Relaxation Processes and Glass Transition in Polymer Filled with Nanoparticles

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Summary: We report the results of the investigations of the influence of filling of polymer with Aerosil nanosize particles on the glass transition and dynamics of the α- and the β-relaxation processes in poly(n-octyl methacrylate) by dielectric spectroscopy and differential scanning calorimetry (DSC). The polymer was filled with hydrophilic and hydrophobic Aerosil particles of 12 nm diameter. In filled polymers the characteristic frequency of the alpha-process was shifted to higher frequencies in comparison with pure bulk polymer at the same temperature. This suggests that the filling of the polymer with nanoparticles has resulted in the shift of its glass transition temperature T_g. This change in T_g was mainly due to the existence of a developed solid particle-polymer interface and the difference in the dynamic behavior of the polymer in the surface layers at this interface compared to the bulk behavior. This result was in agreement with DSC experiments.

Keywords: dielectric properties; glass transition; nanocomposites

Introduction

Studies of structure, phase and glass transitions as well as the dynamic behavior of complex fluids confined in porous media and their thin films have been very useful in exploring the fundamental physics of condensed matter. The confinement of soft matter can lead to such prominent changes in the physical properties that, even in the case of a one component isotropic fluid, a clear physical picture explaining these changes has not been achieved.

Recently there has been much interest in the physical properties of thin polymer films. Despite great success in research on the physical properties of thin polymer layers and films, there are still open questions in the understanding of the influence of surface and interfacial layers on physical properties of polymers.[1–5]

Many studies have examined whether the glass transition[6,7] in the confinement of thin supported or freely standing films is altered in comparison to that in the bulk polymer. Both increases and decreases of the glass transition temperature were found by using different experimental techniques and were attributed to strong or weak interactions between the polymer and its boundary (see review[4]). Heterogeneous systems based on polymers are materials extremely important for applications as well as fundamental condensed matter physics. Recently another polymer based system, which is polymer filled with inorganic nanoparticles attracted substantial attention.[8,9] The behavior of polymers at interface or in thin surface layers in such systems as polymers confined/dispersed in pores or filled with nanoparticles, in particular, remains an insufficiently investigated area of condensed matter physics.

In this paper we report on the influence of filling of polymer with nanoparticles on glass transition in poly(n-octyl methacrylate) as investigated by dielectric spectroscopy and differential scanning calorimetry. In order to estimate the role of surface effects at nanoparticle-polymer interface in filled polymers we used two types of Aerosil particles: hydrophilic and hydrophobic.

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The results for filled polymer are compared with those of bulk POMA. We restrict our consideration to the results for α-relaxation, which provide information on glass transition, and DSC experiments. Due to the limited length of this paper, the analysis of the results on β-relaxation process will be published separately. However it should be noted that the filling of the polymer with both hydrophilic and hydrophobic particles does not affect the β-relaxation process.

Experimental Part

Poly(n-octyl methacrylate) with average molecular weight $\langle M_w \rangle = 10^5$, was purchased from Scientific Polymer Products 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%, 5%, and 10% 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 minutes. 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 network. In hydrophobic Aerosil, about 70% of the surface hydrophilic groups are replaced by hydrophobic groups modifying the interaction between the particles polymer. The agglomeration even of 2–3 volume percent of Aerosil particles in polymer forms a stable three-dimensional network dividing the polymer into domains with liner size of several hundred nm, depending on the concentration of filling particles. This is illustrated in Figure 1, which represents typical arrangements of Aerosil particles in nanocomposite.

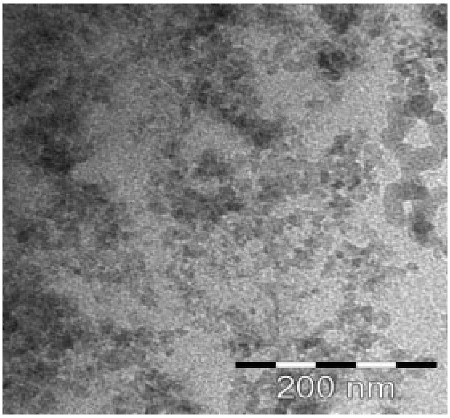

Figure 1.
TEM micrograph of POMA filled with hydrophilic Aerosil nanoparticles - concentration 10wt%.

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 using equipment described in Ref.[10] The dielectric spectra were analyzed using superposition of two the Havriliak-Negami functions: one each for α- and β-processes. The HN function for each process had a form:[11]

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

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. At low frequencies a contribution from conductivity to the imaginary part of the dielectric permittivity was observed and it was taken into account. We performed DSC measurements using Perkin Elmer Pyris Diamond DSC-6. The cooling/heating rate in these experiments was 10 K/min.

α-Relaxation and Glass Transition

Poly(n-alkyl methacrylate)s, such as poly-(n-octyl methacrylate), are polymers, which have been investigated in detail by different methods including dielectric spectroscopy[12,13] and DSC.[14] The dielectric spectra we measured for bulk and confined POMA were alike and the spectra for bulk POMA were similar to what is known from literature.[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. The comparison of results for bulk and filled POMA details of the spectra are presented in Figure 2 and 3 for temperature 283 K.

Despite the fact the spectra for bulk and confined polymer are alike, it should be stressed that the characteristic frequencies, which determine the relaxation times of α-process, were higher for filled polymer than for bulk.

The reduction of the relaxation time of α-process in filled polymer was observed for all temperatures. Figure 4 shows the temperature dependencies of relaxation times of the α-process of bulk POMA and POMA filled with both hydrophilic and hydrophobic particles.

It is clear from this figure that the relaxation times of the α-process are faster for the filled polymer than for the bulk state. This implies that filling of the polymer with nanoparticles has an influence on the relaxation time of the α-process of the polymer in the entire temperature range, suggesting that glass transition temperatures for bulk and confined polymer should be different. These changes in the rate of the relaxation process, and therefore, in the temperature of the glass transition were due to the formation of surface layers on the nanoparticle-polymer interface in filled POMA with properties and glass transition temperature different from those in bulk polymer.[15,16] The glass transition temperatures for all samples could be calculated from the comparison of experimentally determined relaxation times with the Vogel-Fulcher formula $\tau = \tau_0 \exp[B/(T-T_0)]$.

The data analysis on the bases of this formula shows that the temperature dependencies of relaxation times of α-process for bulk and filled polymers are describe by the Vogel-Fulcher formula, with parameters B and T_0 in agreement with values of these parameters obtain earlier for bulk POMA and reported in reference.[13] If we determine[17] the glass transition temperature T_g as the temperature at which $\tau = 100$ s, then we obtain $T_g = 235$ K for bulk POMA,

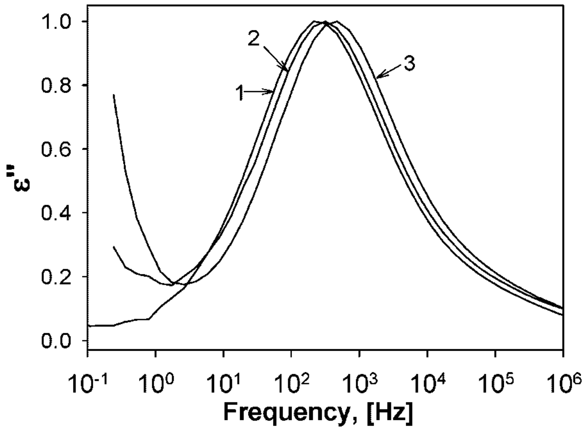

Figure 2.

Normalized dielectric spectra of bulk (1) and filled with 5wt% hydrophilic (2) and 5wt% hydrophobic (3) Aerosil particles measured at 283 K.

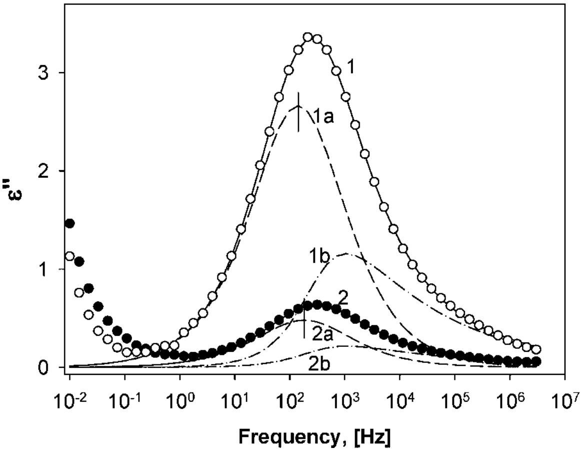

Figure 3.
Dielectric spectra at T = 283 K for bulk POMA (1, 1a, 1b) and POMA filled (2, 2a, 2b) with hydrophilic particles 5 wt% concentration. 1,2: superposition of α- and β-processes; 1a, 2a: α-process, 1b, 2b: β-process. Symbols – experiment, lines (dashed and solid) – fitting. Vertical lines indicate frequencies corresponding to relaxation times of α-relaxation process.

$T_g = 233$ K for POMA filled with hydrophilic particles (5% wt concentration) and 230 K for POMA filled with hydrophobic particles (5% wt concentration). The reduction in T_g was slightly bigger in the case of hydrophobic particles than in samples filled with hydrophilic particles with the same their concentration.

Differential Scanning Calorimetry

The results of our DSC experiments were in agreement with conclusions that can be made on the basis of dielectric spectroscopy experiments. Bellow we illustrate how the concentration of filling particles affects the glass transition temperature. DSC results presented in Figure 5 for bulk POMA and

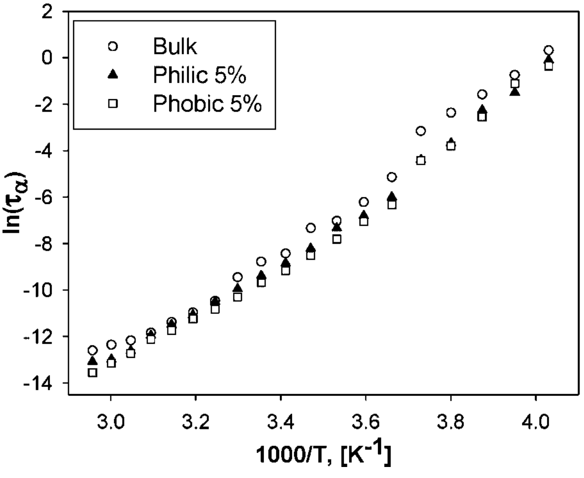

Figure 4.
Arrhenius diagram for α-relaxation process in bulk and filled POMA.

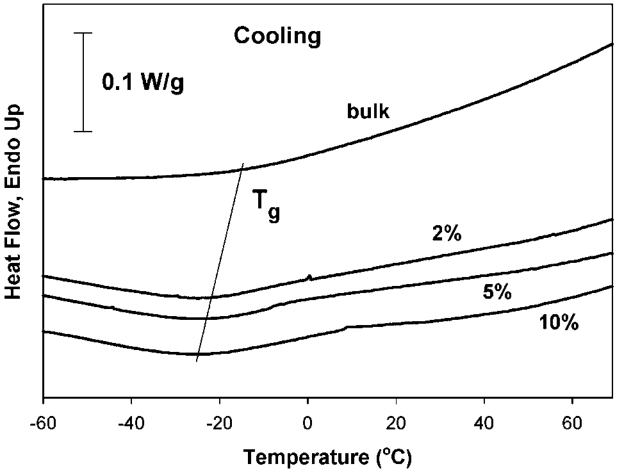

Figure 5.
DSC curves of bulk and filled POMA with hydrophilic Aerosil nanoparticles at various filler concentrations: 2 wt%, 5 wt% and 10 wt%. The line labeled T_g indicates a tendency of decrease of T_g with increase of the concentration of filling nanoparticles.

filled with hydrophilic particles at different filling concentrations. The heat flow curve for bulk POMA reproduces previously published[14] result of DSC experiment on the same bulk polymer: the glass step transforms to bend.[14]

It is very difficult to make quantitative conclusion about shift of glass transition temperature in polymers filled with 12 nm Aerosil particles. However, DSC experiments suggest that in filled POMA T_g lowers from bulk value as the concentration of same surface Aerosil particles increases. It should be mentioned that the similar tendency in shift of glass transition temperature of POMA as function of concentration of filling particles was observed for hydrophobic particles with slightly stronger reduction of T_g than in the case of the hydrophilic particles. This result was in agreement with dielectric spectroscopy results illustrated in Figure 2.

Conclusion

Filling of polymers with Aerosil particles with hydrophilic and hydrophobic surfaces has resulted, in the fact that relaxation times of α-relaxation process (sensitive to glass transition) in both filled polymers are faster than those of bulk POMA measured at the same temperatures. This might be interpreted as reduction of T_g in filled polymers. Semiquantitatively this reduction is in accordance with the Vogel-Fulcher data analysis of the temperature dependencies of α-processes relaxation times and with results of DSC experiments.

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