

Dielectric Spectroscopy of PVAc at Different Isobaric-Isothermal Paths

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Received December 30th, 2011; revised January 29th, 2012; accepted February 29th, 2012

ABSTRACT

We studied broadband dielectric spectroscopy of a glass from systems that the dynamics of the primary α - and the Johari-Goldstein (JG) β -processes are strongly correlated in Poly(vinyl acetate) over a wide temperature T and pressure P range. Analysing the temperature and pressure behaviour of the α - and (Non-JG) β -processes, a correlation has not been found between the structural relaxation time, the (Non-JG) β -processes relaxation time and the dispersion of the structural relaxation. These results support the idea that the (JG)-processes relaxation acts as a precursor of the structural relaxation and therefore of the glass transition phenomenon but it is not clear relation in the (Non-JG) β -processes and structural relaxation at PVAc.

Keywords: Dielectric Relaxation; Nan-Size Motion; Pressure and Temperature

1. Introduction

Usually in the Glass former materials we can find complex relaxation pattern, which evolves over several time decades. A technique that it is useful for study the dynamic of relaxation inside the liquid and glass state is Dielectric spectroscopy [1-3]. It has turned out that in such a broad dynamic range several molecular processes take place, and usually most of them are characterized by non-exponential relaxation functions. In polymeric materials the slowest of these processes is called normal mode: simplifying, if we consider a vector connecting the two ends of a polymeric chain, the normal mode reflects the motion of such vector. In non polymeric materials the slowest process is usually called main, structural or α -relaxation [2-6]. It reflects the cooperative motion of the molecules and its characteristic time can be related to the overall viscosity of the material. The origin of the structural α -relaxation is ascribed to cooperative motions that involve an increasing number of molecules and slow down dramatically when the glass transition is approached, for example either by decreasing temperature T or increasing pressure P (*i.e.*, density) [1-3]. So, it is challenging to distinguish between intermolecular and intramolecular secondary processes also in systems with a complex molecular structure, even showing more than one secondary process.

In this work, we contribute to such discussion by investigating the relation between the structural and the

secondary processes in the poly (vinyl acetate) (PVAc) in an interval of pressure ranging from 0.1 to 600 MPa and temperature from 100 to 350 K. The main goal is to find relation between alpha and secondary relaxation in PVAc and compare this system with relation of alpha and secondary relaxation in the mixture of the rigid polar molecule quinaldine (QN) and tristyrene.

2. Experiment and Materials

The complex dielectric constant $\epsilon = \epsilon' - i\epsilon''$ was measured in the frequency range from 10^{-2} Hz up to 10^7 Hz at different isothermal and isobaric conditions using Novo-control Alpha analyser. The temperature at atmospheric pressure was varied from 100 K and 320 K by means of a conditioned nitrogen flow cryostat. The high pressure experiment was carried out by means of an hydrostatic press and silicon oil as a pressure transmitting medium. A Teflon membrane prevented the oil to contact the dielectric cell. The temperature of the whole pressure chamber was controlled by a thermal jacket connected to a liquid circulator.

Poly (vinyl acetate) (PVAc), with M.W. = 167 Kg/mol, and $T_g = 310.7$ K is purchased from Aldrich. PVAc has interesting structural variations and can be obtained in the atactic, and thus amorphous form, which is crucial for investigations of the glass transition. PVAc has been often chosen to test the current aspects of various theories related with glass transition phenomena. An ample dipole

moment makes PVAc a good candidate of dielectric spectroscopy [7-10].

3. Results

Dielectric loss spectra, $\varepsilon(\omega) = \varepsilon' - i\varepsilon''$ of PVAc was measured from above to below the glass transition. We applied the different thermodynamic paths to studied the relation between the structural and the secondary relaxation close to T_g (P).

We acquired dielectric spectra along isothermal paths by varying pressure from 0.1 MPa up to the maximum value of 600 MPa, with step of 10 MPa in the supercooled liquid and step of 50 MPa in the PVAc, **Figure 2**. We also measured dielectric spectra by varying temperature at high pressure from 100 to 300 K in supercooled liquid and in the glass. The increase of pressure slows down the structural relaxation similarly to the decrease of temperature: the structural relaxation peak shifts to lower frequencies until the structure of the liquid is eventually arrested in a glassy state. At ambient pressure in PVAc only the α -structural process is visible above T_g , when spectra are collected in the frequency interval $10^{-2} - 10^6$ Hz. At temperatures below T_g two further relaxation processes, β -, is visible in the frequency interval, **Figure 1**. All the observed relaxation processes move towards lower frequencies on decreasing temperature or increasing pressure, the α -process being the most sensitive and the β - the less. The β -process occurs only at very high frequency and we can measure only at very low temperature at ambient pressure, but never at high pressure due to limitation of the temperature interval, **Figure 1**. In the PVAc below T_g we observe only one secondary relaxation.

Dielectric spectra were fitted with a superposition of different HN and CC functions [1-3], one for each relaxation process. Since for any value of temperature not more than two relaxation processes appear, in the fitting procedure we never used more than two relaxation functions. Moreover, the β -process was usually described by the CC function. The fitting program, based on a least square minimizing procedure, contemporary fits the real and the imaginary part of the dielectric spectrum and furnishes the values of the parameters and the corresponding errors. **Table 1**, report some representative values of the parameters α and β for the considered systems at different pressure and temperature.

Finally, since in all the cases, near T_g , the structural and the secondary relaxations are well separated in the frequency scale we reproduced the structural relaxation peak by the Fourier transform of the KWW function. This further analysis allowed a direct estimation of the stretching parameter characterizing the broadness of the structural peak.

Table 1. Parameters of α -(structural), β -(secondary) relaxation at different pressure and temperature for PVAc.

P (MPa)	T (K)	α -relaxation		β -relaxation	
		α	β	α	β
250	323	0	0	0.55	1
300	323	0	0	0.56	1
350	323	0	0	0.57	1
400	323	0	0	0.58	1
51	342	0	0	0.56	1
101	342	0	0	0.56	1
0.1	244	0	0	0.66	1
0.1	244	0	0	0.68	1

As model independent parameter for the characteristic time scale of the process we considered the maxima of frequency, $\nu_{\max}^i = 1/(2\pi\tau_{\max}^i)$ corresponding to the loss peak maximum frequency, which was calculated by

$$\nu_{\max}^i = 1/2\pi\tau_i \times \left\{ \sin \left[\frac{((1-\alpha_i) \times \pi)}{(2+2 \times \beta_i)} \right] \right\}^{1/(1-\alpha_i)} \times \left\{ \sin \left[\frac{((1-\alpha_i) \times \beta_i \times \pi)}{(2+2 \times \beta_i)} \right] \right\}^{-1/(1-\alpha_i)} \quad (1)$$

The temperature dependence of ν_{\max}^α can be well fitted by a Vogel-Fulcher-Tammann, VFT, equation,

$$\nu_{\max}^\alpha = \nu_0^\alpha \exp(DT_0/(T-T_0))$$

over the entire temperature interval. The pressure dependence of ν_{\max}^α can be well fitted by a Vogel-Fulcher-Tammann like, PVFT, equation, $\log(\nu_{\max}^\alpha) = \log(\nu_{0\max}^\alpha) + [A \times P/(B-P)]$

over the entire pressure interval. In the isothermal paths, pressure dependence of ν_{\max}^α below T_g are well reproduced by the Arrhenius equation,

$$\nu_{\max}^\alpha = \nu_0 \exp(-P \cdot \Delta V_\beta / k_B T)$$

(where ΔV_β is the activation volume of the secondary β -relaxation), and in isobaric condition the temperature dependence of ν_{\max}^α below T_g is well reproduced by the Arrhenius equation,

$$\nu_{\max}^\beta = \nu_0^\beta \exp(-E_a / (k_B T))$$

The different VFT and Arrhenius parameters for the isobaric dielectric relaxation spectra of the different are listed in **Table 2**.

The value of the glass transition temperature, T_g , determined by $\tau_\alpha(T_g) = 10$ s at ambient temperature is ($310 \text{ K} \pm 2 \text{ K}$) for PVAc. From the **Figure 2**, it is clear that the position of secondary relaxation at T_g for isobaric paths, **Figure 2(a)**, isn't the same of isothermal path, **Figure 2(b)**.

4. Discussion

The combined variation of both temperature and pressure allows to reach dynamic states characterized by the same value of structural relaxation time, but different thermal

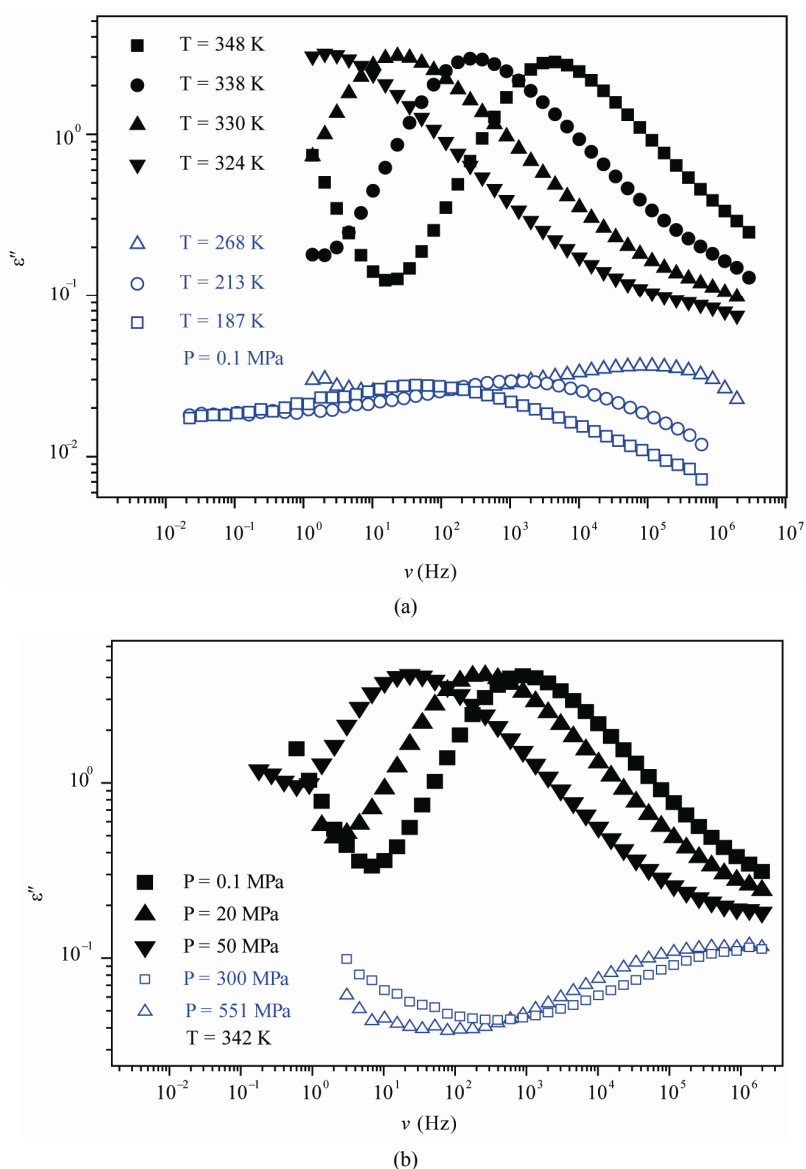


Figure 1. (a) Isobaric (0.1 MPa) dielectric loss spectra of PVAc measured at different temperatures (values reported in the figure); (b) Isothermal (342 K) dielectric loss spectra of PVAc measured at different pressure (values reported in the figure). The black spectra are measured in the supercooled liquid and are dominated by the α -peak and the blue open symbols spectra are measured in the glassy state and are dominated by the β -peak.

Table 2. The glass transition temperature and the relevant VFT parameter for three different systems, as determined by dielectric relaxation measurement [parameter of A and B come from the equation, $\log(\nu_{\max}) = \log(\nu_{0\max}) + A \cdot P/(B - P)$].

P (MPa)	T (K)	$\log(\nu_{0\alpha})$	DT_0 (K)	$T_g(P)$ (K)	$\log(\nu_{0\max})$	A	B (MPa)	$P_g(T)$ (MPa)
#	342	2.99	#	342 ± 1	16.6	16.6	618.3	132.9 ± 0.1
#	323	0.49	#	322 ± 1	98.8	98.8	1777.5	57.3 ± 0.1
0.1	318.4	13.7	2.95	318 ± 1	#	#	#	0.1 ± 0.1

energies and densities. The relative role of density and thermal energy on the slowing the structural relaxation on approaching the glass transition is a matter of study. Even if a similar behavior can be found for materials belonging to the same class, the detail of their relative

role varies for each system [11]. From the dynamic point of view the glass transition is traditionally defined by considering the structural relaxation time being a fixed long value. In other words, at different of temperature and of pressure the ratio $\tau_\alpha(P, T)/\tau_\beta(P, T)$ isn't con-

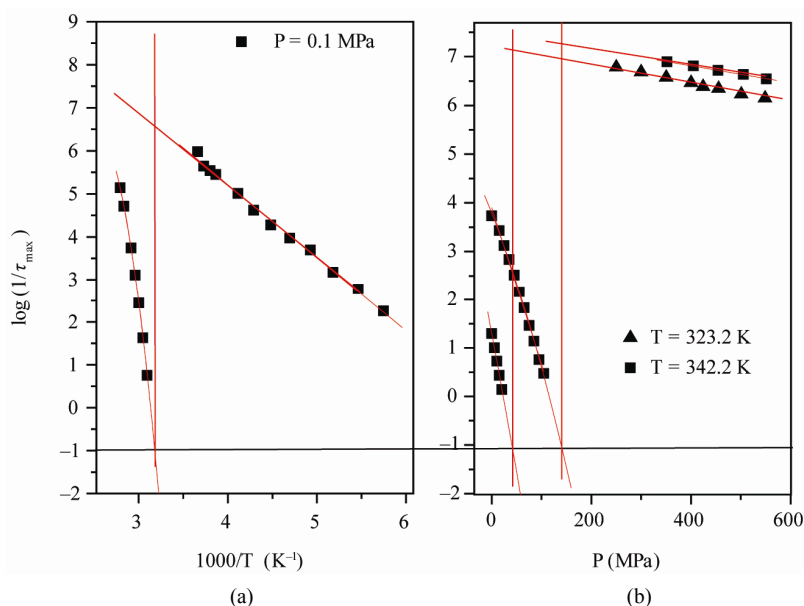


Figure 2. (a) Pressure dependence of the logarithmic of τ_{\max} for the α - (full symbols) and the β - (secondary) process, at two different values of T : 342K (squares), and 323.2 K (triangles) of PVAc (b) Temperature dependence of the logarithmic of ν_{\max}^{α} for the α - (full symbols) and the β - (secondary) process, at ambient pressure: 0.1 MPa (squares) of PVAc. In both panels the continuous lines represent fit with the VFT (α -relaxation) and Arrhenius (β -relaxation) equations. The horizontal dotted line show the relaxation time value used to define the glass transition. Crosses represent the values of τ_{\max} at $(T, P)_g$.

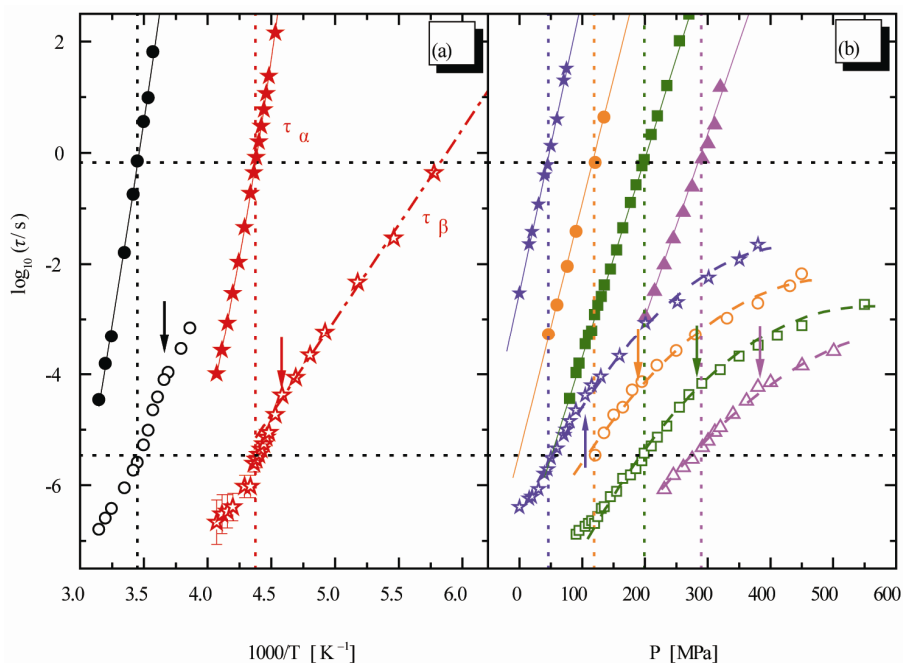


Figure 3. Relaxation map for the mixture 10% QN in tristyrene. (a) Isobaric data: 0.1 MPa (stars), 380 MPa (circles). (b) Isothermal data: 238 K (stars), 253 K (circles), 263 K (squares), 278 K (triangles). The ratio $\tau_{\alpha}(P, T)/\tau_{\beta}(P, T)$ is constant [12].

stant for PVAc for all thermodynamic paths. It is likely to suppose that the connection between α - and β -dynamics isn't a universal feature of all β -processes, but only of those local processes intimately connected to the cooperative structural dynamics. For comparison of β -

process at JG and Non-JG relaxation we compare the Non-JG relaxation at PVAc with JG relaxation at mixture of quinaldine (QN) with tristyrene.

At mixtures of quinaldine (QN) with tristyrene, **Figure 3**, ref. [12], the $\tau_{\alpha}(P, T)/\tau_{\beta}(P, T)$, T is constant for all

the isobaric-isothermal paths but at PVAc the $\tau_\alpha(P, T)/\tau_\beta(P, T)$ isn't constant. So, it is likely to suppose that the connection between α - and β -dynamics isn't a universal feature of all β -processes, but only at the JG relaxation.

5. Conclusion

We investigated the relation between secondary and structural dynamics of PVAc under variations of temperature and pressure. We found that the Non-JG relaxations and α -relaxation inside of PVAc is not relation to each other that it is different behaviour than the JG relaxation inside the mixture systems. The analysis consists in investigating the ratio τ_α/τ_β for different values of pressure and temperature (density and thermal energy), but the same value of structural relaxation time. According to such analysis we evidenced that the β -process in PVAc is not related with the structural dynamics at the glass transition.

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