

Dielectric Spectroscopy of Poly(Ethyl Methacrylate)-Carbon Dioxide System

Keti Vezzù¹, Matteo Petterle¹, Alberto Bertucco¹, Vito Di Noto²

¹*Dipartimento di Principi e Impianti di Ingegneria Chimica, Università di Padova
via Marzolo, 9 - I-35131 Padova PD ITALY*

²*Dipartimento di Scienze Chimiche
via Marzolo, 1 - I-35131 Padova PD ITALY*

* e-mail:

fax:

The investigation on the interactions of polymers with sub and supercritical fluids (SCFs) by dielectric spectroscopy was the aim of this work. The dissolution of the dense gas in the polymeric matrix causes different phenomena, such as the reduction of glass transition temperature and melting point. These effects are due to the increase of the chain and segmental mobility of the polymer and are referred to as “dense gas plasticization”. To study them, dielectric spectroscopy measurements of poly(ethyl methacrylate) (PEMA) were carried out in carbon dioxide (CO₂) at high pressure. Real and imaginary components of dielectric spectra are analyzed in order to study the relaxation phenomena of this macromolecular system.

INTRODUCTION

In the last decade, the use of supercritical fluids (SCFs) in polymer technology has seen an exponential interest, thanks to their properties. The application of SCFs to polymers allows the possibility to exploit their physical properties in order to change the polymer structure. In general, any compressed gas is quite soluble in a polymer at relatively high pressure, causing considerable matrix swelling and plasticization due to lowering of both the glass transition temperature (T_g) and the melting point (T_m) [1].

Supercritical carbon dioxide (CO₂) is the gas mostly used for applications to polymers. For instance, it is applied for chemical synthesis, for production of polymeric foams, fibres, micro-particles [2, 3] and blend [4 - 5], for polymer impregnation with chemical additives [6, 7] and for separation of gas mixtures using polymer membranes [8].

SCFs have been recently applied also in the field of polymer electrolytes (PEs) [9 - 13] to improve the conductivity of amorphous PEs. Sumita *et al.* [9 - 11] reported that the effect of CO₂ is related to the improvement of chain mobility, the enhancement of salt dissociation and the lowering of activation volume for conduction. CO₂ molecules are likely to be involved in Lewis acid-base interactions with electron donor species (such as carbonyl groups), producing plasticization of polymer electrolytes as it was previously found for other polymeric materials [10]. The result can be different in the case of hybrid organic-inorganic materials [12, 13], where the kind of atom ligands plays an important role. In this case, the glass transition of the treated material was reduced also after CO₂ had been removed, and the mobility of the segment was increased, but the conductivity turned to be reduced due to decrease of ion trapping phenomena.

The possible interaction among polymers, salts and dense gas is an important field for understanding the possible use of SCFs in polymer technology and the effect on the properties of final product.

The local motion of bonds, movement of polymer segments and relaxation of chains [14] can be studied by dielectric spectroscopy. In this work, a homemade high pressure cell for dielectric measurement was used to study the effect of solubilization of carbon dioxide (CO₂) in poly(ethyl methacrylate) (PEMA) films [15].

PEMA was chosen because its relaxation peaks are well defined and do not overlap with changing temperature; in addition its glass transition temperature is not far from room temperature. Kamiya et al. [16] studied the system PEMA-CO₂ and saw the plasticization effect of the dense gas, ascribed to a shift towards higher value of the relaxation peak frequency. Opposite results were obtained when employing helium as pressure generating medium.

In this work, the interaction between CO₂ and PEMA is analyzed in the range 50 – 75 °C for temperature and 15 – 80 bar for CO₂ pressure. The relaxation peaks are shifted to higher frequencies with increasing pressure due to the plasticizing effect of carbon dioxide, which prevails on the hydrostatic effect.

I - MATERIALS AND METHODS

The poly(ethyl methacrylate) (PEMA, molecular weight of 515 kDa, glass transition temperature at 63 °C) and toluene were bought from Sigma-Aldrich (Milan, Italy).

The CO₂ was supplied by Sapio srl (Monza, Italy).

The polymeric film was obtained by solvent casting of 2.5% (w/w) PEMA/toluene solution on a glass plate. The surface of the film was gilded by a ion sputtering technique.

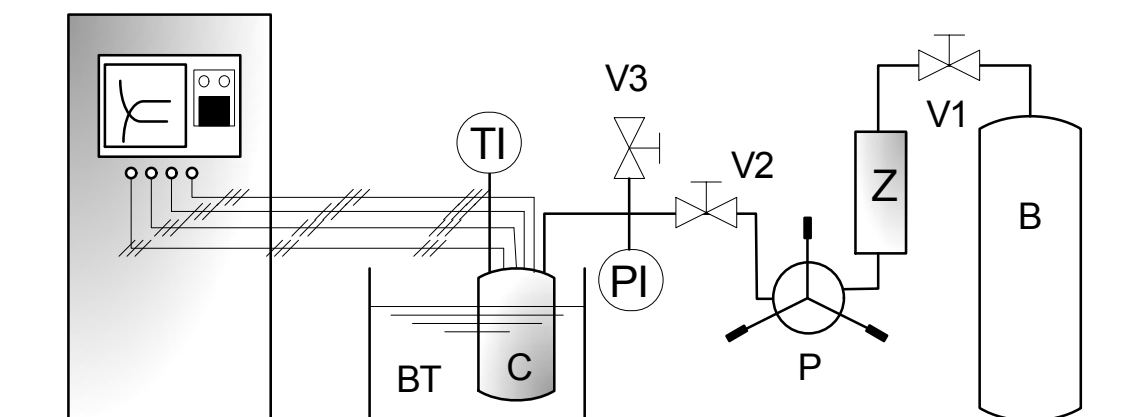


Figure 1. Experimental plant for high pressure dielectric measurements: C high pressure cell; P manual pump; Z zeolites dried bed; BT thermostatic bath; B CO₂; V1, V2, V3 on-off valves, PI pressure indicator; TI temperature indicator

The apparatus (Figure 1) is principally done by an Agilent 4294A precision Impedance Analyzer instrument and by the high pressure cell (C). The description of the cell is reported elsewhere [15]. It is heated by a thermostatic bath (BT), whose temperature is regulated by an external bath to reduce the possible electrical interference in the dielectric measurements. The temperature is measured by a PT 100Ω sensor (TI) with accuracy of ± 0.1 °C. The pressure is measured by precision Boundon gauge (PI). CO₂ is dried by zeolites (Z) and loaded into the cell by opening the valves V1 and V2. To obtain a pressure higher than that of CO₂ tank (B),

a manual screw pump (P) is used. The pump is cooled and CO₂ kept at liquid state by an ice bath.

The film is assembled between the two stainless steel electrodes, which are precisely located and kept in position by three compressing springs, to ensure a constant thin thickness during the measurement. Then the high pressure cell is closed and heated up to the desired temperature. When a steady temperature condition is reached, CO₂ is fed up to the desired pressure value. Dielectric measurements are performed in the range 20 Hz – 1 MHz when the equilibrium of the system is reached.

II - RESULTS

Dielectric measurement of PEMA films (thickness from 40 to 60 μm) were carried out in 50 – 75°C range of temperature and from 15 to 70 bar of CO₂ pressure. The maximum pressure reached during the experiment at 75 °C was 40 bar, because at higher pressure an electrical short circuit occurred. This fact could be due to the high plasticization of the materials, which caused a decrease of its mechanical properties.

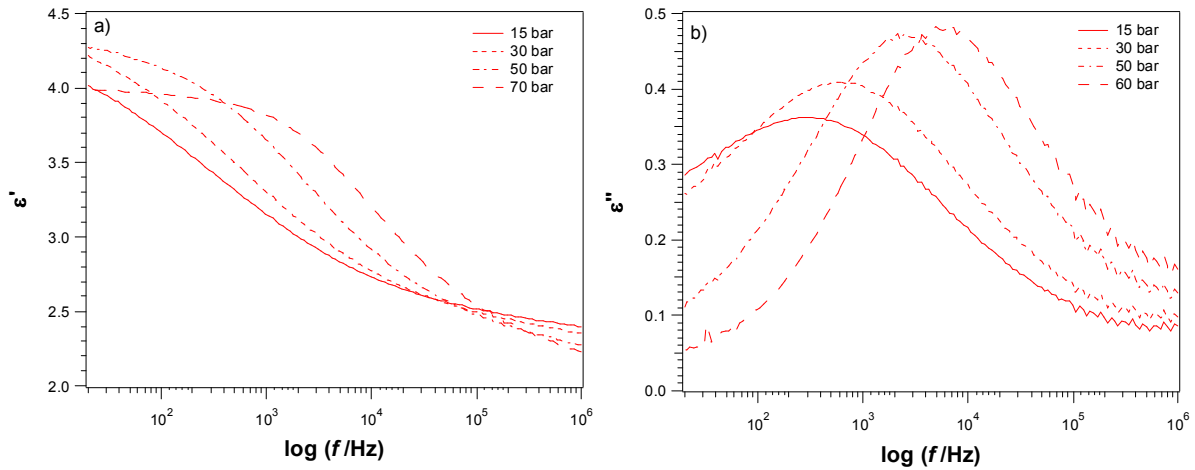


Figure 2. Some spectra of real (a) and imaginary (b) part of dielectric constant as function of $\log[f/\text{Hz}]$ and pressure at 50°C.

In Figure 2, an example of measured spectra is reported. It is possible to see the real (a) and imaginary spectra (b) of the permittivity of PEMA-CO₂ system as a function of frequency and pressure. For sake of clearness, only four measurements are reported. Note that the spectra obtained at lower pressure are different from those at higher pressure. This is due to the dissolution of CO₂ inside the polymer, which reduces the glass transition temperature, increases the chain mobility and so modifies the polarization moment. This fact is more evident in the spectra of imaginary permittivity, where the relaxation peak is more visible: it is also possible to see the shift of the relaxation peak versus higher frequency values with increasing pressure. This peak became higher and narrower when CO₂ pressure is raised from 15 bar to 70 bar.

To determine the position of the relaxation peak, the real and imaginary part of permittivity were analyzed [17, 18] by the general equation:

$$\epsilon(\omega) = \epsilon' - i\epsilon'' = \epsilon_{\infty} - i \left(\frac{\sigma_0}{\epsilon_0 \omega} \right)^s + \sum_{k=1}^n \frac{\Delta\epsilon_k}{\left(1 + (i\omega\tau_k)^{\alpha_k} \right)^{\beta_k}} \quad (1)$$

where τ_k is a characteristic relaxation time related to the peak frequency f_k , σ_0 is the direct current conductivity, s is a parameter that defines the frequency dependence of the conductivity term, $\Delta\varepsilon_k$ is the relaxation strength, α_k and β_k are the shape parameters which account for the symmetric and asymmetric broadening of the k -th relaxation peak.

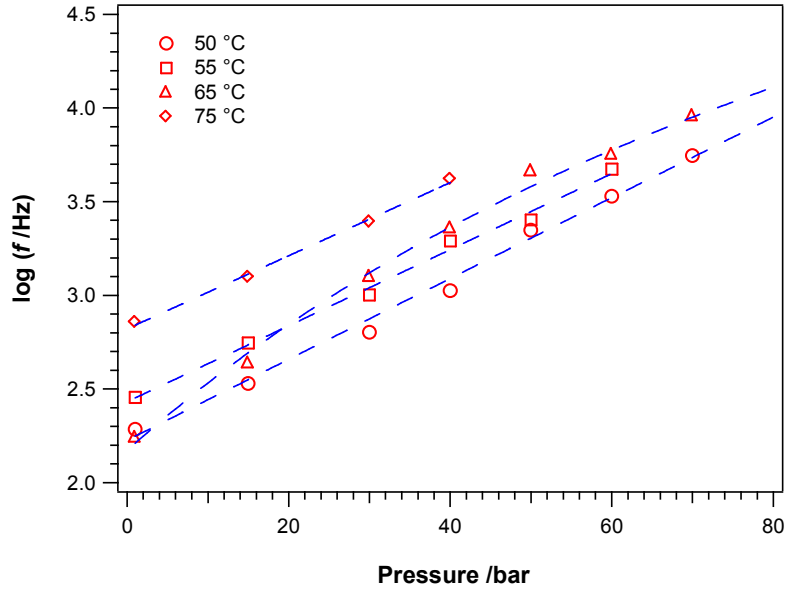


Figure 3. Relaxation peak frequency as a function of pressure and temperature.

From this analysis, one relaxation peaks is obtained for the PEMA-CO₂ system. Figure 3 shows the shift to higher frequency of this peak with increasing pressure. This fact is due to the plasticization effect of absorbed CO₂; in the case of prevalence of hydrostatic effect, the relaxation peak would shift to lower frequency when pressure was increased.

The value of the peak frequency was lower than that found by Kamiya *et al.* [16]. This fact can be due to the different ways used to characterize the relaxation process or to perform the dielectric measurements. In this work, the generalized Havriliak-Negami equation (HN) is used. Kamiya *et al.* [16] applied a different equation. Indeed, the equation used by these authors correspond to a generalized HN equation if α_k and β_k are equal to 1 and the term due to the conductivity is neglected. From the experimental viewpoint, an air gap method was employed, where only one electrode is contacted with the sample and the other is in contact with the gas.

In the case of the system under analysis, it is possible to neglect the conductivity term, but the data obtained from the dielectric measurement are well correlated using $0.4 \leq \alpha_k \leq 0.9$ and $0.5 \leq \beta_k \leq 1$. The higher values are obtained at higher pressure for α_k , while at low pressure for β_k . The asymmetry in the peak lead to a shift in the position of the maximum corresponding to the time of relaxation.

If we consider the segmental process as purely activated, then the activation volume (ΔV^\ddagger) can be obtained from [19]:

$$\Delta V^\ddagger = 2.303RT \left(\frac{\partial \log \tau}{\partial P} \right)_T \quad (2)$$

where R is the ideal gas constant and T is the temperature (K). The mean value found for ΔV^\ddagger was $1.31 \pm 0.05 \text{ dm}^3/\text{mol}$.

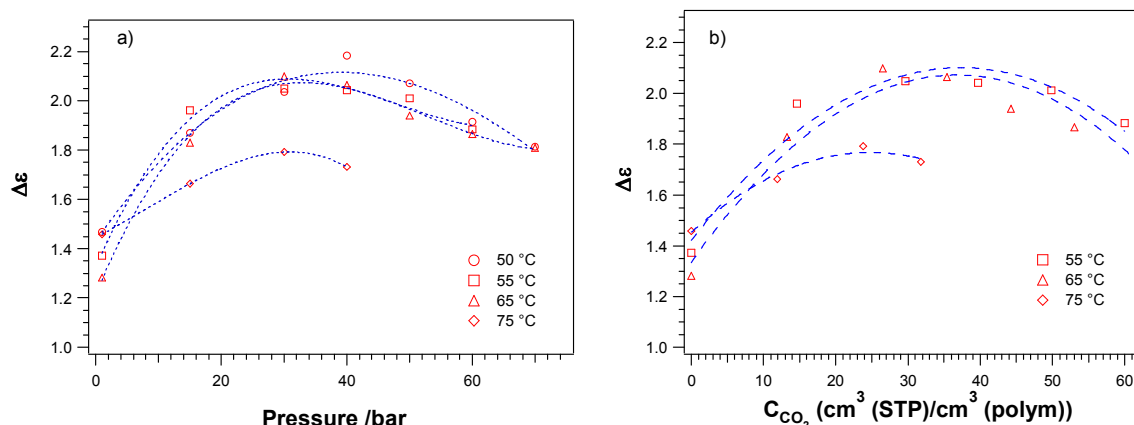


Figure 4. Dielectric strength of relaxation peak as function of pressure and temperatures (a), and as a function of the CO_2 concentration inside the polymer (b). The lines are only guide for eyes.

In Figure 4a, the dielectric strength of the relaxation peaks ($\Delta\epsilon$) as a function of pressure and of temperature are shown. It is possible to see a bell shape behavior. The curves have a maximum around 30 – 40 bar and then decrease. For the experiments carried out from 50° to 65 °C, the values of dielectric strength are slightly different, while a strong effect of pressure is registered at 75 °C. If the dielectric strength is plotted against the CO_2 concentration inside the polymer (Figure 4b), determined using data reported in literature [20], it is clear that $\Delta\epsilon$ increases up to a concentration of about 25 cm^3 (STP)/ cm^3 (polymer), then it becomes quite constant. This fact can be due to the compensation between the plasticization and the hydrostatic effect of the CO_2 pressure. Thus, a higher solubilization of dense gas could cause an increase in the distance between the polymeric chains and so enhance the chain mobility; on the other hand, the pressure tends to increase the polymer density and so the interaction between polymer segments.

CONCLUSION

Dielectric measurements of PEMA- CO_2 system were carried out in the 50 – 75 °C temperature range and 1 – 70 bar pressure range. The width of the relaxation peak decreased with increasing of pressure at constant temperature, while there was not sensible change (variation less than 5%) at constant pressure and different temperature.

Furthermore, an increase of relaxation peak frequency with increasing of pressure and temperature was detected. This fact is easily explained by considering the dissolution of CO_2 inside the polymeric matrix, which is responsible of the reduction on the glass transition temperature of polymer and of the increase of its free volume.

REFERENCES:

- [1] WISSINGER, R.G., PAULAITIS, M.E., J. Polym. Sci. Part B: Polym. Phys., Vol. 25, **1987**, p. 2497
- [2] ELVASSORE, N., BERTUCCO, A., CALICETI, P., J. Pharm. Sci., Vol. 90, **2001**, p. 1628.
- [3] SIEVERS, R.E., KARST, U., SCHAEFER, J.D., STOLDT, C.R. AND WATKINS, B.A., J. Aerosol Sci., Vol. 27, **1996**, p. S497
- [4] TANG, M., WEN, T.-Y., DU, T.-B., CHEN, Y.-P., European Polymer Journal, Vol. 39, **2003**, p. 143
- [5] ZHOU, H., FANG, J., YANG, J., XIE, X., Journal of Supercritical Fluids, Vol. 26, **2003**, p. 137
- [6] NGO, T.T., LIOTTA, C.L., ECKERT, C.A., KAZARIAN, S.G., J. of Supercritical Fluids, Vol. 27, **2003**, p. 215
- [7] SICARDI, S., MANNA, L., BANCHERO, M., Ind. Eng. Chem. Res., Vol. 39, **2000**, p. 4707

- [8] JUNG, J., PERRUT, M., *Journal of Supercritical Fluids*, Vol. 20, **2001**, p. 179
- [9] KWUAK, G.-H., TOMINAGA, Y., ASAI, S., SUMITA, M., *Electrochim. Acta*, Vol. 48, **2003**, p. 4069.
- [10] TOMINAGA, Y., KWUAK, G.-H., HIRAHARA, S., ASAI, S., SUMITA, M., *Polymer*, Vol. 44, **2003**, p. 4769.
- [11] KWUAK, G.-H., TOMINAGA, Y., ASAI, S., SUMITA, M., *Electrochim. Acta*, Vol. 48, **2003**, p. 1991.
- [12] VEZZÙ, K., ZAGO, V., VITTADELLO, M., BERTUCCO, A., DI NOTO, V., *Electrochimica Acta*, in press.
- [13] DI NOTO, V., VEZZÙ, K., PACE, G., VITTADELLO, M., BERTUCCO, A., *Electrochimica Acta*, Vol. 50, **2005**, p. 3904
- [14] RUNT, J.P., FITZGERALD, J.J., “Dielectric Spectroscopy of Polymeric Materials: Fundamentals and Applications”, American Chemical Society, Washington, DC, **1997**, cap. 3.
- [15] VEZZÙ, K., ELVASSORE, N., DI NOTO, V., BERTUCCO, A., Convegno GRICU: “Nuove Frontiere di Applicazione delle Metodologie dell’Ingegneria Chimica” - September 12th – 15th 2004, Porto d’Ischia (Napoli), Italy
- [16] KAMIYA Y., MIZOGUCHI, K., NAITO, Y., *J. Polym. Sci. Part B: Polym. Phys.*, Vol. 28, **1990**, p. 1955
- [17] VITTADELLO, M., SUAVEZ, S., CHUNG, S.M., FUJIMOTO, K., DI NOTO, V., GREENBAUM, S.G., FURUKAWA, T., *Electrochim. Acta*, Vol. 48, **2003**, p. 2227.
- [18] FLOUDAS, G., GRAVALIDES, C., REISINGER, T., WEGNER, G., *Journal of chemical physics*, Vol. 111, **1999** 9487
- [19] WILLIAMS, G., *Trans. Faraday Soc.*, Vol. 61, **1965**, p. 1564
- [20] KAMIYA Y., HIROSE, T., MIZOGUCHI, K., NAITO, Y., *J. Polym. Sci. Part B: Polym. Phys.*, Vol. 27, **1989**, 879