

Molecular mobility and phase transitions in confined liquids

Research Team

P.Pissis, *Professor*

K.Christodoulides, *Assoc. Professor*

L. Apekis, *Assoc. Professor*

D. Daoukaki, *Assoc. Professor*

S. Kriptomou (*Research Student*)

D. Fragiadakis (*Research Student*)

National Technical University of Athens, Greece

Introduction

Molecular dynamics and phase transitions in glass-forming liquids and in polymers confined in small volumes were investigated in the frame of the project. Special attention was paid to the investigation of the glass transition and the associated α relaxation (dynamic glass transition). The glass transition, that is the freezing of a supercooled liquid into an amorphous solid, is a central problem of condensed-matter physics [1-3]. There exist several theoretical approaches to but no generally accepted theory of it. The investigation of effects on glass transition induced by confinement of glass-forming liquids and of amorphous polymers in mesoscopic volumes may provide additional information on the dynamics of glass transition and may help to check theories and models proposed for it [4]. This expectation is based on the central role of the cooperativity concept in many theories and models for the glass transition (however not in the very popular mode coupling theory [2]).

In the first part of the project glass-forming liquids including glycerol, propylene glycol (PG) (both hydrogen bonded liquids) and the non-associating N-methyl- ϵ -caprolactan (NMEC), confined in model geometries of 1-10nm size were investigated. Work with these liquids had started previously [5-8] and was completed within the project. The second part of the project was devoted to polymers confined within nanocomposites, hybrid organic-organic systems and interpenetrating polymer networks (IPNs). Investigation of these more realistic systems is interesting from the fundamental point of view for two reasons. The first is related to the possibility to extend studies to confining geometries with additional characteristics. The second is that detailed studies of molecular dynamics and phase transitions in nanostructured polymeric systems, which take properly into account effects of confinement, may make a valuable contribution to a better understanding of structure-property relationships in these systems. The investigation of these relationships is one of the central topics in Materials Science.

Experimental

In the case of the glass-forming liquids model geometries of Vycor glass, Gelsil glasses and butyl rubber (BR) with hydrophilic inclusions were employed, details being given elsewhere [4-8]. Confinement in the two glass systems is 2-dimensional, whereas the last system provides a possibility for 3-dimensional confinement. Molecular dynamics and phase transitions in these systems were investigated by dielectric techniques, including broadband dielectric relaxation spectroscopy (DRS) and thermally stimulated depolarization currents (TSDC). Details of preparation of the samples and of measurements have been given previously [4-8].

The polymeric systems investigated include: epoxy resin/carbon (ER/NCP) nanocomposites [9], polycarbonate/carbon nanotube nanocomposites [10], two hybrid systems of polyimide (PI) with poly dimethylsiloxane (PDMS) [11] and polyethylene glycol (PEG) [12], respectively, a hybrid system of polycyanurate (PCN) modified with flexible crosslinks of polytetramethylene glycol (PTMG) [13] and IPNs and copolymers of poly(butyl acrylate) (PBA) and poly(methyl methacrylate) (PMMA) [14]. Several experimental techniques were employed to investigate local structure and morphology of the complex polymeric systems. Details of the preparation of the materials and the structural-morphological characterization have been given elsewhere [9-14]. Molecular dynamics and phase transitions were investigated by DRS, TSDC, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and creep rate spectroscopy (CRS).

Results and Discussion

Figure 1 shows results for the shift ΔT_g of the glass transition temperature T_g of PG ($\Delta T_g = T_g(\text{bulk}) - T_g(\text{confined})$) against size, d , of confinement for different confining geometries: 2-dimensional confinement in pores of Gelsil and Vycor glasses and 3-dimensional confinement in the form of droplets in BR. T_g has been determined by DRS, as the temperature where the dielectric relaxation becomes 100s, and by TSDC, as the peak temperature of the corresponding TSDC peak [8]. The dielectric data measured by DRS for the α relaxation in PG are effective values, as they refer to the composite material consisting of the glass or polymer matrix and the liquid inclusions. Effective medium theories can be used to calculate the dielectric data for the confined liquid from the data measured on the composite material. This procedure is straightforward in the case of BR, where the liquid is confined in spherical droplets, as indicated by SAXS measurements [8]. In this work the Maxwell-Garnett theory [8] was used. The corrections are expected to be smaller in the glasses [8]. In all systems studied T_g is lower in the confined liquid compared to bulk. For the same system ΔT_g decreases with increasing d . The effects are stronger in BR than in the glasses. For both systems ΔT_g vanish at $d \approx 10-12\text{nm}$. This allows us to determine the cooperativity length ξ of the glass transition [3] as $\xi \leq 5-6\text{nm}$.

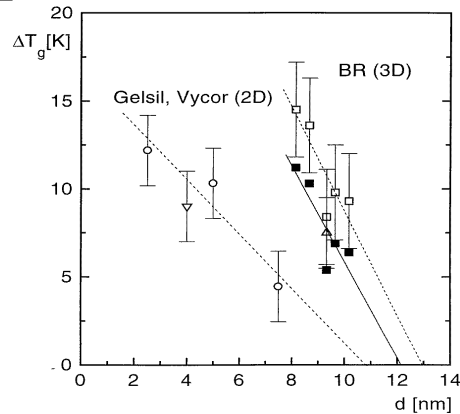


Figure 1. Glass transition temperature depression, $\Delta T_g = T_g \text{ bulk} - T_g \text{ confined}$, against size of confinement (nominal pore/droplet diameter d) for PG in BR with (!) and without correction after Maxwell-Garnett theory (∇) and in Gelsil ($-$). 8 and X denote TSDC data for PG in BR and in Vycor glass, respectively. Vertical bars indicate experimental errors. The lines are to guide the eyes.

In the case of the hybrid PCN/PTMG networks, with molecular weight of the flexible PTMG crosslinks incorporated into the PCN network equal to 1.000g/mol and weight fraction of PTMG equal to 0, 10, 20, 30 and 40wt%, DMA, DSC, TSDC and DRS data show, in agreement to each other, a single glass transition/ α relaxation, indicating (microscopically) homogeneous mixing of the two components. The existence of heterogeneity at nm scale (nanoheterogeneity) was followed by DRS. Figure 2 shows the Arrhenius plot for the α relaxation. We observe a systematic shift of the relaxation to lower temperatures/higher frequencies with increasing amount of PTMG. For the sample with 30% PTMG we observe, however, a change of the dynamics from that of the cooperative α relaxation at higher temperatures to that of the Goldstein-Johari β relaxation at lower temperatures. These results suggest that at high temperatures α relaxation occurs through the cooperative rearrangement of the polymeric chains, whereas at lower temperatures, with the cooperative length increasing, cooperativity is suppressed, due to spatial nanoheterogeneity of the sample. Other dielectric results support this interpretation, in agreement with SAXS data obtained with the same samples [15].

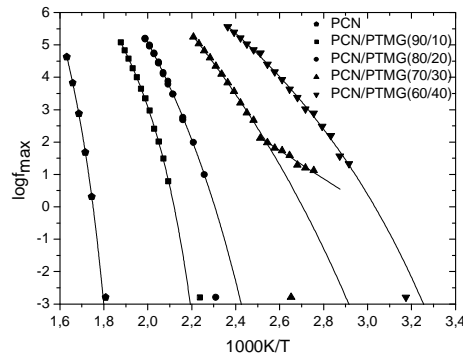


Figure 2. Arrhenius plot of the α relaxation in pure PCN and the hybrid networks indicated on the plot. TSDC data are included at the equivalent frequency of 1.6 mHz. The lines are fittings of the VTFH and the Arrhenius equation (for the hybrid network PCN/PTMG(70/30)) to the DRS data for the α relaxation.

Figure 3 shows DRS results obtained with the epoxy resin/carbon (ER/NCP) nanocomposites at various weight fractions of NCP: real (ϵ') and imaginary (ϵ'') part of dielectric permittivity versus temperature at a constant frequency of 80,805 Hz. The data have been recorded isothermally by frequency scanning and have been replotted here to facilitate a comparison with DSC and dynamic mechanical data. A relatively high frequency has been chosen for the presentation to eliminate conductivity effects present at lower frequencies. An overall increase of the molecular mobility can be observed in Figure 3 (in agreement with TSDC data not shown here), in the sense that, at each temperature, ϵ' and ϵ'' increase with increasing filler content. This is to a large extent related to the formation of a percolation structure of the nanoparticles, as confirmed by the dependence of ϵ' (at a frequency of 1 Hz and a temperature of -50 °C) on Φ of NCP in the inset of Figure 3 (a). The well-known equation for the dependence of ϵ' on Φ from percolation theory has been used:

$$\epsilon'(\Phi) = \epsilon'_m + A|\Phi - \Phi_c|^{-t} \quad (1)$$

where ϵ'_m is the dielectric constant of the matrix and t is the critical exponent. The values of Φ_c and t have been determined to be 7.4% and 0.69, respectively.

Two relaxations, a secondary (β) relaxation at lower temperatures and a primary (α) relaxation at higher temperatures, associated with the glass transition of the ER matrix, can be observed in Figure 3. For both relaxations, the strength [i.e., the magnitude of the peak in $\epsilon''(T)$ and the corresponding step in $\epsilon'(T)$] increases in the nanocomposites, particularly for the sample above Φ^* . The timescale (temperature position) of the response shows, however, a different behavior. For the local β relaxation, it does not change with the composition, whereas for the cooperative α relaxation, the peak temperature increases slightly in the nanocomposites, particularly at higher filler contents, at which it shifts out of the temperature range of Figure 3. (measurements at higher temperatures and lower frequencies are less conclusive for higher content nanocomposites, as the results are masked by conductivity effects). Thus, the DRS results allow us to discuss molecular mobility in terms of the relaxation strength and the timescale of the response. The increase in the relaxation strength for both β and α can be understood in terms of increased free volume, in agreement with results obtained for other nanocomposites. The slowdown of the cooperative α relaxation (dynamic glass transition) provides additional evidence for the immobilization of polymer chains in the interface layer around the particles (the formation of a bound polymer).

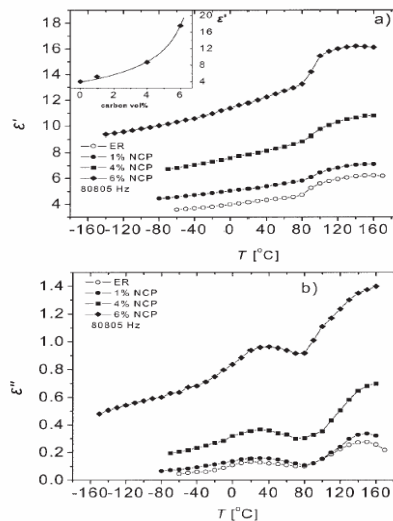


Figure 3. (a) Real part (ϵ') and (b) imaginary part (ϵ'') of the dielectric permittivity versus the temperature (T) at 80,805 Hz. The inset shows ϵ' (measured at 1Hz and -50°C) versus the NCP volume concentration. The line is a fit of eq 1 to the data.

Figure 4 shows results obtained with the random copolymers and the IPNs of PBA and PMMA [14]. The main interest in this study was to follow the merging of the main α and the secondary β relaxations of PBA and PMMA in the IPNs in comparison to the copolymers. In both cases a high amount (10wt%) cross-linking agent was used, resulting in a high cross-linking density, to force a certain degree of compatibility of the IPNs, as shown by DMA and TSDC results [14]. DRS was then employed to follow details of the relaxations over a wide frequency range. In neat PMMA the β relaxation dominates over the α relaxation, whereas the opposite is the case in neat PBA. This is reflected in Figure 4, where the Arrhenius equation is fitted to the neat PBA data and the Vogel-Tammann-Fulcher-Hesse (VTFH) equation to the neat PMMA data. The numbers in Figure 4 following the designations COP and IPN give the weight percentage of PBA. The main result in Figure 4, confirmed also by analysis of the

magnitude of the relaxations (dielectric strength) [14], is the very different behavior of a copolymer network and an IPN with the same average composition. It seems that in the case of the IPNs the effect of the cooperative α relaxation disappears. This fact can be ascribed to the distribution of the glass transition in a broad temperature interval, what makes that at any temperature only a small part of the chain segments contribute to the cooperative conformational rearrangements that are responsible for the α relaxation. Thus, the characteristics shown by the overall relaxation process are those of the secondary relaxation that predominates in the whole temperature interval.

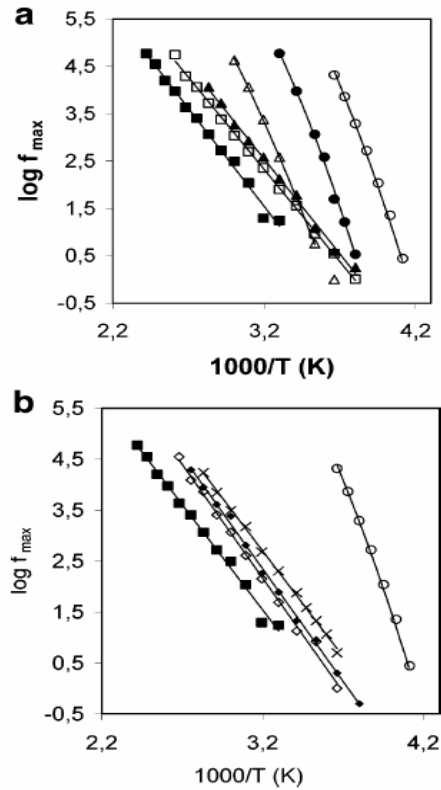


Figure 4. Arrhenius diagram showing the position of the relaxation peaks in the frequency axis at different temperatures: (a) (!) *net*-PMMA, (∇) COP20, (Δ) COP40, (8) COP 60, (.) COP80, and (O) *net*-PBA; (b) (!) *net*-PMMA, (M) IPN42, (7) IPN50, (\square) IPN59, and (O) *net*-PBA. The lines in these plots correspond to the Arrhenius behavior in the case of secondary relaxations and to the VFTH equation in the case of pure α relaxations.

Conclusions

The results obtained within the project contribute to a better understanding of molecular dynamics in glass-forming liquids and polymers under conditions of geometrical confinement, in particular with respect to the glass transition (segmental dynamics). The decrease of T_g (faster dynamics) in model confining geometries of size comparable to the cooperativity length at T_g becomes less clear in more complex systems and IPNs, due to contribution of various effects. More work is needed, by combining complementary techniques to study various aspects of molecular dynamics, to further clarify this point.

References

1. Jackle, J.: "Models of the glass transition", *Rep. Prog. Phys.*, **49**, 171, 1986
2. Goetze, W.: *Liquids, Freezing and the Glass Transition* (Berlin: Akademie), 1991
3. Donth, E.: *The Glass Transition. Relaxation Dynamics in Liquids and Disordered Materials* (Springer, 2001)
4. Kremer, F. and Schönhals, A.: *Broadband Dielectric Spectroscopy* (Springer – Verlag, Berlin Heidelberg, 2003)
5. Pissis, P., Daoukaki-Diamanti, D., Apekis, L. and Christodoulides, C.: "The glass transition in confined liquids", *J. Phys.: Condens.Matter*, **6**, L325-L328, 1994
6. Barut, G., Pissis, P., Pelster, R. and Nimtz, G.: "Glass transition in liquids: two versus three-dimensional confinement", *Phys. Rev. Lett.* **80**, 3543, 1998
7. Daoukaki, D., Barut, G., Pelster, R., Nimtz, G., Kyritsis, A. and Pissis, P.: "Dielectric relaxation at the glass transition of confined N-methyl- ϵ -caprolactam", *Phys. Rev. B*, **58**, 5336, 1998
8. Pissis, P., Kyritsis, A., Daoukaki, D., Barut, G., Pelster, R. and Nimtz, G.: "Dielectric studies of glass transition in confined propylene glycol", *J. Phys.: Condens. Matter*, **10**, 6205, 1998
9. Kotsilkova, R., Fragiadakis, D., Pissis, P.: "Reinforcement Effect of Carbon Nanofillers in an Epoxy Resin System: Rheology, Molecular Dynamics, and Mechanical Studies", *J. Polym. Sci.: Part B: Polym. Phys.*, **43**, 522, 2005
10. Pissis, P., Fragiadakis, D.: "Broadband dielectric spectroscopy for studying morphology and interfacial effects in polymer nanocomposites", presented at: *11th European Conference on Composite Materials-ECCM1*, Rhodes (Greece), May-June 2004
11. Kripotou, S., Pissis, P., Bershtein, V. A., Sysel, P., Hobzova, R.: "Dielectric Studies of Molecular Mobility in hybrid polyimide-poly(dimethylsiloxane) networks", *Polymer*, **44**, 2781, 2003
12. Kripotou, S., Pissis, P., Sysel, P., Sindelar, V. and Bershtein, V. A.: "Structure-property relationships in novel poly (imide-amide)-poly (ethylene glycol) hybrid networks", in preparation
13. Kripotou, S., Pissis, P., Kontou, E., Fainleib, A.M., Grigoryeva, O. and Bey, I.: "Structure –property relationships in brittle polymer networks modified by flexible cross-links", submitted to *Materials Science Poland*
14. Berzosa, A.E., Ribelles, J.L.G., Kripotou, S. and Pissis, P.: "Relaxation spectrum of polymer networks formed from butyl acrylate and methyl methacrylate monomeric units", *Macromolecules*, **37**, 6472, 2004
15. Bershtein, V.A., David, L., Egorov, V.M., Fainleib, A., Grigoryeva, O., Bey, I. and Yakushev, P.N.: "Structural/compositional nanoheterogeneity and glass transition plurality in amorphous polycyanurate-poly(tetramethylene glycol) hybrid networks", submitted.