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Relaxation processes in polymers filled with nanoparticles

Ivan Joel Lopez, Vladimir Dolidze, Fouad M. Aliev *

Department of Physics, P.O. Box 23343, University of Puerto Rico, San Juan, PR 00931-3343, USA

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A B S T R A C T

We report on the influence of filling poly(n-alkyl methacrylates) with 12 nm in diameter Aerosil nanoparticles on relaxation processes and glass transitions, as investigated by dielectric spectroscopy and differential scanning calorimetry. The agglomeration of Aerosil particles in polymer formed a three-dimensional network dividing the polymer into random domains. The filling of polymers with nanoparticles had at least two effects: random field effects imposed by the network and a large particle surface area that imposed an interfacial effect on the polymer. In order to study the role of interfacial effects on the nanoparticle–polymer interface we used two types of Aerosil particles: with hydrophilic and hydrophobic surfaces. We found that the relaxation times of α-relaxation process (sensitive to glass transition) in polymers filled with both hydrophilic and hydrophobic particles were faster than those of bulk polymers measured at the same temperatures. This might be interpreted as reduction of the glass transition temperature in the filled polymers. Semi quantitatively this reduction is in accordance with the Vogel–Fulcher data analysis of the temperature dependencies of the α-process relaxation times. The β-relaxation process was slower for bulk than for filled polymers, but the activation energies of this process were about the same for pure and filled polymers.

1. Introduction

High values of surface to volume ratio in systems comprised of soft matter, such as polymers or liquid crystals, confined in nanoporous media, filled with nanoparticles, or in very thin film leads to significant changes in their physical properties [1–5]. Despite increasing knowledge on the physical properties of thin polymer layers and films, understanding of the influence of surface and interfacial layers on physical properties of polymers is inadequate [1–5]. Both increase and decrease of the glass transition temperature in thin polymer film have been found [6] by using different experimental techniques. These changes in glass transition temperature were attributed to strong or weak interactions between the polymer and its boundary (see review [4]). Recently another polymer-based system, where polymer is filled with inorganic nanoparticles, has attracted substantial attention [7–9]. Current problems with glass transition in nanofilled and nanoconfined materials were summarized in [10]. According to [10], changes in the dynamic properties of the nanoconfined materials vary greatly depending on the nature of the interfaces, the chemical structure of the nanoconfined glass-former, the experimental methods used, and, in the case of polymers, the length-scale of the dynamics probed. For example, it has been shown [11] that wetting conditions at solid surface–polymer interface greatly affect glass transition temperature in polymers filled with nanoparticles. In this paper we report on the influence of filling of polymer with Aerosil nanoparticles on glass transition in poly(n-octyl methacrylate) (POMA) and poly(n-butyl methacrylate) (PBMA) as investigated by dielectric spectroscopy and differential scanning calorimetry (DSC). Poly(n-alkyl methacrylate)s, such as poly(n-octyl methacrylate), are polymers, whose bulk properties have been investigated in detail by different methods, including dielectric spectroscopy [12,13] and DSC [14].

In order to estimate the role of surface effects at nanoparticle–polymer interface in filled polymers we used two types of Aerosil particles: with hydrophilic and hydrophobic surfaces. However, due to limited volume of this paper, we restrict presentation of the results and their discussion to polymers filled with hydrophobic particles, in which the influence of filling of polymer was stronger than in case of hydrophilic particles. We just provide glass transition temperatures for polymers filled with hydrophilic particles obtained from dielectric spectroscopy. For qualitative illustration of the influence of filling of polymer with hydrophilic particles we present results obtained by differential scanning DSC for these samples. The results for filled polymers are also compared with those of bulk POMA and PBMA.

2. Experimental details

POMA with average molecular weight $\langle M_w \rangle = 10^5$, and PBMA ($\langle M_w \rangle = 1.8 \times 10^5$) were purchased from Scientific Polymer Products

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* Corresponding author. Tel.: +1 (787) 764 0000x7554; fax: +1 (787) 756 7717.
E-mail address: fmaliev@uprrp.edu (F.M. Aliev).

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in 23.8 wt% toluene solution. We used Aerosil-200 (specific area about 200 m^2/g) hydrophilic particles and Aerosil-R974 (specific area about 170 m^2/g) hydrophobic particles to prepare nanocomposites, which contained 2% and 5%, weight concentration of Aerosil. The samples were prepared by adding the desirable amount of Aerosil particles to the solution, and then the solution was sonicated for about 45 min. After that, the solvent was slowly (during approximately 30 days) evaporated until the polymer + Aerosil particles composites were completely dry. The information on particle distribution in the polymer was obtained using TEM LEO ZEISS 922. Hydroxyl OH groups on the surface of the Aerosil particles form hydrogen bonds between different particles, leading to the formation of a network. In hydrophobic Aerosil, about 70% of the surface hydrophilic groups were replaced by hydrophobic groups, modifying the interaction between the particles and the polymer. The agglomeration even of 2–3 volume percent of Aerosil particles in the polymer forms a stable three-dimensional network [15], dividing the polymer into domains with liner size of several 100 nm, depending on the concentration of filling particles.

Measurements of the real (ε') and imaginary (ε'') parts of the complex dielectric permittivity (ε^*) in the frequency range 0.01 Hz–1 MHz were carried out as in Ref. [16]. The dielectric spectra were analyzed by using a superposition of two Havriliak–Negami (HN) functions: one for each relaxation process observed in our samples. The HN function for each process is given [17] by:

$$\varepsilon^*(\omega) = -i\frac{\sigma_o}{2\pi\varepsilon_o f^n} + \frac{\Delta\varepsilon}{(1+(i2\pi f\tau)^{\alpha})^{\beta}} + \varepsilon_\infty, \tag{1}$$

where the first term on the right represents contributions from the dc conductivity, ε_o represents the permittivity of free space, f is the frequency of the probing electric field, τ is the mean relaxation time of the corresponding process, α and β describe the symmetric and asymmetric distribution of relaxation times, $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$, and ε_s and ε_∞ are the low frequency and high frequency limits of the real part of dielectric permittivity. Fitting parameter n accounts the contribution of conductivity. In the case of pure ohmic conductivity $n = 1$. At low frequencies a contribution from conductivity to the imaginary part of the dielectric permittivity was observed and it was taken into account. In our samples, this contribution to ε'' from conductivity was integrated effect, which arose from presence of ionic impurities in both polymer and Aerosil. We performed DSC measurements using equipment described in Ref. [15] with cooling/heating rate of 10 K/min.

3. Dielectric spectra

Dielectric spectra measured for bulk and filled polymers were alike and were similar to spectra for bulk poly(alkyl methacrylates) [12,13]. The main feature of these spectra was the lack of clear separation of the α- and β-relaxation processes because the amplitudes of these processes are comparable especially at low temperatures. As a result substantial broadening and asymmetry of spectra were observed. This is illustrated in Fig. 1. Solid lines in this figure represent fitting to the HN formula and are the superposition of two functions describing the α- and β-relaxation processes. Although the spectra for bulk and filled polymer were alike, the characteristic frequencies, which determined the relaxation times of both processes, were higher for filled polymer than for bulk, indicating that the relaxation processes in these samples were faster than those of the bulk. This was observed for both polymers and all temperatures. The temperature dependencies of relaxation times of α- and β-relaxation processes for both bulk and filled polymers are presented and discussed in next sections.

4. Temperature dependencies of relaxation times

Fig. 2 shows the temperature dependencies of relaxation times of the α-process in POMA and PBMA bulk and filled with hydrophobic particles with their weight concentration of 5%. It is clear from Fig. 2 that the relaxation times of the α-process were faster for the filled polymers than for pure bulk polymer. This implied that filling the polymer with nanoparticles influenced the relaxation time of the α-process of the polymer in the entire temperature range, suggesting that glass transition temperatures for bulk and filled polymer should be different. The data analysis of the temperature dependencies of relaxation times of the α-process on the basis of the Vogel–Fulcher formula $\tau_\alpha = \tau_{0\alpha}\exp[B/(T - T_0)]$ shows that these dependencies for bulk and filled polymers obey this formula, with parameters B and T_0 in agreement with values of these parameters obtain earlier for bulk POMA and reported in Ref. [13]. The dynamic glass transition temperatures for all samples could be calculated using the Vogel–Fulcher formula. If we determine [18] the glass transition temperature T_g as the temperature at which $\tau = 100$ s, then using the Vogel–Fulcher formula we obtain for POMA: $T_g = 244.2$ K (bulk), $T_g = 236.0$ K (filled with hydrophobic particles – 5 wt% concentration), and for PBMA: 291.6 K (bulk), 288.2 K (filled with hydrophobic particles – 5 wt% concentration). The glass transition temperatures obtained in the same manner

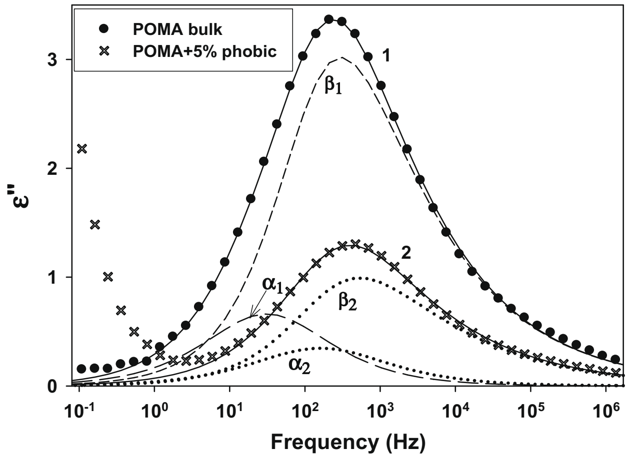

Fig. 1. Dielectric spectra at $T = 283.1$ K of bulk POMA (1) and POMA filled (2) with hydrophobic particles with 5 wt% concentration. Lines 1 and 2 represent superposition of α- and β-relaxation processes. Symbols – experiment, lines (dashed and solid) – fitting.

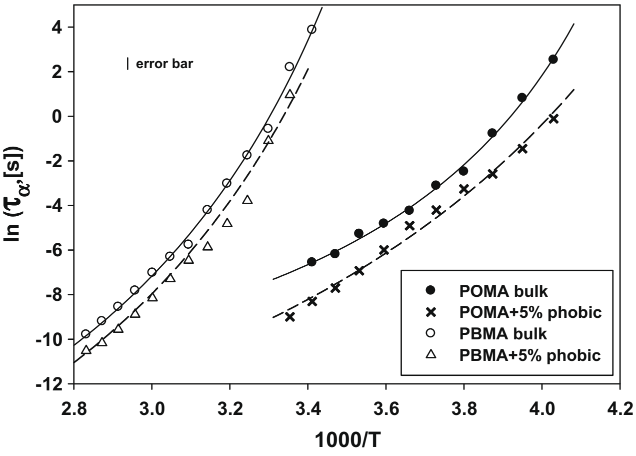

Fig. 2. Arrhenius diagram (T in K) for α-relaxation process in bulk and filled POMA and PBMA. Lines (solid and dashed) are drawn according to Vogel–Fulcher formula using parameters obtained from the fitting of experimental data.