Thermal Expansion of Polymers Submitted to Supercritical Carbon Dioxide as a Function of Pressure

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Pressure-Controlled Scanning Calorimetry (PCSC) has been used to study interactions of polymers with compressed supercritical CO_2. Global cubic thermal expansion coefficients α_p for MDPE and PVDF saturated with supercritical CO_2 have been determined at 352.4 K over the pressure range from 0.1 MPa to 100 MPa. In both cases the isotherms of global α_p exhibit minima near 20 MPa. At pressures below the minimum α_p for the PVDF- CO_2 system are higher than for the MDPE- CO_2 system, while at pressures above the minimum the opposite was observed. This proves that incorporation of CO_2 in PVDF is stronger than in MDPE. The appearance of the minimum is attributed to the action of compressed CO_2 molecules, which at higher pressures are forced to enter deep inside the interstitial or other voids in the polymer and cause their mechanical distension, which must be associated with an endothermic effect. The measurements have been performed on polymers used for fabrication of pipelines.

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[2] S.A.E. Boyer, S.L. Randzio and J-P. E. Grolier, "Thermal expansion of polymers submitted to supercritical CO_2 as a function of pressure." *J. Polym. Sci. B: Polym. Phys.* **44**, 185-194 (2006).