Fluid Phase Equilibria 449 (2017) 83–90

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Evaluation of solubility enhancement of carbon dioxide in polystyrene via introduction of water

Hao Wu [a, b], Zhongjie Du [a], Hongfu Zhou [b, *], Xiangdong Wang [b], Jianguo Mi [a, **]

[a] State Key Laboratory of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing, China
[b] School of Materials and Mechanical Engineering, Beijing Technology and Business University, Beijing, China

ARTICLE INFO

Article history:
Received 23 January 2017
Received in revised form
23 May 2017
Accepted 20 June 2017
Available online 22 June 2017

Keywords:
CO_2–H_2O co-blowing agent
PS foaming
Density functional theory
Dissolution equilibria
Interfacial properties

ABSTRACT

It is generally believed that CO_2 and H_2O acting as a supercritical co-blowing agent in the process of polystyrene (PS) foaming can offer lower foam density and uniform cell morphology for better thermal insulation. However, the solubilities of the co-blowing agent in PS have not been measured, since the dissolution equilibria are very difficult to establish in experiments. In this work, the dissolution equilibria and interfacial properties of the CO_2–H_2O–PS ternary system have been quantitatively predicted via a density functional theory. It is found that, in the presence of water, CO_2 dissolution and PS swelling have been enhanced. For instance, after the introduction of 0.05 mass fraction of water into PS melt, which can be realized at higher pressure (over 16 MPa), CO_2 solubility can be increased by 50%, whereas the corresponding interfacial tension of gas–melt can be reduced by 40%.

1. Introduction

Polymer foam with good heat resistance, mechanical properties and degradability have attracted considerable attention to their potential applications in mechanical equipments, domestic appliance, instruments, packing materials, building materials, and many others [1–5]. The solubility of supercritical blowing agent in polymer matrix is one of the most important physical properties during the development of polymer foams. To get a high agent-solubility, it is undoubtedly necessary to suppress the foaming pressure, reduce the interfacial tension, promote polymer plasticization, and therefore improve the comprehensive performance of foaming materials.

Foaming polystyrene (PS) with supercritical CO_2 as the blowing agent was extensively investigated and has been accepted as an economically and environmentally benign process for producing thermally insulating foams [6–12]. However, because of its very low dielectric constant and polarizability [13,14], CO_2 possesses poor compatibility with PS matrix. In order to circumvent these problems, a multitude of investigations were devoted to developing new blowing agents or co-agents [15–18]. Many PS foaming processes were performed by supercritical CO_2, together with alcohol (e.g. ethanol), ketone (e.g. acetone), nitrogen, or water as plasticizing co-blowing agents, to improve the foamability [19–27]. Among these co-blowing agents, both ethanol and acetone are flammable volatile organic vapors, which can lead to serious safety and environmental problems. Nitrogen has a lower solubility, resulting in a low volume expansion. In contrast, water is non-toxic, non-flammable, low-cost, and possesses very high heat capacity and latent heat. In addition, the introduction of water is helpful to achieve a higher plasticization effect, which can eliminate blowholes or pores in foams associated with supercritical CO_2 dissolution issues. Therefore, it is a desirable co-blowing agent for providing both internal cooling and foaming capacity in the extrusion foaming process. In recent years, some studies have demonstrated that, as a co-blowing agent, water not only offers benefits such as enlarged cell size and thus a lower foam density for better thermal insulation, but also creates uniform cell morphologies without a noticeable reduction in mechanical properties [28–32].

Very recently, water has been introduced as a co-blowing agent to support supercritical CO_2 via emulsion polymerization, suspension polymerization, activated carbon absorption, etc. In these cases, water is not directly dissolved in PS matrix through dissolution equilibrium. Nevertheless, determination of the solubility of

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[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: zhouhf@th.btbu.edu.cn (H. Zhou), mijg@mail.buct.edu.cn (J. Mi).

http://dx.doi.org/10.1016/j.fluid.2017.06.020
0378-3812/

co-blowing agent in PS is of importance in the polymerization and foaming process. The solubilities of pure CO_2 in water or PS have been extensively studied by theories and experiments [33–38]. For the co-blowing agent of CO_2 and H_2O dissolved in PS, however, there is scarce information about experimental measurement or theoretical quest.

Although experimental technology is undoubtedly necessary to accumulate data, theoretical models, which are capable of evaluating the dissolution capacities, are also important for providing data more efficiently and for mechanism explanation. From a practical standpoint, a reliable thermodynamic model should be applicable to the systems containing simple molecules and polymer chains in homogeneity or inhomogeneity. Moreover, it is also supposed to be computationally simple, be reliable over wide ranges of temperature, pressure, and composition, and have few or no adjustable parameters.

In this work, we attempt to calculate the dissolution equilibria and interfacial properties of the CO_2–H_2O–PS ternary system within the framework of classical density functional theory (DFT) to figure out the effect of water on promoting the dissolution of CO_2 in PS and reducing the interfacial tension of gas-melt. This theoretical approach has already displayed good performances for binary systems [12,39–41]. In this ternary system, CO_2 is nonpolar molecule, PS is long chain molecule, whereas water is polar molecule with strong hydrogen bonding, thus the most important issue is to construct a new free-energy functional via integrating these asymmetric interactions that are generated by their different chemical and geometric attributes.

Unlike previous investigations for gas dissolved in polymer melts, where the solubilities have been calculated but the polymer swellings have been overlooked [42,43], we obtain the solubilities of the supercritical co-blowing agent from the phase equilibria of CO_2–H_2O–PS, such that the solubilities and polymer swellings can be obtained simultaneously, and the enhancement effect of water on CO_2 dissolution can be clearly distinguished. The increment of volumetric expansion of PS and the decline of interfacial tension with respect to water concentration can be distinguished to account for the effect of water on PS plasticization and interfacial regulation. Without introduction of any regressed parameters, this work is expected to provide a theoretical basis for quantitatively evaluating the dissolving, swelling, and interfacial properties of polymer matrix dissolved with co-blowing agent.

2. Theoretical section

We employ a coarse-grained force field to summarize the correlations of various sites in PS chains. Therefore, a PS molecule is modeled as a semi-flexible chain with 40 repeat monomers, and each monomer contains two independent sites to represent the vinyl backbone and side phenyl ring group. We find that, once the number of repeat units reaches 40, the effect of chain length on CO_2 solubility is trivial. For the CO_2–H_2O–PS ternary mixture, we adopt the Lennard–Jones (LJ) potential to describe the interactions of CO_2–H_2O, CO_2–PS, and H_2O–PS:

$$u_{\alpha\alpha'}(r) = 4\varepsilon_{\alpha\alpha'}\left[\left(\frac{\sigma_{\alpha\alpha'}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\alpha'}}{r}\right)^{6}\right] \tag{1}$$

where α represents CO_2 or H_2O molecule or a site in PS monomers. This potential is also applied to account for the interactions of CO_2–CO_2 and PS–PS. The interactions between water molecules are generally given by Lennard–Jones and Coulombic terms:

$$u_{\mathrm{water}}(r) = 4\varepsilon_{\mathrm{O}}\left[\left(\frac{\sigma_{\mathrm{O}}}{r}\right)^{12} - \left(\frac{\sigma_{\mathrm{O}}}{r}\right)^{6}\right] + \frac{1}{4\pi\varepsilon_0}\sum_i\sum_j\frac{q_i q_j}{r} \tag{2}$$

where the subscript O denotes an oxygen atom in water molecule, ε_0 is the permittivity of free space, q is the charge of hydrogen or oxygen.

Within the framework of DFT, all thermodynamic properties of the system can be obtained from the grand potential, $\Omega[\rho(\mathbf{r})]$, or equivalently the intrinsic Helmholtz free energy, as a functional of density distribution:

$$\Omega[\{\rho_\alpha(\mathbf{r})\}] = F[\{\rho_\alpha(\mathbf{r})\}] - k_{\mathrm{B}}T\sum_\alpha\int\rho_\alpha(\mathbf{r})\mu_\alpha d\mathbf{r} \tag{3}$$

where k_{B} is the Boltzmann constant, μ_α stands for the bulk chemical potential of component α. The total Helmholtz free-energy functional can be expressed as:

$$F[\{\rho_\alpha(\mathbf{r})\}] = k_{\mathrm{B}}T\sum_\alpha\int\rho_\alpha(\mathbf{r})[\ln(\rho_\alpha(\mathbf{r})) - 1]d\mathbf{r} + F^{\mathrm{ex}}[\{\rho_\alpha(\mathbf{r})\}] \tag{4}$$

where the first term on the right-hand side is the free-energy of ideal gas, $F^{\mathrm{ex}}[\{\rho_\alpha(\mathbf{r})\}]$ accounts for the excess free-energy contribution. For a ternary system, the excess free-energy can be generalized as:

$$\begin{aligned} F^{\mathrm{ex}}[\{\rho_\alpha(\mathbf{r})\}] = {} & F^{\mathrm{hs}}[\{\rho_\alpha(\mathbf{r})\}] + F^{\mathrm{att}}[\{\rho_\alpha(\mathbf{r})\}] + F^{\mathrm{assoc}}[\{\rho_\alpha(\mathbf{r})\}] \\ & + F^{\mathrm{chain}}[\{\rho_\alpha(\mathbf{r})\}] + F^{\mathrm{stiff}}[\{\rho_\alpha(\mathbf{r})\}] \end{aligned} \tag{5}$$

to account for the contributions arising from the hard-sphere repulsion, dispersive attraction, hydrogen bonding of water, chain connectivity, and chain stiffness of PS, respectively.

The fundamental measure theory is commonly used to describe the contribution of hard-sphere repulsion, which is expressed as [44]:

$$F^{\mathrm{hs}}[\{\rho_\alpha(\mathbf{r})\}] = k_{\mathrm{B}}T\int\Phi^{\mathrm{hs}}[n_\gamma(\mathbf{r})]d\mathbf{r} \tag{6}$$

with

$$\begin{aligned} \Phi^{\mathrm{hs}}[n_\gamma(\mathbf{r})] = {} & -n_0\ln(1-n_3) + \frac{n_1 n_2 - \mathbf{n}_{V1}\cdot\mathbf{n}_{V2}}{1-n_3} \\ & + \frac{1}{36\pi}\left(n_3\ln(1-n_3)\right. \\ & \left. + \frac{n_3^2}{(1-n_3)^2}\right)\frac{n_2^3 - 3n_2\mathbf{n}_{V2}\cdot\mathbf{n}_{V2}}{n_3^3} \end{aligned} \tag{7}$$

where the detail information of $\Phi^{\mathrm{hs}}[n_\gamma(\mathbf{r})]$ can be seen in Ref. [45].

According to the weighted density approximation, the attractive contribution can be represented by Ref. [46]:

$$F^{\mathrm{att}}[\{\rho_\alpha(\mathbf{r})\}] = k_{\mathrm{B}}T\sum_\alpha\int(\rho_\alpha(\mathbf{r})\{F_1[\overline{\rho}_\alpha(\mathbf{r})] + F_2[\overline{\rho}_\alpha(\mathbf{r})]\})d\mathbf{r} \tag{8}$$

in which the expressions of $F_1[\overline{\rho}_\alpha(\mathbf{r})]$ and $F_2[\overline{\rho}_\alpha(\mathbf{r})]$ are given by the first-order mean spherical approximation expansion [46]: