Modeling the phase behavior of commercial biodegradable polymers and copolymer in supercritical fluids

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Abstract

Biodegradable polymers have received much attention as materials for reducing environmental problems caused by conventional plastic wastes. In this work, the thermodynamic behavior of binary and ternary systems composed by commercial biodegradable polymers and high-pressure fluids [poly(D,L-lactide) + dimethyl ether, poly(D,L-lactide) + carbon dioxide, poly(D,L-lactide) + chlorodifluoromethane, poly(D,L-lactide) + difluoromethane, poly(D,L-lactide) + trifluoromethane, poly(D,L-lactide) + 1,1,1,2-tetrafluoroethane, poly(butylene succinate) + carbon dioxide and poly(D,L-lactide) + dimethyl ether + carbon dioxide] and binary systems formed by commercial biodegradable copolymers and supercritical fluids [poly(butylene succinate-co-butylene adipate) + carbon dioxide] were studied. The Perturbed Chain-SAFT (PC-SAFT) and the Sanchez–Lacombe (SL) non-cubic EoS were used to model the liquid–fluid equilibrium (LFE) for these binary systems, by fitting one temperature-dependent binary interaction parameter. For comparison, the same data were also modeled by using the traditional Peng–Robinson (PR) cubic EoS. The three pure-component parameters of PC-SAFT and SL EoS and two pure-component of PR EoS were regressed by fitting pure-component data (liquid pressure–volume–temperature data for polymers and copolymer and vapor pressure and saturated liquid molar volume for fluids). The estimation of pure-component and binary interaction parameters was performed by using the modified maximum likelihood method with an objective function that includes the cloud point pressure. An excellent agreement was obtained with the PC-SAFT EoS, while the performance of the SL and PR EoS was less satisfactory.
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1. Introduction

Along with the increase in the quantity of plastics production, plastic disposal has been regarded as a serious problem; therefore, biodegradable polymers have received much attention in recent years as one of the approaches to solve the problem [1]. A biodegradable polymer is a high molecular weight polymer that, owing to the action of micro- and/or macro-organisms or enzymes, degrades to lower molecular weight compounds [2]. Biodegradable polymers have received much attention as materials for reducing environmental problems caused by

conventional plastic wastes; consequently, production of these materials has been studied and their commercial applications are growing progressively. In the 1960s, poly(D,L-lactide) (PLA) was proposed as a biocompatible, biodegradable and bioresorbable material for biomedical applications [3]. In recent years, environmental concerns have led to an escalated interest in PLA, as well as others biodegradable polymers, as an alternative to traditional commodity plastics [4]. PLA has the advantage of being not only biodegradable but also renewable since, the raw material, lactic acid, may be produced by microbial fermentation of biomass. PLA is a polymer well known from applications in the biomedical field. It has been used for more than 20 years for surgical devices such as sutures or clips. In recent times, these biomedical applications have been extended to controlled drug delivery systems and larger parts, such as screws for fracture fixation. In the biomedical field, PLA is highly accepted because of its good mechanical properties combined with is biocompatibility and its ability to

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degrade both in vivo and in vitro [5]. Poly(butylene succinate) (PBS) and poly(butylene succinate-co-adipate) (PBSA) are also biodegradable plastics produced from 1,4-butanediol, succinic acid and adipic acid as principal raw material. PBS and PBSA are also known commercially as Bionelle, a biodegradable aliphatic polyester [6]. Imaizumi et al. [7] found that PBS has viscoelastic properties and processability for direct extrusion gas foaming.

The phase behavior of polymer solutions depends strongly on the energetic interactions and on size differences between polymer and solvent molecules. At higher temperatures (near to the solvent critical point), polymer precipitates due to the free volume effect. This type of phase transition is known as the lower critical solution temperature (LCST), which is characterized by the increase of pressure transition values with temperature. At lower temperatures, differences of energetic interaction between polymer and solvent molecules may lead to another phase transition (limited polymer solubility and phase split) known as the upper critical solution temperature (UCST) [8]. Fig. 1 presents a typical PT diagram for an amorphous polymer + solvent systems. If the asymmetry between polymer and solvent molecules increases, the LCST and UCST curves approach one of other and eventually, they can be mixed in a single denominated U-LCST curve [9].

For these reasons, it is important to know the location of the phase boundaries for polymer–solvent mixtures in industrial production of these biodegradable polymers and copolymer. In this work, the thermodynamic behavior of binary and ternary systems composed by commercial biodegradable polymers and copolymer with high-pressure fluids (PLA + DME [10], PLA + CO$_2$ [11], PLA + CDFM [12,13], PLA + DFM [12], PLA + TFM [12], PLA + TFE [12], PBS + CO$_2$ [14], PBSA + CO$_2$ [14] and PLA + DME + CO$_2$ [10]) were studied. The PC-SAFT [15,16] and SL [17] non-cubic EoS and the well-known PR cubic EoS [18] were used to model the phase

equilibrium for these binary systems, by fitting one temperature-dependent binary interaction parameter (κ_{ij}), determined using the modified maximum likelihood method [19], including the cloud point pressure in the objective function.

2. Thermodynamic models

2.1. Perturbed-chain statistical associating fluid theory (PC-SAFT)

The PC-SAFT EoS [15,16] has the reference hard-sphere chain and the perturbation contribution terms,

$$\tilde{a} = \tilde{a}^{hc} + \tilde{a}^{pert} \tag{1}$$

where $\tilde{a} = A/NkT$. The hard chain contribution [20] was based in the first-order thermodynamic perturbation theory:

$$\tilde{a}^{hc} = \bar{m}\tilde{a}^{hs} - \sum_i x_i(m_i - 1)\ln g_{ii}^{hs}(\sigma_{ii}) + \tilde{a}^{ideal} \tag{2}$$

where m, x and g^{hs} are the segment number, mole fraction and the radial pair distribution function, respectively and $\bar{m}$ is the arithmetic average of the segment number:

The contribution of hard-sphere, $\tilde{a}^{hs}$, depends on the temperature dependent segment number, d, and the total number density of molecules, ρ, where d_i is calculated as $d_i = \sigma_{ii}[1 - 0.12\exp(-3\varepsilon_{ii}/kT)]$.

The perturbation contribution [21] is predicted from the first ($\tilde{a}_1$) and second-order ($\tilde{a}_2$) perturbation terms:

$$\tilde{a}^{pert} = \tilde{a}_1 + \tilde{a}_2 \tag{3}$$

where $\tilde{a}_1$ and $\tilde{a}_2$ depend on the total number density of molecules, ρ, the average of the segment number, $\bar{m}$, the reduced density, η, and VDW mixing rules (one fluid) represented in the form of

$$\overline{m_{i,j}\varepsilon_{i,j}^l\sigma_{i,j}^k} = \sum_i\sum_j x_i x_j m_i m_j \left(\frac{\varepsilon_{ij}}{kT}\right)^l \sigma_{ij}^k \tag{4}$$

Conventional combining rules are used to determine the cross parameters:

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_{ii} + \sigma_{jj}) \tag{5}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}(1 - \kappa_{ij}) \tag{6}$$

where κ_{ij} is an adjustable parameter used to evaluate the segment-segment interactions. So, m, σ and ε are the pure-component parameters for the PC-SAFT model.

2.2. Sanchez–Lacombe (SL)

The SL lattice-gas EoS [17] is composed of a VDW-type attractive term and a lattice-gas repulsive term which can be shown in its reduced form as:
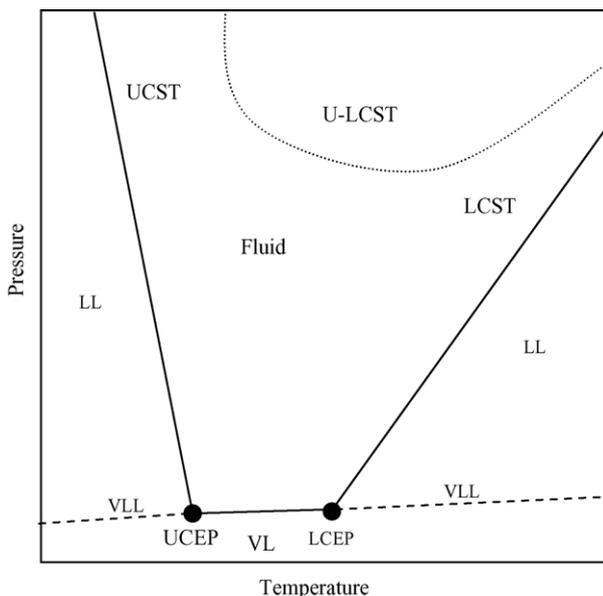
Fig. 1. PT projection for the high-pressure phase behavior for polymer + solvent systems.

$$\rho_R^2 + P_R + T_R\left[\ln(1 - \rho_R) + \left(1 - \frac{1}{r}\right)\rho_R\right] = 0 \tag{7}$$