

Modeling phase equilibria in CO₂ + polymer systems



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ABSTRACT

This work reviews thermodynamic models for the correlation and prediction of the phase behavior of CO₂ + polymer systems. Advantages and shortcomings of cubic equation of state, the SAFT equation, and Lattice fluid models are discussed. Perspectives and future directions in the development of thermodynamic models for CO₂ + polymer systems are presented.

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Abbreviations: PEA, poly(ethyl acrylate); PE, poly(ethylene); PMA, poly(methyl acrylate); PMMA, poly(methyl methacrylate); MMA, methyl methacrylate; PTFPME, poly(tetrafluoroethylene-co-perfluoromethylvinyl ether); PTFE, poly(tetrafluoroethylene); PVDF, poly(vinylidene fluoride); PC, poly(carbonate); PS, poly(styrene); LDPE, low density polyethylene; HDPE, high density polyethylene; PBS, poly(butylene succinate); PBMA, poly(butyl methacrylate); PP, poly(propylene); PTFE, Polytetrafluoroethylene; PVAc, poly(vinyl acetate); PEG, poly(ethylene glycol); PDDMA, poly(dodecyl methacrylate); DDMA, dodecyl methacrylate; DME, dimethyl ether; PVC, poly(vinyl chloride); EVA, poly(ethylene-co-vinyl acetate); PVME, poly(vinyl methyl ether); PLA, poly(lactic acid); PLGA, poly(lactide-co-glycolide); PCL, poly(ϵ -caprolactone); PEG, poly(ethylene glycol); CFC-22, chlorodifluoromethane; PPO, poly(2,6-dimethyl phenylene oxide); PEO, poly(ethylene oxide); PES, poly(ether sulfone); PIB, poly(iso-butene); L61, (PEO)2-(PPO)31-(PEO)2; L81, (PEO)3-(PPO)42-(PEO)3; L62, (PEO)5-(PPO)34-(PEO)5; 17R2, (PEO)15-(PPO)10-(PEO)15; 17R4, (PEO)15-(PPO)26-(PEO)15; 25R2, (PEO)22-(PPO)14-(PEO)22; PA-11, nylon polyamide-11; PDMS, poly(dimethyl siloxane); PEMS, poly(ethylmethyl siloxane); PHMA, poly(hexyl methacrylate); POMA, poly(octyl methacrylate); PDMA, poly(decyl methacrylate); PFHMA, poly(1H,1H,2H,2H-tetrahydroperfluoro hexylmethacrylate); PFOMA, poly(1H,1H,2H,2H-tetrahydroperfluoro octylmethacrylate); PFDMA, poly(1H,1H,2H,2H-tetrahydroperfluoro decyl methacrylate); PBA, poly(butyl acrylate); PEHA, poly(ethylhexyl acrylate); PODA, poly(octadecyl acrylate); PIPA, poly(isopropyl acrylate); PIDA, poly(isodecyl acrylate); PDA, poly(n-decyl acrylate); IDA, isodecyl acrylate; PIPMA, poly(isopropyl methacrylate); PPA, poly(n-propyl acrylate); IPA, isopropyl acrylate; IPMA, isopropyl methacrylate; PCHA, poly(cyclohexyl acrylate); PCHMA, poly(cyclohexyl methacrylate); CHA, cyclohexyl acrylate; CHMA, cyclohexyl methacrylate.

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1. Introduction

The use of carbon dioxide as a solvent and/or reactant for the synthesis and processing of polymers is well-established and has been the subject of several reviews [1–5]. CO₂ has also been used to manipulate sorption, cloud points, and swelling in polymer systems, as well as to manipulate mechanical properties such as the elastic modulus and creep compliance [1,5,6]. Fig. 1 summarizes key thermodynamic properties that influence the use of CO₂ in polymer processing and some of the applications of CO₂ in this field. Many of these applications have been reviewed by Duarte et al. [4], Tomasko et al. [6], Kazarian [5], Nalawade et al. [7], Kendall et al. [2], Cooper [1], and Yeo and Kiran [3], among others. Reviews published between 2008 and 2013 are listed in Table 1.

The solubility of CO₂ in polymers and, conversely, the solubility of polymers in CO₂ is governed by temperature, pressure, concentration, molecular weight (MW), polydispersity of the polymer, free volume difference between the polymer and CO₂, van der Waals interactions between the polymer and CO₂, as well as specific (complex-forming) interactions between polymer segments and CO₂. Thermodynamic models for CO₂ + polymer systems must therefore take into account all these interactions in describing phase behavior necessary for the design and optimization of polymer processes [6].

1.1. CO₂–polymer interactions

Interactions between CO₂ and polymers can be non-specific (due to dispersion forces and forces between dipoles or quadrupoles) or specific (due to hydrogen bonding or Lewis

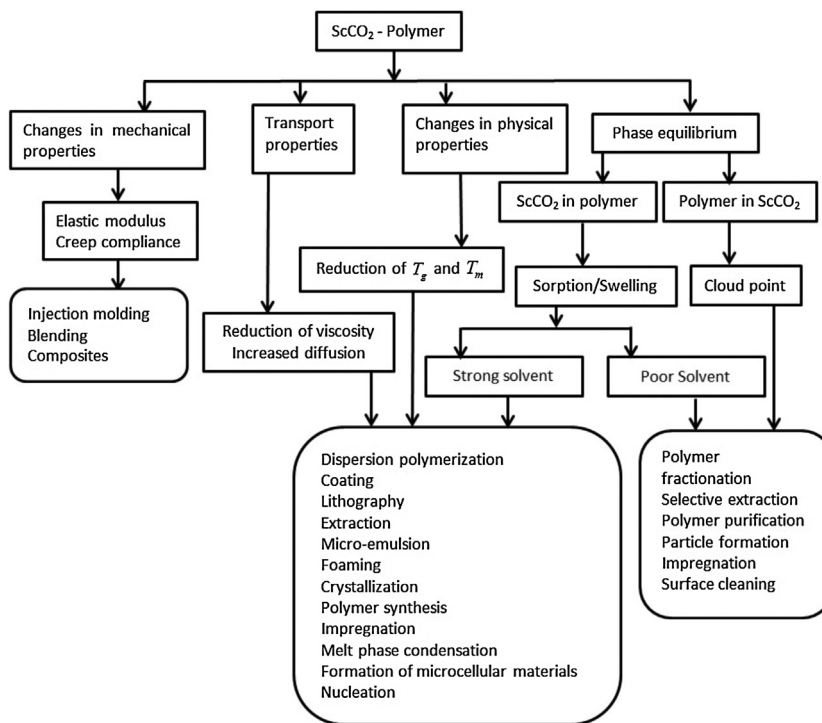


Fig. 1. Properties and applications of CO₂ + polymer systems.

acid–base complex formation). Non-specific interactions are generally weak and of the order of -1 to -10 kJ/mol [8]. On the other hand, specific interactions can be stronger and have a significant effect on CO₂ + polymer phase behavior. It has been suggested that CO₂ can act either as an electron donor or electron acceptor to form electron donor–acceptor (EDA) complexes with acidic or basic functional groups in polymers [9,10]. FTIR evidence of complex formation has been obtained by several authors [9,11,12] and the strength of specific interactions involving EDA complexes has been shown to lie between -4 and -50 kJ/mol [9,13]. By comparison, the strength of hydrogen bond interactions can vary from -1 to -162 kJ/mol [14–16]. There are several thermodynamic models that consider specific interaction explicitly in their formulation [17–19] and employ FTIR measurements, molecular dynamics simulations or quantum calculations to estimate these interactions [9,11,20]. However, no single model has demonstrated the ability to predict vapor–liquid (VLE), liquid–liquid (LLE), and vapor–liquid–liquid equilibrium (VLLE) simultaneously over wide ranges of conditions in polymer systems. The present review focusses on some of the more widely-used models used in

process calculations and outlines their successes and challenges in describing CO₂ + polymer systems.

2. Models for CO₂ + polymer systems

We have divided published models into three classes: (1) cubic EOS models, (2) perturbation models and (3) models based on the Lattice Fluid (LF) theory [7].

2.1. Cubic EOS models

Cubic equation of state (EOS) models are popular because of their simplicity and availability in process simulation software. Many of these models, including the van der Waals (vdW) equation, the Soave–Redlich–Kwong–Soave (SRK) equation, and the Peng–Robinson (PR) equation, have achieved some success in describing the behavior of specific CO₂ + polymer systems [7,21]. More success has been achieved with the Sako–Wu–Prausnitz (SWP) model which is based on the modified van der Waals partition function for chain molecules [22]. As is well-known, the SRK and PR equations incorporate two characteristic parameters (a and b) for pure substances, and these are generally obtained from critical point and vapor pressure data of the substance of interest. The SWP equation includes an additional pure component characteristic parameter c , which is the number of external degrees of freedom and accounts for the density dependence of the rotation and vibration of large molecules. When $c = 1$, the SWP equation reduces to the RKS EOS for small molecules, but $c > 1$ for large molecules. Finally, classical van der Waals mixing rules are generally used to extend the SRK, PR, and SWP EOS to polymer systems [7,22–24] and these have proved adequate for specific CO₂ + polymer systems. The SWP EOS, in particular, has been used successfully to investigate high pressure phase equilibria in the ethylene + polyethylene system and extended to calculate the solubility of gases in polymers by Chen et al. [24]. However, calculated solubilities were generally poor for small gases in molten and semi-crystalline polymers [24].

Table 1
Review papers published in 2008–2013 dealing with CO₂ + polymer systems.

Area of application	Reference
Tissue engineering	[4,97–99]
Polymer purification	[100]
Particle formation	[101–104]
Membrane separation	[105–107]
Fuel cells	[108]
Nano-composites	[109,110]
Catalytic reaction	[111]
Drug delivery	[112–115]
Phase equilibrium measurements	[116–118]
Polymer processing	[119–121]
Foaming	[122]
Polymer synthesis	[123]
Thermodynamic modeling	[124]
Formation of micro-emulsions	[125]

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