Journal of Thermal Analysis and Calorimetry, Vol. 91 (2008) 3, 733–736

SOME COMMENTS ON NATURE OF THE STRUCTURAL RELAXATION AND GLASS TRANSITION

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We report on an experiment and new formula revealing dynamic and structural heterogeneity observed in liquids and polymeric systems. The formula applied to data obtained by mechanical spectroscopy reveals the glass-forming system behaviour giving the parameters previously postulated. The presented results are compared with data obtained for liquids (oligomers) confined to nanoporous media. To explain the behaviour of the polymeric systems the three-phase model is considered.

Keywords: *glass transition, relaxation time, structural heterogeneity*

Introduction

Cooling a liquid below some temperature usually results in crystallisation. However under special conditions, the same liquid undergoes an increase of the viscosity without crystallisation, the glass transition, that leads to glass formation. Owing to this fact, the glass may be defined as a material of a thermally arrested molecular arrangement of a liquid state. Hence, the generally used glass transition temperature, T_g, depends on cooling rate and thermal history. The glass transition is one of the most debated problem in condensed matter physics. Most materials of interest are densely packed interacting molecular systems. A many-body effects and mutual interactions between subsystems make the understanding of the phenomenology of the glass transition and the structural relaxation (this relaxation, assigned as α_c, is intimately related to the glass transition) difficult. Especially the strong temperature dependence of the characteristic relaxation time is intrigue. This has prompted a lot of efforts but a complete understanding is still lacking. There are many data on many kind of glass-forming substances, which can be organised into a number of well-established general properties [1]. The dynamic heterogeneous nature of relaxation has been reported through experimental studies [2–5]. The results exhibited a complex time dependence for the relaxation function, $\varphi(t)$ [1], associated with the given physical magnitude (e.g. neutron scattering, dielectric spectroscopy, calorimetry, nuclear magnetic resonance). The function displays a short-time exponential decay crossing over to a non-exponential regime close to the crossover time, t_c. $\varphi(t)$ depends on temperature through the relaxation times, τ, hence, the adequate temperature, T^*, can be determined [6]. At $T>T^*$ the relaxation is governed by the Arrhenius equation whereas below T^* by non-Arrhenius formulae (e.g. the Vogel–Fulcher or the power function). The glass-forming system is further complicated by the presence of crystallites and their random distribution in an amorphous matrix. One can easy find that a role of crystalline domains in structural relaxation have been addressed incidentally [7–9]. In this paper, some of the topics of polymer physics are discussed briefly: dynamic and structural heterogeneity; ‘crossover’ temperature; confinements of chain mobility. More detailed discussion and a set of new data will be presented in a full paper.

Experimental

Poly(4-methyl-1-pentene) (PMP) used in the experiments was originally produced by Mitsui & Co. Ltd. and distributed as a TPX-granulate [7]. This granulated PMP has been used to prepare films from the following solvents: toluene (TOL); trichloroethylene (TRI) and carbon tetrachloride (CT). The polymer cast-films (4 mass% – the polymer concentration in a solution) were investigated by using mechanical spectroscopy (TA DMA Q800) in a tensile mode. The frequency and temperature ranges were 0.01–200 Hz and 123–480 K, respectively. A heating rate was 1 K min^{-1}.

Results and discussion

Advantage of new formula

Both the dynamical heterogeneity and the coexistence of the crystal and amorphous phases were tested by new formula recently [9–11]. The formula giving the

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1388–6150/$20.00

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temperature dependence of the relaxation time is presented below (its detailed description was done previously [12]):

$$\tau=\tau_1\exp\left(\frac{\Delta H_\alpha}{\Delta C_\mathrm{p}(T_\mathrm{g})}\frac{1}{T}\right) \tag{1}$$

$$\Delta H_\alpha=n_\alpha H_1 \tag{2}$$

$$n_\alpha=n_1\left(1-\frac{1}{1+\left(\frac{T}{T_\mathrm{c}}\right)^\beta}\right) \tag{3}$$

Another characteristic of the formula is the structure heterogeneity approach. The three-phase model was applied. In this way, the structural relaxations (α relaxations) occurred in 'real' and 'ordered' amorphous phases were described using new formula. These fractions of the amorphous phase were characterised by the mobility of the molecules built the fractions. Moreover the formula considers the many-body nature of the α relaxation, its origin, and possible relation to the glass transition studied by differential scanning calorimetry [13, 14]. Both facts were revealed in the temperature dependence of the activation enthalpy of the relaxation. An application of the sigmoidal function ($n_\alpha \rightarrow f(T)$) for the process description gave looks-like a crossover effect at some characteristic temperature, T_{99}. According to the function definition it is a temperature at which all mers (a basic unit of chain) of each basic relaxing segment (composed of several mers) are thermally activated for a cooperative motion within the frame of one segment [12]. It was found that this characteristic temperature for the 'ordered' amorphous structure is much lower than for 'real' amorphous one (for details, one can see Table 2 in [10]). Unfortunately, this temperature was not experimentally observed by relaxation technique. However, T_{99} would relate to the 'universal' value proposed earlier [15] and to the T^* value defined in a neutron scattering experiments (so-called 'crossover' temperature [6]). The T_{99} values estimated for the 'real' amorphous phase (the new equation was tested for semi-crystalline poly(4-methylene-1-pentene), PMP, liquid crystalline polynorbornene, SCLC, and polyethylene, PE) was much higher than the temperature of a polymer degradation [10]. Moreover, the new formula shows how the system dynamics changes from a local (segmental) to a global (cooperative) due to a step activation of the polymeric chain. The feature of the step activation and the correlation between the data obtained by different experimental techniques are presented in Fig. 1. It was taken $T_\mathrm{c}\neq T_\mathrm{g}$ for the fitting procedure in earkier papers [8, 9, 10]. Owing to the fact, that both values were similar (always $T_\mathrm{g}<T_\mathrm{c}$), in new approach [11], $T_\mathrm{c}=T_\mathrm{g}$. It reduced the number of fitting parameters. T_c is the temperature at which 50% of the mers (segments) take part in the collective motion.

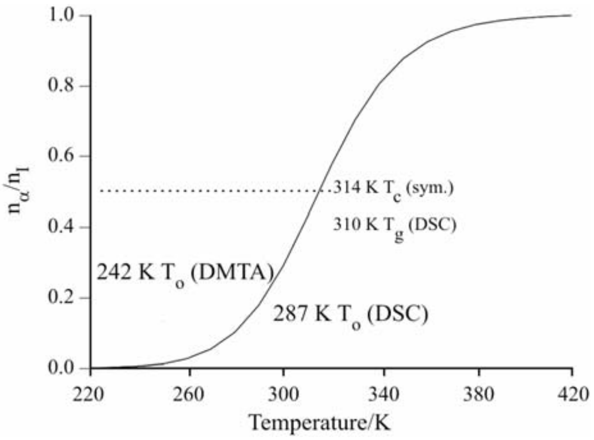

Fig. 1 Temperature dependence of the number of mers taking part in the structural relaxation. T_c – parameter of the fitting procedure, T_g and T_o(CMTA) taken from DSC and DMTA measurements, respectively. T_o (DSC) is the temperature at which the initial deviation from the base-line can be found in the DSC curve

As was mentioned above, the formula could be successfully applied to the 'real' amorphous fraction of the amorphous phase as well as to the 'ordered' one. It was assumed that the latter fraction is a result of the coexistence of crystal and amorphous phases in one polymeric system. The 'ordered' fraction represents restricted chain mobility that makes it similar to a 'rigid' fraction of the amorphous phase [16]. The latter term described the restricted mobility obtained by various factors whereas the former one concern the restriction caused by the crystallites (an internal factor).

Structural heterogeneity

A characteristic topology for semi-crystalline polymers is a distribution of crystallites in an amorphous matrix that would lead to existence of an interphase of various supermolecular structure. This three-phase model ('real' amorphous, 'ordered' amorphous and crystalline phases) was used for the data explanation concerning biodegradable polymers recently [17]. The authors combined mechanical spectroscopy, small-angle X-ray scattering and differential scanning calorimetry. More spectacular presentation of the interphase existence in real systems was done for dielectric spectroscopy applied to liquids [18] and polar oligomeric systems (polymers with a low molecular mass) [19]. The studied systems were prepared as a glass (there was no sign of crystallites) in nanoporous media, hence, biphasic nature of the supermolecular structures of the oligomers (only 'real' and 'ordered' fractions) could not be a result of the influence of the arrangement of the chains built the crystal phase on the amorphous regions. It must be emphasised that this biphasic effect only resulted from an interaction of the confined macromolecules with the internal surface of the medium (a porous matrix). The thermal data did not show crystallisation or melting of the oligomers. In all cases, the dielectric response revealed two relaxations. The one at lower temperature corresponded with the α relaxation of bulk oligomeric material and the second one at higher temperatures strongly depended on the pore size and the character of the internal surface of pores. Therefore that latter relaxation was assigned to the chain segments forming an interfacial layer close to the pore wall. Their mobility was essentially lower than in the centre of the pore [19]. One can easy find that mentioned above studies not only are convergent to our previous results concerning the origin of two α relaxations but also confirm our idea on the miscellaneous supermolecular structure of the amorphous phase implicating various segment mobility. In our experiments, the restricted mobility resulted from the fact that some part of the long chain was between crystallites, which acted as bounds (topological nodes). The same effect, as concerned the chain mobility, was achieved in the nanoporous medium. However in this case, the existence of the bonds was the results of the chemical reaction between the ends of the short chains and the chemically reactive groupsm which are the part of the molecules covering the surface of the porous medium. The reaction occurred only on the internal surface of the pores. Hence, the chains in the centre part of the pore behaved like in the bulk material.

New factor of mobility restriction–PMP example

In order to study the influence of various crystallites on mobility of the chains in the 'ordered' amorphous region, PMP films cast from different solutions were investigated by mechanical spectroscopy, DMTA. Results of other experimental techniques are taken into account, too. Detailed description will be done in a separate paper. DMTA spectra for different samples obtained for 10 Hz are presented in Fig. 2. When PMP is dissolved in various solvents, different crystal phase is formed in PMP films. Five crystal modification, prepared under different conditions, were described for PMP [20]. One can easy find that the sample preparation influenced both relaxations. The temperature of *E*" maximum for relaxation signed as α_g is the highest for the sample prepared from melt (ME) and shifts towards low value for the samples prepared from solutions. It should be mentioned here, that the studied films did not contain residual amount of solvents and no reaction occurred between the used solvents and PMP. The effect of residual solvent on both relaxations was described previously for chosen systems [21]. The relaxation signed as α_c differ for studied samples, too. The curve for the film cast from toluene (TOL) exhibits two well separated maxima in the temperature region of the α_c relaxation. The maximum at lower temperature is in good agreement with the maximum observed for the film obtained from melt whereas the second maximum is almost at the same position in the temperature scale as the maximum found for the film cast from trichloroethylene (TRI). One can see that the maximum for the α_c relaxation of the film cast from carbon tetrachloride (CT) is located between the maxima found for TOL. It was postulated that the α_c relaxation reveals the influence of the crystalline domains on the amorphous phase. In such a case the 'ordered' amorphous phase (interphase) is formed [7]. Owing to the fact that various crystalline is formd in the cast films, the deviation of the α_c peak seems to be understandable.

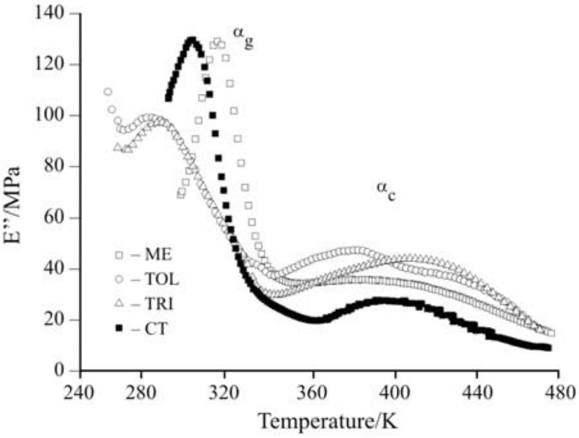

Fig. 2 Imaginary part of Young's modulus, *E*", as a function of temperature for studied samples cast from: □ – melt (ME); ○ – toluene (TOL); △ – trichloroethylene (TRI); ■ – carbon tetrachloride (CT). Relaxations of the 'real' and 'ordered' amorphous regions are signed as α_g and α_c, respectively

Conclusions

In summary, we have shown that the systems obtained in the nanoporous matrix and these one studied for semi-crystalline polymers exhibit similar behaviour. It means that the internal surface and the crystalline phase influence the amorphous regions similar. Moreover, both factors act like bounding layers restricting the mobility of the chains as compared to bulk, totally amorphous, material. It was surprisingly found that the α_c relaxation splits into two well separated relaxations. The predicted temperature of the ‘crossover’ effect, T^*, is well reproduced by new formula under the assumption of the structural heterogeneity of the amorphous phase, i.e. three-phase model. The dynamic heterogeneity is revealed by new function, which shows the step thermal activation of the mers taking part in the structural relaxation. This function links a description of the local and global motions influencing macroscopic properties of polymers, too.

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Received: July 29, 2007
Accepted: August 14, 2007

DOI: 10.1007/s10973-007-8651-1