CORRELATION BETWEEN THE α RELAXATION AND THE EXCESS WING FOR POLYCHLORINATED BIPHENYLS AND GLYCEROL

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Abstract

Data are presented for three glass formers, each having an excess wing in the low temperature dielectric loss spectra. Two polychlorinated biphenyls, whose α relaxations have equivalent temperature dependences, exhibit excess wings that are clearly different. Comparison of the spectra for glycerol at atmospheric pressure and at P=0.9 GPa reveals a different response of the α relaxation and the excess wing. These findings cannot be reconciled with the notion that the excess wing is an inherent part of the α relaxation. Interpretation of the spectra as a superposition of distinct α and β processes, however, is consistent with the observed behavior.

Keywords: dielectric loss and relaxation, glass transition

Introduction

The frequency dependent dielectric loss, $\varepsilon''(\nu)$, of glass forming materials is dominated by the structural relaxation (α relaxation), which dramatically slows down as the glass transition is approached. In addition to the α relaxation, present in the $\varepsilon''(\nu)$ spectra is a secondary relaxation (β relaxation), which can often be resolved as a distinct second peak. However, if these relaxation times are very close, it is difficult to resolve the secondary peak, especially if it is of low strength. In recent years, much attention has been given to materials like glycerol and propylene carbonate [1–4] whose dielectric loss spectra evidence a high frequency power law $\varepsilon''(\nu) \sim \nu^{-b}$ distinguished from the power law describing the high frequency flank of the α relaxation $\varepsilon''(\nu) \sim \nu^{n-1}$; however a secondary peak per se is never resolved. A current debate concerns whether the observed wing is part of the α relaxation or a submerged secondary relaxation. Investigation of such materials to determine if any correlation exists between the two phenomena (e.g. the α peak and the wing) can be informative.

Dielectric spectroscopy measurements on two polychlorinated biphenyls (PCB) of different chlorine content were carried out over a broad frequency range. The dielectric loss spectra for both the PCBs are very similar to those observed for glycerol, with a

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structural relaxation and a high frequency wing. Moreover, the fragility of the PCBs are intermediate between the respective fragilities of glycerol and propylene carbonate.

Another interesting case is the effect of pressure on the dielectric relaxation of glycerol. We examine previously published data with the objective of looking for any correlation between the α relaxation and the excess wing [5].

Experimental

The two PCB (obtained from J. Schrag and manufactured by Monsanto) are referred herein as PCB42 and PCB62, having 42 and 62% by mass chlorine, respectively. PCB are mixtures of biphenyls containing one to nine chlorines per molecule; the presence of various homologs suppresses crystallization. The primary species in PCB42 and PCB62 are trichlorobiphenyl and heptachlorobiphenyl, respectively.

Dielectric measurements were carried out over 13 decades of frequency (10^{-4} to 10^{9} Hz), using an IMASS time domain dielectric analyzer, a HP4284A LCR meter and a HP491A impedance analyzer.

Dielectric measurements on PCB

The glass transition temperature, defined as the temperature at which the relaxation time ($\tau_{max}=1/2\pi f_{max}$) equals 100 s, was measured to be T_g=221 and 269 K for PCB42 and PCB62, respectively. Notwithstanding this difference, from the analysis of the temperature dependence of f_{max}, the two materials were found to have equivalent T_g normalized temperature dependences over the entire temperature range. To quantify their fragility, we calculated the steepness index $m=-d\log(f_{max})/d(T_g/T)\big|_{T=T_g}$, obtaining m=63 [6]. This value falls in between that of glycerol and propylene carbonate, glass formers having an excess wing but not a distinct β relaxation.

Displayed in Fig. 1 are four dielectric loss spectra (normalized to their peak value) for each sample at temperatures for which the f_{max} are very close. The solid lines are the Laplace transforms of the Kohlrausch–Williams–Watts (KWW) function [7, 8]

$$\phi(t)=\exp[-(t/\tau_{kww})^{1-n}], \ 0\leq n<1 \qquad (1)$$

where τ_{KWW} is the relaxation time and the parameter n characterizes the departure from exponential decay. In the coupling model (CM) [9], n increases with intermolecular interaction strength [10], so that by comparing n for different glass formers at their respective T_g, it is possible to discern differences in coupling strength (intermolecular cooperativity). Moreover, the non-exponentiality of the dielectric dispersion (and therefore n) have been found to correlate with the fragility [11].

Although the peaks in Fig. 1 change with temperature, it is noteworthy that for equal f_{max}, n is equal for the two materials. Therefore, both τ and n for the α relaxation of the two materials have equivalent temperature behavior. This is particularly interesting if we want to investigate the nature of the excess wing in the PCBs. If the wing
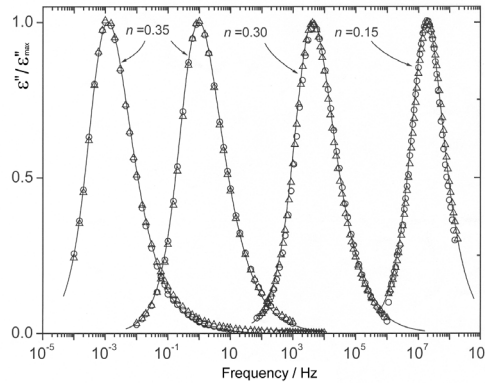
Fig. 1 Dielectric loss spectra for PCB62 (o) and PCB42 (△) normalized to the maximum without any frequency shift. For PCB42 the temperatures are (from left to right): 220.2, 231.7, 249.1 and 288.6 K. For PCB62 the temperatures are (from left to right): 268.1, 281.6, 304.2 and 347.5 K. The solid lines are KWW functions (Eq. (1)), the value of n are indicated in the figure

is part of the α relaxation, from the previous results we would expect that the excess wing for the two materials should be the same.

In Fig. 2 is shown the normalized loss peak for PCB62 and PCB42 at T=268.1 and T=220.2 K, respectively, together with fits to the KWW function (dashed line). Evident for both materials is a departure from the power law of the α relaxation ($\varepsilon'' \alpha \, \nu^{n-1}$), giving rise to a second power law $\varepsilon'' \alpha \, \nu^{-b}$ with $b < 1-n$. It is also apparent that the wings for the two samples are different. Given the similarities of the primary α relaxation, this indicates that the wing is a separate β relaxation.

Accordingly, the spectra were analyzed as a superposition of two relaxations, represented by a KWW and Cole–Cole [12] function respectively

$$\varepsilon''(\nu)=\Delta\varepsilon_\alpha \int_0^\infty dt \exp(-i2\pi t)\exp(-d\exp[-(t/\tau_\alpha)^{1-n}]/dt)+\Delta\varepsilon_\beta Im\left[\frac{1}{1+(i2\pi\nu\tau_{cc})^{1-\alpha_{cc}}}\right] \quad (2)$$

where $\Delta\varepsilon_\alpha$ and $\Delta\varepsilon_\beta$ are the relaxation strengths, τ_{cc} is a relaxation time, and α_{cc} is a shape parameter. The individual contributions of the two β relaxations are indicated by the dotted lines in Fig. 2. The fit of the β relaxation yields $\Delta\varepsilon_\beta/\varepsilon''_{max}=3.7\square10^{-2}$, $\tau_{cc}=0.6$ s and $\alpha_{cc}=0.57$ for PCB62, and $\Delta\varepsilon_\beta/\varepsilon''_{max}=9.5\square10^{-2}$, $\tau_{cc}=0.8$ s and $\alpha_{cc}=0.65$ for PCB42. This analysis shows that the relaxation times of the two β relaxation times are very close, while there is a marked difference between their dielectric strengths and α_{cc}. This finding is in agreement with the correlation found between $\tau_\beta(T_g)$ and n [13]. In terms of the CM, in fact, the more cooperative the α relaxation (larger n), the more α will be separated from the non–cooperative β relaxation. By the same token, for close values of n, a similar separation is expected between the two processes. In Fig. 2 the β peaks for the two PCBs are almost coincident at temperatures at which the values of τ_α are equal.
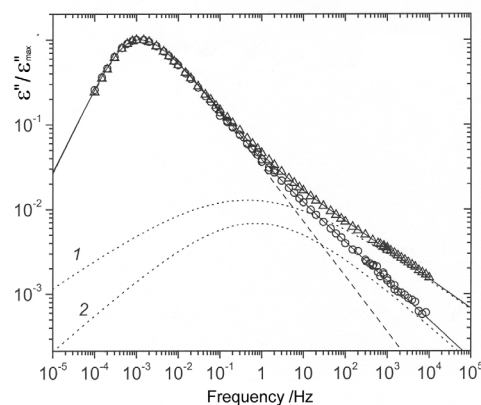
Fig. 2 Dielectric loss spectra, normalized to their maximum, for PCB42 at T=220.2 K
(o) and PCB62 at T=268.1 K ($\triangle$). The frequencies are as measured. The solid
lines are the best fit to Eq. (2) with n=0.35, the dashed line indicates the α relax-
ation contribution (the same for both the materials) and the dotted line is the
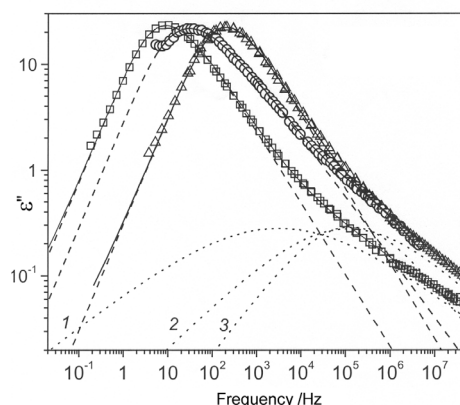β relaxation contribution (curve 1: PCB62; curve 2: PCB42)

Fig. 3 Dielectric loss spectra for glycerol, from Lunkenheimer [14] at atmospheric
pressure T=204 K ($\square$) and T=213 K ($\triangle$) and from Forsman *et al*. [5] at
P=0.9 GPa and T=243 K (o). The solid lines are the best fit by using Eq. (2),
the dashed lines are the α relaxation contribution, and the dotted lines the
β relaxation contribution (curve 1 – T=204 K and P=0.1 MPa; curve 2 –
T=213 K and P=0.1 MPa; curve 3 – T=243 K and P=0.9 GPa)

Dielectric measurements on glycerol

The dielectric properties of glycerol have been measured by many investigators. For
example, Menon *et al*. [4] carried out dielectric spectroscopy over 14 decades of fre-
quency, and more recently Lunkenheimer undertook an extensive study reporting
data for more than 17 decades of frequency [14]. The interpretations of the excess

wing observed in glycerol are quite different: as an inherent part of the structural relaxation [15, 16] or as unresolved β relaxation [2]. Physical aging of glycerol, which causes a slowing down of the structural relaxation, has been shown to effect the emergence of a peak at frequencies associated with the excess wing [1].

We can further elucidate this issue by analysis of the ambient pressure spectra reported by Lunkenheimer [14], with spectra of glycerol under high pressure from Forsman *et al.* [5]. In Fig. 3 are two dielectric loss spectra at T=204 K (open squares) and T=213 K (open triangles) measured at atmospheric pressure along with a spectrum measured at T=243 K and P=0.9 GPa (open circles). This figure makes evident that the α relaxation at elevated pressure is broader, with the 'wing' more separated from the α relaxation. The individual contributions of the α and β relaxations for the three spectra estimated using Eq. (2) are reported in Fig. 3 (dotted lines for β relaxations, dashed lines for α relaxations). It is evident that the maximum of the β relaxation at P=0.9 GPa and T=243 K is at a frequency very close to that of the maximum of the β relaxation at T=213 K and atmospheric pressure, while f_{max} of the α relaxation is about one order of magnitude lower. This result is in agreement with the correlation between n and the separation between α and β relaxation [13]. In fact, the increase of pressure evidently causes an increase of the parameter n (and therefore the intermolecular cooperativity) of the α relaxation; consequently, the α and β relaxations results more separated in the frequency domain.

Conclusions

Herein we presented data for three glass formers, each showing the presence of an excess 'wing' in their low temperature spectra. Both the PCBs have α relaxations with equivalent temperature dependencies (of both τ and n), while their excess wings are clearly different. An analysis of the low temperature spectra shows that the relaxation times of the two β processes are very close for the two materials.

A comparison of results on glycerol at atmospheric pressure and at P=0.9 GPa showed that pressure influences both the shape of the α relaxation and the separation between α and β peaks. In particular, an analysis of the spectra using Eq. (2) revealed an increase of the separation with increasing n.

These findings are consistent with the CM, in that an increase of the coupling parameter, reflecting an increase in intermolecular cooperativity, results in a larger temporal separation between non-cooperative (β relaxation) and cooperative motions (α relaxation).

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