface equal or shorter than about 100 nm. This
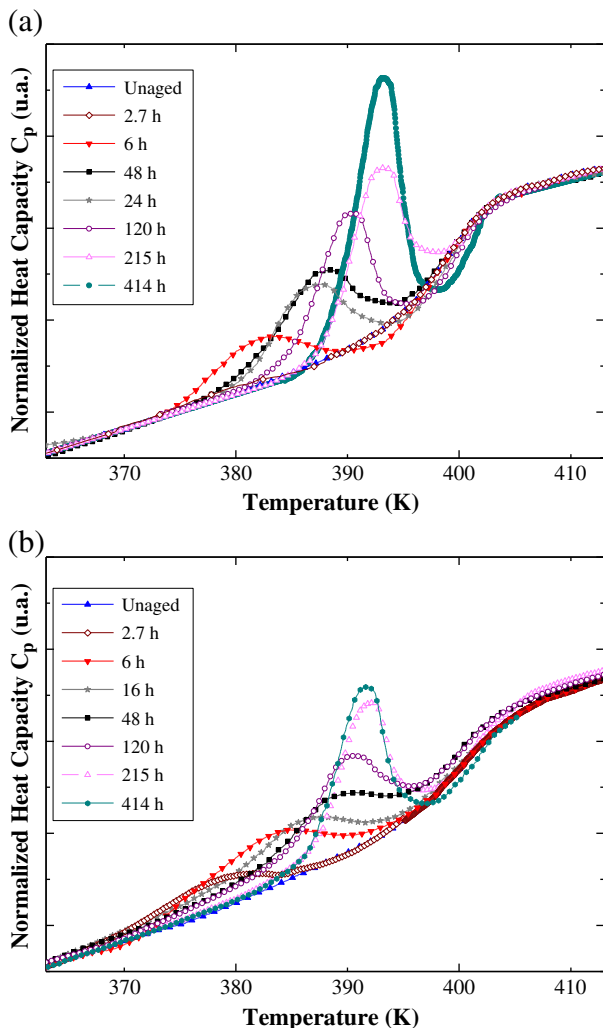

Fig. 5. Calorimetric response of pure PMMA (a) and V10 (b) after different aging times at 353 K.
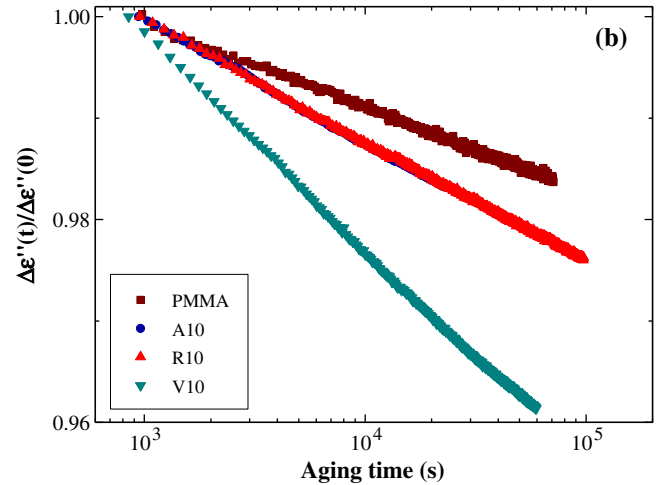

Fig. 6. Time evolution during physical aging at 353 K of the dielectric strength of PMMA β process, normalized to the value at the beginning of the aging process, for all PMMA/silica nanocomposites and pure PMMA.

assumption arises from the fact that a decrease of the size of free volume holes rather than their number occurs. This would rule out the possibility of diffusion of free volume holes towards the interface, as recently proposed by several studies [14,16,17]. The diffusion mechanism would likely provoke the decrease of the number of free volume holes. We argue here that the details of the evolution of the free volume microstructure do not necessarily allow discarding the hypothesis of the diffusion mechanism. A possible explanation to reconcile the positron annihilation lifetime results with the diffusion might reside in the rearrangement of free volume microstructure after the migration of the free volume holes to the interface. Furthermore, several arguments can be put forward to question the hypothesis of enhanced mobility in a layer beside the interface of around 100 nm. First of all, enhanced mobility over such a distance can have an observable effect on the macroscopic dynamics. In the case of PMMA/ silica nanocomposites investigated in this work, the typical interparticle distance is of the order of 1 μm and, therefore, an effect on the dynamics in the first 100 nm from the interface would certainly be visible in the macroscopic dynamical response. Our experimental data – showing no influence of silica nanoparticles on the dynamics – do not support such possibility. Neither effects on the dynamics have been observed in thin polymer films with thickness as small as around 10 nm [23,24]. In
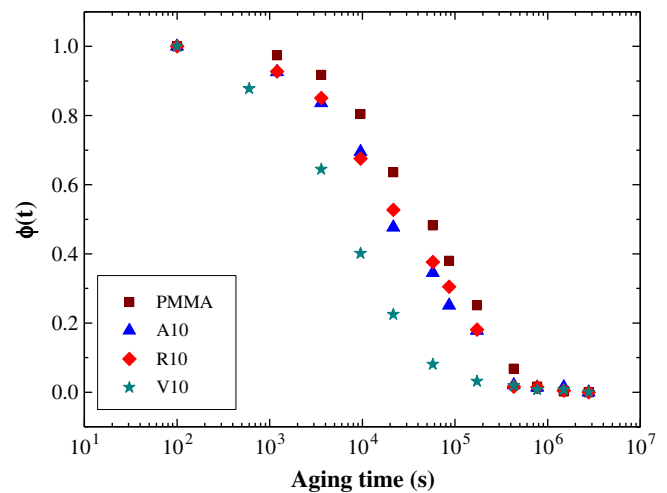

Fig. 7. Time evolution during physical aging at 353 K of the relaxation function associated to the enthalpy relaxation (see text) for all PMMA/silica nanocomposites and pure PMMA.

addition, molecular dynamics simulations on confined Lennard-Jones liquid by Scheidler et al. [11] and solvation dynamics experiments by He et al. [12] provide evidence that effects on the mobility are present only in the very first nanometres beside the confining surface. Thus, in our view, the mechanism based on free volume diffusion towards the interface still represents a valid explanation to rationalize the length scale dependence of the rate of physical aging. The quantitative soundness of the diffusion mechanism will be reported elsewhere [18,25].

Finally, it is worth to discuss briefly our results in light of recent results on the physical aging of nanostructured systems with typical length scale shorter than 100 nm. Most of them, with some exceptions [21], point towards a reduction, or even suppression, of physical aging [26–29]. Thus, these results apparently conflict with ours as well as those previously presented for thin polymer films [13,14,22]. One possible explanation to explain such a discrepancy may reside on the experimental inability of catching the very first stages of physical aging in nanostructured glasses with very short typical length scale. In other words, the absence of evolution of the measured property can be just the consequence of a rapidly achieved equilibrium not detectable due to the inevitable time-lag before the beginning of data collection in standard physical aging experiments. Recent results by Rowe et al. [30], measuring the permeability in several glassy polymers, seem to confirm this hypothesis. In particular, they show that, although for ultra-thin polymer films (less than 50 nm) the time evolution of the permeability is dumped in comparison to the thickest films, the initial value of this property is consistently reduced with respect to the "bulk" value. In light of these results, the idea that the rate of physical aging is strongly enhanced in nanostructured systems with relatively small length scale is not just the results of speculation but it is rather a highly reliable scenario.

4. Conclusions

We have focused on the study of physical aging of PMMA/silica nanocomposites with particular attention to whether any modification of the rate of such a process depends or not on a corresponding change of PMMA dynamics. We have found that, despite the lack of influence of silica nanoparticles on the dynamics of PMMA, all nanocomposites display accelerated physical aging in comparison to bulk PMMA. Furthermore, the acceleration is more pronounced the shorter is the interparticle distance, whereas samples with the same interparticle distance but different silica surface present equal rates of physical aging. These results have been obtained monitoring physical aging by means of dielectric spectroscopy and DSC. The general agreement between the trends of the physical aging rate obtained by the two techniques indicates that the accelerated physical aging is a

general behaviour of PMMA/silica nanocomposites. We have discussed the implications of such acceleration in light of the diffusion model. According to it, the densification of the glass during physical aging would be due to the disappearance of free volume holes at the interface between the polymer and silica nanoparticles, after their diffusion from the core of the polymer to the interface.

Acknowledgements

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