Polymer 97 (2016) 95–103

Contents lists available at ScienceDirect

Polymer

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

Dimethyl ether's plasticizing effect on carbon dioxide solubility in polystyrene

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ARTICLE INFO

Article history:
Received 3 March 2016
Received in revised form
29 April 2016
Accepted 6 May 2016
Available online 7 May 2016

Keywords:
Solubility
Co-blowing agent
Simha-Somcynsky equation-of-state
Ternary system
Plasticization

ABSTRACT

The solubility of carbon dioxide (CO_2) and dimethyl ether (DME) blends in polystyrene (PS) is studied as a function of the temperature and the pressure. The solubility was measured by means of the gravimetric method and a visualizing dilatometer which determined the swollen volume to compensate for the buoyancy change due to swelling. The solubility of the blend gases for the ternary PS/CO_2/DME system is also predicted by the Simha-Somcynsky (SS) equation of state (EOS). The theoretical prediction of the blend solubility was in agreement with the experimental results. Adding DME to PS not only decreased the pressure required to dissolve CO_2 in PS but the effects of plasticization were also observed. The remarkable plasticization effect due to the presence of DME increased the CO_2 solubility via an increased free volume of PS.

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1. Introduction

Thermoplastic foams, which have cellular core structures, are created by the phase separation of polymer/gas mixtures. Under high pressure, a polymer/gas system's total Gibbs free energy decreases as gas is dissolved in the polymer matrix up to the solubility limit. This process typically swells the polymer volume [1,2]. Thus, the thermal and physical properties are changed [3–7]. For example, the glass transition temperature (T_g) is reduced due to the plasticization effect of the dissolved gas. The concentrated gas within the polymer matrix causes the T_g depression of a polymer/gas mixture. As the diluents' concentration is increased, regression in the T_g becomes more pronounced. This is due to an increase in the inter-chain distance and in the polymer segment's mobility, which increases the free volume [8]. This degree of swelling and the solubility is a sensitive function of the pressure and the temperature. Therefore, a sudden pressure or temperature alteration induces a thermodynamic instability within the polymer/gas mixture, which would result in foaming of the polymer when the degree of the instability is high enough to overcome the bubble nucleation barrier and when enough gas is available to promote bubble growth. As such, the solubility of the gas in the polymer is a critical parameter in controlling the phase separation and, eventually, the foam morphology.

Numerous past theoretical studies have been conducted on binary polymer/gas systems to determine the solubility of gas in the polymer [9–11]. Their fundamental data have helped researchers to achieve the desired foam structure by optimizing the processing conditions based on the solubility data. The foam structure is typically characterized by the cell size, the cell density, the expansion ratio, and the open-cell content. A certain combination of these structural parameters allowed the foamed plastics to be effectively used in the structural, packaging, automotive, and sports industries [12,13].

Although binary systems have been used to produce polymeric foams in numerous commodity applications, a ternary system further enabled us to fabricate a more complex foam structure for specific functionalities. Gong et al. used a ternary polystyrene (PS)/CO_2/pentane system to produce PS foams with a small cell size and a large expansion ratio (17-fold) for thermal insulation [14]. CO_2 was used to create a large bubble density, and pentane was used to achieve a large expansion ratio. Zhang et al. used a ternary PS/CO_2/water system to produce PS foams with bimodal cell morphology [15,16]. Lee et al. used a ternary low-density polyethylene (LDPE)/CO_2/butane system to produce LDPE foams with open-cell morphology [17,18]. However, unlike the binary systems, accurate

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http://dx.doi.org/10.1016/j.polymer.2016.05.018
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solubility data for the ternary systems are scarce, and a fundamental understanding of the role of each gas within the ternary system is lacking.

On the other hand, a number of gases have been used as blowing agents in the foam industry. Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrocarbons (HCs), and hydrofluorocarbons (HFCs) have been used due to their low diffusivity and high solubility for low-density foam processing. However, most of these commonly used blowing agents are environmentally hazardous, flammable, and/or expensive. For instance, CFC's contribute heavily to the depletion of the stratospheric ozone layer, and the Montreal Protocol banned their production in 1996 [19]. HFCs, as replacement blowing agents, have zero ozone depletion potential (ODP), but its emission control was required by Kyoto Protocol due to their high global warming potential (GWP). HCs (zero ODP and low GWP) are highly flammable, and the recently developed hydrofluoroolefins (HFOs) are too expensive for industrial-scale usage. Due to aforementioned environmental reasons, carbon dioxide (CO_2), which is less environmentally threatening and economically viable, has been used as a replacement. However, CO_2 tends to be relatively less soluble in polymer compared with the previously noted blowing agents. This, in turn, affects the processing conditions to produce the desired cell morphology of the foam. As a consequence, the processing pressure required to dissolve the less soluble CO_2becomes very high. Therefore, in order to circumvent this critical drawback of CO_2's low solubility, other highly soluble co-blowing agents are also blended together with CO_2. Ethanol, 2-ethyl hexanol, dimethyl ether (DME), and acetone [20–23] are a widely used co-blowing agent with CO_2 due to their high solubility in polymers. Also, these gases are less environmentally threatening and are more economically viable [24]. In particular, DME has an outstanding secondary blowing agent characteristic along with CO_2 in that it has a zero ODP, a low GWP, and non-toxicity [25]. Most importantly, DME interacts favorably with PS [26]. Furthermore, DME has a lower boiling temperature (−24.8 °C) compared to other highly soluble blowing agents such as hydrocarbons and alcohols, so it will remain in a gaseous phase at most ambient temperatures during winter. Hence, the shrinkage of the blowing agent during cooling within PS foams will be much less for DME than for hydrocarbons and alcohols which can liquefy easily. Therefore, the PS foams blown with DME will have a less shrinkage problem in environments where temperature drops considerably.

Despite their great potential, the literature describing the blend gases, which are limitedly used in industrial polymer-foam processes [15–18] is scarce. It contains no information on their solubility or on how they affect each other. Such information is vital to the design of an optimal polymer foam process because it provides the critical information such as the minimum pressure to be maintained to keep a single-phase polymer/blend-gas mixture in the processing system, and the location of cell nucleation inside the die lip [27,28].

In this study, the solubility of blend gases was experimentally and theoretically investigated in PS. A very interesting phenomenon regarding the co-blowing agent's role in enhancing the solubility of the inherently low-soluble CO_2 within the polymer was discovered. The solubility of CO_2, determined using the Simha-Somcynsky (SS) equation-of-state (EOS) was observed to increase in the presence of DME. DME was found to act as a plasticizer by increasing the free volume within the PS. It appears that the PS swells with the dissolved DME and thereby the solubility of CO_2 in PS increases. The changes in the CO_2 solubility are analyzed as a function of the DME content. To further confirm DME's plasticizing effect, the depression of the T_g caused by the dissolution of each gas was also observed.

2. Theoretical background

Theoretical models have been created to describe the interactions between polymer and gas with a view to optimizing the processing conditions. Two of such models used in the past are the Sanchez-Lacombe (SL) equation-of-state (EOS) and the Simha-Somcynsky (SS) EOS [29,30]. The two models were compared to the experimental findings for a binary system in our earlier work, and the SS-EOS was found to be closer to the experimental results compared to the SL-EOS [11,31]. Both the models can be traced back to the Flory-Huggins model and both allow for the holes to allow for entropy generation within the lattice hole theory. But, unlike the SL-EOS, the SS-EOS also accommodates the entropic contribution of the each lattice. This is resulted due to the presence of an additional characteristic parameter such as the flexibility of the molecules and the total number of mers present in a molecule. These differences may have contributed in the similarity of the SS-EOS prediction with the experimental findings over the SL-EOS for the binary polymer/gas systems. The effectiveness of the SS-EOS for describing the polymer/gas mixtures was also observed for ternary polymer-blend gas systems [26]. The experimentally measured volume swelling of polymer-blend gas mixtures was adequately described by the SS-EOS. Therefore, we used the SS-EOS in this work to predict the solubility of the blend gases in the ternary system.

A detailed explanation of the ternary based SS-EOS is described in Ref. [32]. A brief description of the ternary model is presented here. The pressure - specific volume - temperature (PVT) behavior of the mixture was obtained by solving Eqs. (1) and (2) of the SS-EOS as follows:

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = [1-\eta]^{-1} + \left(\frac{2y}{\tilde{T}}\right)Q^2 \times \left[1.011Q^2 - 1.2045\right] \tag{1}$$

and

$$\frac{s}{3c}\left[\frac{s-1}{s} + \frac{\ln(1-y)}{y}\right] = \frac{\eta - 1/3}{1-\eta} + \left(\frac{y}{6\tilde{T}}\right)Q^2\left[2.409 - 3.033Q^2\right] \tag{2}$$

As required by the SS theory, the volume of the gas molecules should match those of the molar repulsion volume of polymer segment; this was achieved by adjusting the polymer segment size [33]. Hence, in line with the polymer/gas system we studied, the SS scaling parameters for the PS and the gases involved were obtained. Table 1 lists all the scaling parameters for each component.

According to the classical thermodynamic theory, the chemical potential (μ) for each gas component (1 or 2) is identical in all phases (that is, the vapor phase and the polymer/gas mixture phase) under equilibrium conditions [35,36]. Therefore, the criterion for the phase equilibrium in the ternary system can be expressed by Eqs. (3)–(5):

$$\mu_1^V(P,T,m_1) = \mu_1^P(P,T,n_1,n_2) \tag{3}$$

$$\mu_2^V(P,T,m_2) = \mu_2^P(P,T,n_1,n_2) \tag{4}$$

Table 1
Scaling parameters for the SS-EOS.

Substance	P^* (MPa)	V^* (cm^3/g)	T^* (K)	Mn	s	c	Reference
PS	807.8	0.96475	16,044	190,000	7309	1142	[26]
CO_2	954.2	0.586	2960	44.01	1	1	[34]
DME	1318.9	0.5508	4025	46.07	1	1	[26]

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