

NOTE

Dielectric relaxation study of the crystalline chain motion of poly(vinylidene fluoride) under carbon dioxide

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Polymer Journal (2010) 42, 419–422; doi:10.1038/pj.2010.19; published online 24 March 2010**Keywords:** carbon dioxide; crystalline chain motion; *in situ* dielectric relaxation; poly(vinylidene fluoride)

INTRODUCTION

Carbon dioxide (CO₂) can dissolve into a free volume of amorphous polymers because of the low viscosity and/or high diffusivity of CO₂.¹ The dissolved CO₂ causes a plasticization effect such as dilation,² depression of glass transition temperature^{3,4} and decrease in viscosity.⁵ Hence, for example, CO₂ is used as a plasticizer in polymer processing. The plasticization effect on amorphous polymers has been verified in terms of molecular motion by using *in situ* dielectric relaxation measurement under CO₂; that is, the dielectric relaxation spectrum for the amorphous chain (α_a relaxation) shifts to a higher frequency by pressurized CO₂, suggesting that the molecular motion of the amorphous chain is accelerated by the plasticization effect of CO₂.^{6,7}

In crystalline polymers, a crystalline region coexists with an amorphous one. The packing of the chain in the crystalline region (crystalline chain) is tight in crystalline polymers, whereas the chain is randomly arranged and free volume exists in amorphous polymers. Hence, the sorption and solubility of CO₂ into crystalline polymers are much smaller than those of amorphous polymers, suggesting that CO₂ is insoluble in the crystalline region.^{3,8} Because CO₂ is insoluble in the crystalline region, whereas it dissolves in the amorphous region, dissolved CO₂ in the molten state is excluded from the crystal growth front during crystallization. Owing to the exclusion, characteristic porous structures such as layered and rod-like ones are obtained when the bubbles nucleate and grow by supersaturation of the excluded CO₂ in the constrained intercrystalline amorphous region.⁹ On the other hand, a decline in melting temperature is observed under CO₂ in several crystalline polymers, suggesting the plasticization effect of CO₂ on the crystalline chain.^{4,10,11} Thus, the solubility and plasticization effects of CO₂ on the crystalline chain are controversial. However, thus far, the solubility of CO₂ in the crystalline chain has not been clarified on a molecular scale.

If CO₂ is dissolved in the crystalline region, the molecular motion of the crystalline chain should be accelerated by its plasticization effect.

Dielectric relaxation measurement is a powerful tool to estimate the molecular motion of the crystalline chain under CO₂. In this paper, we investigate the molecular motion of the crystalline chain by *in situ* dielectric relaxation measurement of a crystalline polymer under CO₂ at various pressures. Here, we chose poly(vinylidene fluoride) (PVDF) as the crystalline polymer because the decline in its melting temperature can be observed under CO₂¹¹ and the dielectric relaxation spectra of the crystalline chain (α_c relaxation) are seen near 120 °C under air at ambient pressure.^{12,13} The dissolution of CO₂ in the crystalline region is discussed in terms of the molecular motion of the crystalline chain.

EXPERIMENTAL PROCEDURE

The PVDF powder used in this study was supplied by Kureha Chemical Industry Co., Ltd (Tokyo, Japan) (KF-1000, $M_w=250\,000$). To obtain a crystallized film specimen with a thickness of 0.4 mm, the PVDF powder was compression molded between two cover glasses at 200 °C for 5 min, and then gradually cooled to room temperature.

In situ dielectric relaxation measurement under high-pressure CO₂ was taken using a specially designed custom-made high-pressure cell constructed of stainless steel with an inner volume of 300 ml equipped with two sapphire windows for through view, as schematically shown in Figure 1. The capacitors used for the dielectric relaxation measurement consisted of two indium tin oxide plates. The upper capacitor was hung from a shaft and the lower one was fixed at the lower part of the cell. As the magnet was attached at the upper end of the shaft in a hollow bolt and was held by a magnetic nut on the hollow bolt with screw thread, the upper capacitor could be moved up or down, thereby moving the shaft by rotating the magnetic nut on the hollow bolt. The film specimen was placed on the lower capacitor and high-pressure CO₂ was injected into the cell at room temperature. After the specimen was kept in position for 2 h to dissolve CO₂ in the specimen, the upper capacitor was moved downward until it adhered to the specimen as viewed through the sapphire window. Here, the capacitors were separated by a polyimide spacer of 0.4 mm to determine the thickness of the specimen. The temperature was then

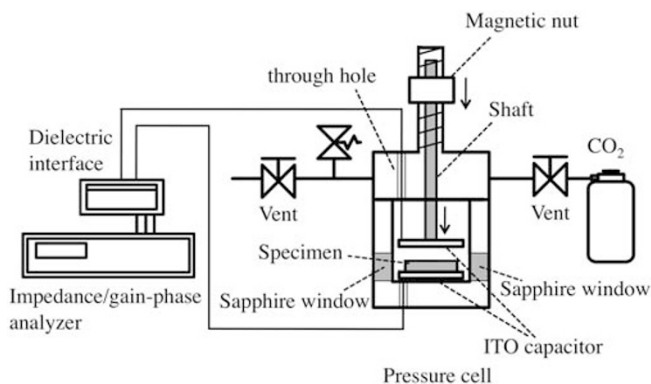


Figure 1 Schematic illustration of the instrumental setup for *in situ* dielectric relaxation measurement.

raised to 120 °C. The pressure of CO₂ was kept constant during the heating process using a back pressure regulator. Dielectric measurements were performed with a Solartron 1260 Impedance/Gain-Phase Analyzer equipped with an impedance transformer (SI 1296 Dielectric Interface, Solartron, Farnborough, UK) under CO₂ pressure up to 10 MPa at a frequency, f , ranging from 10⁻¹ to 10⁷ Hz. The angular frequency, ω , was obtained by $\omega=2\pi f$.

RESULTS AND DISCUSSION

Figure 2 shows the angular frequency, ω , dependence of the dielectric loss, ϵ'' , of the crystallized PVDF at 120 °C under various CO₂ pressures, P_{CO_2} . A peak is detected near 10⁵ s⁻¹ and a broad shoulder is observed near 10² s⁻¹. The peak near 10⁵ s⁻¹ is assigned to the crystalline chain relaxation (α_c relaxation).^{12,13} As the α_c relaxation originates from rotating and twisting with a small lengthwise translation of the crystalline chain,^{14,15} this peak is expected to shift to a higher frequency when the crystalline chain motion is accelerated by dissolving CO₂ in the crystalline region. On the other hand, the shoulder near 10² s⁻¹ is assigned to the relaxation of the interfacial polarization caused by trapping charge carriers at the crystal–amorphous interphase because of the permittivity difference between the amorphous and crystalline regions.^{16,17} A steep upturn with a straight line of slope -1 is seen at a low frequency below 10² s⁻¹. The steep upturn is assigned to ionic conductivity caused by the mobility of ionic impurities in the amorphous region.^{2,18}

As shown in Figure 2b, the $\epsilon''(\omega)$ curve in Figure 2a can easily be resolved into three parts. The peak for the α_c relaxation and the shoulder for the relaxation of the interfacial polarization are described by the Havriliak–Negami equation:¹⁶

$$\epsilon^* = \epsilon_\infty + \sum_j \frac{(\Delta\epsilon)_j}{[1+(i\omega\tau_j)^{\alpha_j}]^{\beta_j}} \quad (1)$$

where ϵ^* is the complex dielectric permittivity; $\epsilon^* = \epsilon' - i\epsilon''$, ϵ_∞ is the limiting high-frequency permittivity; τ_j is the relaxation time of the j th process; $(\Delta\epsilon)_j$ is the dielectric strength of the j th process; and α_j and β_j are the parameters describing the broadening and asymmetry of the j th relaxation time distribution. The upturn for the ionic conductivity is described by

$$\epsilon_{\text{ionic}}^*(\omega) = -\frac{i\sigma_{\text{ionic}}}{\omega\epsilon_0} \quad (2)$$

where σ_{ionic} is the ionic conductivity and ϵ_0 is the permittivity of vacuum (8.854 pFm⁻¹).

Figure 3 shows the peaks for α_c relaxation and interfacial polarization at various CO₂ pressures that are obtained from Figure 2 using

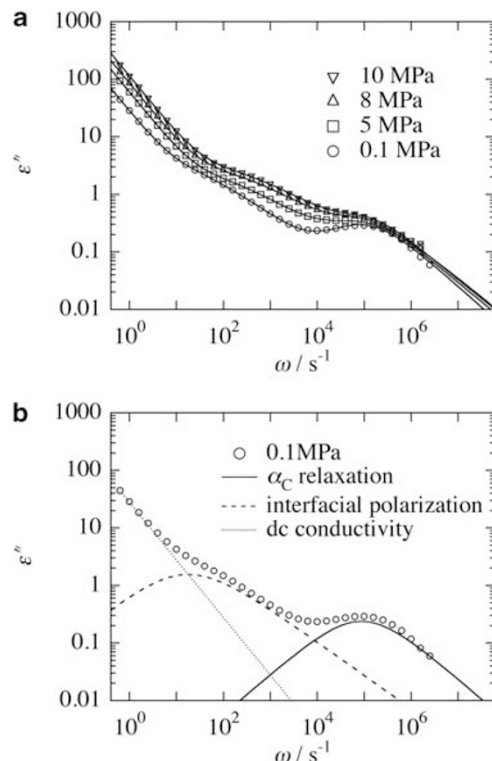


Figure 2 Frequency dependence of dielectric loss ϵ'' . (a) Crystallized PVDF under various CO₂ pressures at a temperature of 120 °C. The solid lines were obtained by the fitting procedure shown in (b). (b) Crystallized PVDF under air at ambient pressure (0.1 MPa) at a temperature of 120 °C. The curve was fitted by Equation (1) for α_c relaxation and interfacial polarization, and by Equation (2) for ionic conductivity.

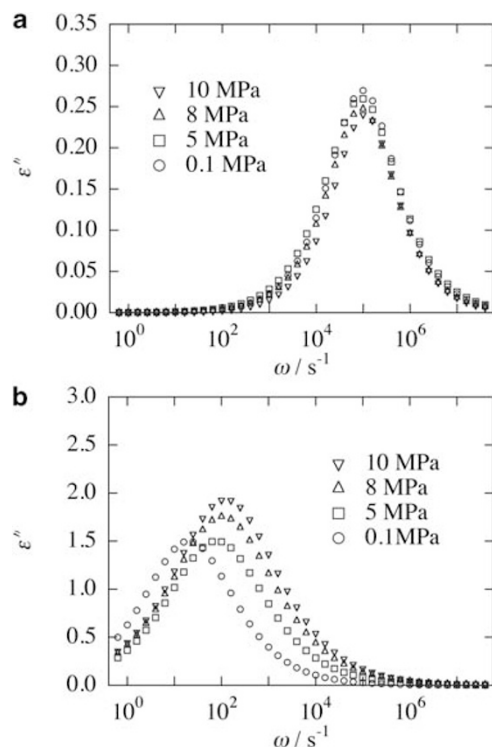


Figure 3 Frequency dependence of the dielectric loss of (a) α_c relaxation and (b) interfacial polarization in the crystallized PVDF under various CO₂ pressures at a temperature of 120 °C.

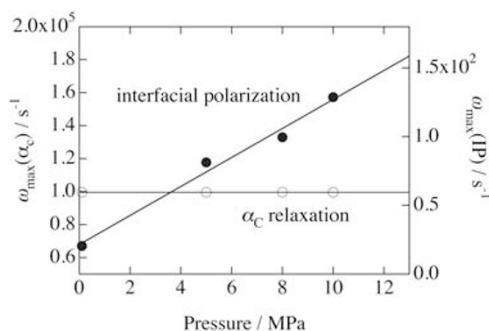


Figure 4 Pressure dependence of the frequency of the peak maximum of the dielectric loss of α_c relaxation and interfacial polarization in crystallized PVDF under CO₂ at a temperature of 120 °C.

Equations (1) and (2). It was found that the shape and peak maximum for the α_c relaxation did not change, although pressurized CO₂ was applied up to 10 MPa (Figure 3a). As shown in Figure 4, the frequency of the peak maximum for the α_c relaxation obtained from Figure 3a, $\omega_{\max}(\alpha_c)$, is almost constant near $10^5 s^{-1}$ with CO₂ pressure. The constant $\omega_{\max}(\alpha_c)$ with CO₂ pressure indicates that the molecular motion of the crystalline chain is not accelerated by applying pressurized CO₂. This result is quite different from that observed in amorphous polymers in which accelerated chain motion by pressurized CO₂ is suggested, that is, the peak maximum for the amorphous chain motion (α_a relaxation) shifts to a higher frequency by several orders of magnitude by applying pressurized CO₂ up to a few MPa.^{6,7} As the molecular motion of the crystalline chain is not accelerated by applying pressurized CO₂, CO₂ is not dissolved inside the crystalline region because of the tight chain packing in the crystalline region. Thus, the plasticization effect of CO₂ is not seen in terms of the molecular motion of the crystalline chain, whereas the decline in melting temperature under CO₂ is suggested. The decline in melting temperature under CO₂ might not be attributed to the accelerated crystalline chain motion inside the crystalline region but to the interaction between CO₂ and the PVDF chain near the surface of the crystalline region. Owing to the interaction near the surface, the surface free energy increases and then the melting temperature declines, as demonstrated by Zhang and Handa.⁴

As shown in Figure 3b, the peak for interfacial polarization shifts to a higher frequency and the strength of the peak increases with increasing CO₂ pressure. The frequency of the peak maximum obtained from Figure 3b, $\omega_{\max}(IP)$, increases with increasing CO₂ pressure (Figure 4). Assuming that the crystalline region is spherical with dielectric constant ϵ_2 and conductivity σ_2 , and is dispersed in a matrix of the amorphous region with dielectric constant ϵ_1 and conductivity σ_1 , the relaxation time of the interfacial polarization, τ_{MWS} , is given by the Maxwell–Wagner–Sillars equation:¹⁷

$$\tau_{MWS} = \frac{2\epsilon_1 + \epsilon_2}{4\pi(2\sigma_1 + \sigma_2)} \quad (3)$$

As CO₂ molecules are not dissolved in the crystalline region, as demonstrated above, ϵ_2 and σ_2 are unchanged with CO₂ pressure. In contrast, CO₂ molecules can dissolve in the amorphous region and the chain mobility in that region is accelerated with increasing CO₂ pressure. The increase in the upturn with increasing CO₂ pressure shown at the low frequency region in Figure 2a suggests an increase in ionic conductivity due to an increase in the mobility of ionic impurities associated with increased chain mobility in the amorphous

region. As conductivity increases with increasing chain mobility, σ_1 becomes larger as the amount of dissolved CO₂ in the amorphous region increases with increasing CO₂ pressure. In contrast, the dielectric constant of PVDF is much higher than that of CO₂; that is, the relative permittivity of PVDF is 12¹⁹ and that of CO₂ at 100 °C is 1.19 under pressures below 15 MPa.²⁰ Hence, ϵ_1 becomes smaller as the amount of dissolved CO₂ in the amorphous region increases with increasing CO₂ pressure. Thus, σ_1 increases, whereas ϵ_1 decreases because of the dissolved CO₂ in the amorphous region. The increase in σ_1 and the decrease in ϵ_1 yield a decrease in τ_{MWS} in Equation (3). The fact that $\omega_{\max}(IP)$ is the inverse of τ_{MWS} might explain the increase in $\omega_{\max}(IP)$ with increasing CO₂ pressure, as shown in Figures 3b and 4.

CONCLUSION

We found by *in situ* dielectric relaxation measurement that the shape and frequency of the peak maximum for the α_c relaxation of the crystallized PVDF did not change, although pressurized CO₂ was applied up to 10 MPa. The result suggests that CO₂ is not dissolved inside the crystalline region and the crystalline chain motion is not accelerated under CO₂. On the other hand, the frequency of the peak maximum for interfacial polarization shifted to a higher frequency with increasing CO₂ pressure because of a decrease in the dielectric constant and an increase in the conductivity in the amorphous region with an increase in the amount of dissolved CO₂ in the amorphous region.

ACKNOWLEDGEMENTS

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