New dynamics in poly(propylene glycol) based glass-forming nanocomposites

M. Głuszek[a], A. Antosik[a], R. Żurowski[a], M. Szafran[a], S.J. Rzoska[b], M. Zalewski[b], E. Pawlikowska[b], S. Starzonek[b],*

[a] Department of Chemical Technology, Warsaw University of Technology, ul. Noakowskiego 3, 00-664 Warsaw, Poland
[b] Institute of High Pressure Physics, Polish Academy of Sciences, ul. Sokołowska 29/37, 01-142 Warsaw, Poland

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ABSTRACT

Results of broadband dielectric spectroscopy and rheological studies of poly(propylene glycol) + SiO$_2$ nanocomposites are presented. They show that the dynamics in high-concentrated composites is dominated by confinement and adsorption effects. The most notable finding is the impact of nanoparticles on fragility, the fractional translational – orientational decoupling and the shift of dynamics towards the pure Vogel-Fulcher-Tammann pattern, associated with the lack of local symmetry preferences.

1. Introduction

Glass transition and related phenomena are considered as one of greatest challenges of the condensed matter physics, soft matter physics and material engineering [1]. One of its most fascinating features are far previtreous effects for dynamic properties, starting even 200 K above the glass temperature (T_g). They exhibit a set of universal patterns, sharing between glass forming systems notably different at the microscopic level. One can recall [1–5]: (i) the non-Debye distribution of relaxation times, (ii) the non-Arrhenius evolution of relaxation times or viscosity or related properties (iii) the 'magic' dynamic ergodic – nonergodic crossover most often occurring at $\tau(T_B) \approx 0.1\mu s$ for the primary relaxation time and $\eta(T_B) \approx 1kPoise$ for viscosity, (iv) decoupling between translational and orientational for $T < T_B$, (v) the emergence of the secondary *beta* relaxation process below T_B. One of paths for approaching the key point of the glass transition mystery can be studies in 'innovative glass formers', revealing some usually hidden features of the phenomenon [6–9].

This report is related to studies in vitrifying nanocomposite, composed of glass forming poly(propylene glycol (PPG) and silica oxide (SiO$_2$) nanoparticles. Such systems seem to constitute a separate class of glass formers due to the beneficial combination of the ultraviscous glass former and solid nanoparticles properties. Worth recalling is the possible practical significance of complex dynamics studies in glass forming nanocomposites, for instance in innovative fuel cells. Studies focused on interactions between molecular hosts and strongly ionic nanoparticles can be found in Refs. [[12–16] and Refs.

therein]. This report presents the preliminary response to aforementioned basic questions.

Studies are based on rheological and broadband dielectric studies, supported by the derivative based pre-analysis of experimental data which includes also the insight into the evolution of the temperature index of the activation energy.

2. Experimental

2.1. Broadband dielectric spectroscopy and previtreous dynamics

Results presented below are based on broadband dielectric spectroscopy (BDS) and supplementary rheological tests, two methods essential for getting insight into dynamics of glass formers [4,5]. Regarding the broadband dielectric spectroscopy (BDS), it offers a simultaneous insight into dynamics for even 15 decades in frequency/time thus yielding a unique tool for studying complex dynamics and previtreous phenomena in glass formers [5]. Moreover, BDS can be relatively easy implemented for high pressure studies although in this case the terminal frequency is limited to now more than 10 MHz, so far [11]. Experimental data from BDS scans can be shown in few representations focusing on translational and orientational processes. The latter is associated with the complex dielectric permittivity as a function of a frequency $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$. The imaginary part of permittivity gives direct access to the distribution and values of the primary relaxation time, namely $\tau = 1/2\pi f_{peak}$ where f_{peak} is the frequency coordinate of the primary dielectric loss curve. The distribution of relaxation times is

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* Corresponding author.
  E-mail address: starzoneks@unipress.waw.pl (S. Starzonek).

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associated with slopes of loss curves and alternatively can be estimated also from $\varepsilon''(f)$ fittings via a set of formulas, among which Havriliak – Negami one is the most general [5]. The temperature evolution of dynamic properties in the ultraviscous domain, where the primary relaxation times plays the key role, can be expressed by the general super-Arrhenius (SA) equation [2,5]:

$$\tau(T) = \tau_0 \, exp\left(\frac{\Delta E_a(T)}{RT}\right) \tag{1}$$

where $\Delta E_a(T)$ denotes the apparent activation energy and τ_0 is the prefactor which can range between $10-11$ s and $10-16$ s in different systems.

In the simplest 'classical' case the apaprent acitivation energy is constant, i.e. $\Delta E_a(T) = \Delta E_a = const,$ and only in this case the activation energy can be easily determined as $\Delta E_a = R\ln\tau(T)/d(1/T).$ For the temperature – dependent apparent activation energy $R\ln\tau(T)/d(1/T)$ $= \Delta H_a(T),$ where $\Delta H_a(T)$ is the apparent activation enthalpy. The routine for non-biased determing of $\Delta E_a(T)$ has been developed in Refs [2,3,17]. The application of the SA Eq. (1) for portraying $\tau(T)$ experimental data is still not possible, and 'ersatz relations' are used. The most important and popular is the Vogel-Fulcher-Tammann (VFT) dependence [1,4,5]:

$$\tau(T) = \tau_0 \, exp\left(\frac{D_T T_0}{T - T_0}\right) \tag{2}$$

where D_T is the fragility strength coefficient related to the temperature of the path of the approaching the glass transition, T_0 is the extrapolated VFT singular temperature, located in the solid glass phase, below the glass temperature T_g.

In the analysis experimental data can conveniently presented via the Arrhenius plot $\log\tau(T)$ or $\ln\tau(T)$ vs. $1/T$ what is followed by the nonlinear fit via Eq. (2) [1,4,5]. However, such procedure introduces notable biased factors which can yield 'effective' and non-physical values of parameters. This can be associated with the erroneously selected fitting domain and the fact that the given relations can appear non-optimal or non-physical. Next issue is associated with the nonlinear fitting procedure, which also may yield non-physical and effective values of parameters. In Refs [18,19]. the simple recipe for solving these problems was proposed. Taking derivatives of Eqs. (1) and (2) and merging resulted equations one can obtain the following dependence [18,19]:

$$\left[\frac{d\ln(\tau)}{d\,(1/T)}\right]^{-0.5} = (\Delta H_a')^{-0.5} = A - \frac{B}{T} \tag{3}$$

Thus the appearance of the linear domain at the plot defined by Eq. (3) indicates the domain of a possible validity of the VFT parameterization and the subsequent basic linear regression fit yields optimal values of key parameters in Eq. (2): $T_0 = |B/A|$ and $D_T = 1/|AB|$ [18]. In fact, the plot $d\log\tau(T)/d(1/T)$ vs. $(1/T)$ was earlier used by Stickel et al. [17,20], but fit was focused solely on the estimation of the location of the so called dynamic crossover temperature and no link to the activation enthalpy was indicated [5,20].

In recent decades few other equations offering a reliable description of the temperature evolution of relaxation time appeared and they seem to offer equally reliable description as VFT, including the support of the preliminary derivative-based analysis [[17–19] and Refs. therein]. Hence, the question remains if the VFT equation is indeed the optimal choice for the given system. This basic problem can be solved the supplementary analysis using the activation energy temperature index $I_{DO}(T)$ [2,3,17]

$$I_{DO}(T) = -\frac{d\ln E_a(T)}{d\ln T}. \tag{4}$$

The form of this index for different relations describing dynamics in the ultraviscous/ultraslowing domain is notable different, thus enabling

the ultimate and unequivocal selection. In the case of the VFT dependence one obtains [2]:

$$I_{DO}^{VFT}(T) = \frac{T_0}{T - T_0}. \tag{5}$$

The determination of $I_{DO}(T)$ values from $\tau(T)$ experimental data requires the knowledge of the apparent activation time $E_a(T)$ in prior. The non-biased way of calculating $E_a(T)$, based on the numerical solution of a differential equation, has been recently proposed in Refs [2,3,17]. Subsequently, it was also discovered that the form of the evolution of the index may be 'universal feature' of glass forming dynamics $I_{DO}^{-1}(T) = a + bT$ [2], i.e. shows the linear behavior for arbitrary glass formers. This feature was shown for the set of ca. 50 glassy systems, ranging from low molecular weight liquids to polymers, liquid crystals and plastic crystals [2,3]. In the case of the VFT equation one obtains [2,3,17]:

$$[I_{DO}^{VFT}(T)]^{-1} = \left(\frac{1}{T_0}\right)T - 1. \tag{6}$$

Notable is the general form of the index: $I_{DO}(T) = nT_S/(T - T_S)$ [17], where T_S is the singular temperature below T_g and the coefficient $n = -1/b$ [2,3]. It was shown in Refs [2,3,17]. that the value of this coefficient reflects the local dominating symmetry and ranges between $0.2 < n < 1.5$. Then only for the special $n = 1$, which is related to the lack of the preferable local symmetry, the VFT equation is physically justified for the given set of experimental data.

In ultraviscous/ultraslowing regime the evolution of translational and orientational motions becomes decoupled, what can be detected via the Debye–Stokes– Einstein relation due to its shift to the fractional form (FDSE) [11]:

$$\sigma_{DC}(T)[\tau_a(T)]^S \tag{7}$$

where σ_{DC} and τ_α stands for DC-conductivity and the primary relaxation time.

The experimental evidence indicates that generally FDSE or FSE behavior with non-zero fractional exponents takes place in the ultraviscous/ultraslow dynamical domain for $T_B < T(\tau) < T_g$. For $T > T_B$ the crossover to Debye–Stokes– Einstein (DSE) occurs when $S = 1$. Study of FDSE behavior is one of the key tools for obtaining insight into dynamic heterogeneities, called cooperatively rearranged regions near T_g [4,5,11]. They are recognized as the most probable reason for the universal patterns in the ultraviscous domain. It was shown that $S = \Delta H_a^\sigma(T)/\Delta H_a^\alpha(T) = m_P^\sigma/m_P^\alpha$, where m is the fragility index, $P = const.$ The most precise calculation in Ref. [11] can be found.

Basing on existing reference experimental results [5,8,9] for ultraviscous PPGs one can note few types of relaxation processes in this system: the normal mode (NM) related to the polymer chains interactions (because PPG is a type-A polymer), α-process/segmental mode (SM) defined as actions of the polymer segments, $\beta-$ and $\gamma-$ processes associated with deep glass motions. So far, the temperature evolution of the α-relaxation is described by the single VFT Eq. (3).

For the given report measurements of the complex dielectric permittivity $\varepsilon^*(f)$ [5] were performed using the broadband dielectric spectrometer (BDS) Novocontrol Alpha Analyzer over a frequency range from 10^{-2} to 10^7 Hz. This enabled 6 digits resolution in dielectric measurements. The temperature was controlled by the Quattro System (Novocontrol) with stability better than 0.2 K [5]. Samples were placed in the measurement capacitor made from Invar, with a gap $d = 0.2$ mm and a diameter $2r = 20$ mm. The Teflon ring was used as the spacer. The latter and the macroscopic gap of the capacitor made it possible to avoid bubbles, distorting results.

2.2. Rheology

Rheological measurements are very useful technique for studying viscosity as a function of the applied shear rate or shear time. The fluids