

Calculation of solubility of supercritical fluids in amorphous and glassy polymers

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The solubility of supercritical fluids in polymers is an important quantity relevant for a variety of applications involving drug delivery systems [1] or polymer coating [2]. The solubility depends strongly on the thermodynamic state of the polymer [3]. Usually, the solubility decreases sharply at the glass transition temperature (T_g), where T_g depends on the presence and concentration of solubilized small molecules. Hereby it was observed that T_G tends to run through an extremum (either maximum or minimum is possible) if the polymer is exposed to a supercritical fluid [4,5]. Therefore, the modelling of the solubility needs the knowledge of T_g as function of the concentration of the solubilized supercritical fluid. For the modelling of the solubility, an additional pressure treated as adjustable constant was introduced [6,7,8]. This contribution aims to a new theoretical framework working without this additional pressure. The assumption that T_g is basically thermodynamic in nature was used to derive a theoretical framework for the calculation of T_g of polymers [9,10,11]. The theory is a synthesis of a thermodynamic equation of state suitable for polymers, the generalized entropy theory for glass-formation in polymer materials, and the rigorous Kirkwood-Buff theory for concentration fluctuations in binary mixtures [10,11]. In the present contribution, this theoretical framework is applied in order to compare the calculated T_g -values as function of the amount of dissolved supercritical fluids with experimental data taken from the literature [5]. Hereby we apply the PC-SAFT equation of state [12]. It is our goal to calculate T_G under the influence of compressed fluids as a function of the dissolved gas in the polymer using the above mentioned theoretical framework. We consider two examples, first carbon dioxide dissolved in polystyrene and second carbon dioxide dissolved in poly(methyl methacrylate).

References

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