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Measurement and prediction of phase equilibria of ethylene + methyl acrylate + poly(ethylene-co-methyl acrylate) systems

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ABSTRACT

The solubilities of ethylene in the methyl acetate (MA) solutions of poly (ethylene-co-methyl acrylate) (EMA) were investigated according to conditions applicable to polymerization. The bubble point pressure (BP) for vapor-liquid equilibrium (VLE) and the cloud point pressure (CP) for liquid-liquid equilibrium (LLE) of ethylene + MA + EMA ternary system (weight ratio of MA: EMA, 9: 1) were measured at temperatures of 373 K and 393 K and at pressures up to 25 MPa with a synthetic method. The BP and CP increased with increasing temperature and ethylene weight fraction, especially the slope of CP against ethylene weight fraction was large. The Sanchez-Lacombe equation of state (SL EoS) could correlate VLE data of ethylene + MA and ethylene + EMA systems by fitting a corresponding binary interaction parameters for each binary to within about 4.7% in pressure. The phase equilibria of the ternary system could be predicted with the SL EoS from binary interaction parameters determined from the binary systems.

1. Introduction

A great number of polymers have been produced and many of these have become necessary for our daily life. With many new applications being proposed, properties required for polymers have also become more demanding in terms of their intended uses. To satisfy these demands, copolymers have attracted much attention, because it is possible to adjust their properties by changing the ratio of their monomers. Poly(ethylene-co-methyl acrylate) (EMA) is used as a modifier and laminate materials due to its excellent low temperature characteristics and adhesiveness.

A high-pressure method (ca. 100 MPa) is used for production of poly(ethylene-co-methyl acrylate) and has common disadvantages of such processes including equipment cost and safety. Catalyst technology in these decades has allowed low pressure polymerization processes to be developed for poly(ethylene-co-acrylate) production [1,2].

In the low pressure polymerization of EMA, the EMA solution includes ethylene and methyl acrylate (MA) for monomer. To optimize the condition for EMA production via solution polymerization, the solubility of ethylene in EMA solution is necessary for the reaction rate analysis. Liquid-liquid equilibria (LLE) data are important for the design of the separation process [3].

The phase equilibria of polymer solutions are influenced by many factors, for example, temperature, pressure, polymer molecular weight, and comonomer content. Therefore, many experimental studies have been carried out to measure the phase equilibria of polymer solutions, so that correlation and prediction methods can be used to extend the range of the data. The Sanchez-Lacombe equation of state (SL EoS) [4,5] and the perturbed-chain statistical associating fluid theory (PC-SAFT) [6–10] have been widely used for polymer solutions.

Some phase equilibria data related to EMA polymerization processes have been reported. Hasch and McHugh [11] reported the phase equilibrium data of ethylene + methyl acrylate system at temperatures from 288 K to 393 K and at pressures up to 12.2 MPa. McHugh and co-workers measured the phase equilibrium at high pressure with a synthetic method for many polymer solution systems, for example, polyethylene, EMA and poly(ethylene-co-acrylic acid), and then used the statistical associating fluid theory (SAFT) and SL EoS for correlation [12–15]. Becker et al. measured the phase equilibrium with a synthetic method for six poly(ethylene-co-(meth)acrylate) solution systems: EMA, poly(ethylene-co-ethyl acrylate), poly(ethylene-co-propyl acrylate), poly(ethylene-co-butyl acrylate), Poly(ethylene-co-methyl methacrylate) and

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Table 1
Purity and source of chemicals used.

Chemical name	Abbreviation	Purity	T_m [K]	Source
Ethylene		>99.5 vol%		Taiyo Nippon Sanso corporation
Methyl acrylate	MA	>99 mass%		Sigma-Aldrich
Poly(ethylene-co-methyl acrylate)	EMA		347.4	An undisclosed source

Table 2
Characteristic parameters of the Sanchez-Lacombe equation of state used in this work.

Substance (component number)	Mw [g/mol]	P^* [MPa]	T^* [K]	ρ^* [kg/m^3]	Ref.
Ethylene (1)	28.054	335	285.1	648	[22]
Methyl acrylate (2)	86.09	436	466	969	This work
Poly(ethylene-co-methyl acrylate) (3)	180000	371	661	956	This work

poly(ethylene-co-butyl methacrylate) at temperatures 353–533 K, pressures up to 212 MPa and the PC-SAFT was used for prediction [16]. However, relatively low pressure phase equilibrium data of EMA solution have not been reported.

Previously, the authors developed an apparatus [17] based on the synthetic method and reported on the solubility of ethylene in cyclic olefin copolymer solutions at polymerization conditions [18,19]. The phase equilibria for ethylene + poly(ethylene-co-vinyl acetate) (EVA) solution at relatively low pressure conditions were also measured and these data were correlated and predicted with the SL EoS [20]. The objective of this study is to investigate relatively low pressure phase equilibrium data of ethylene + MA + EMA mixtures. In this work, the phase equilibrium data of three systems were measured: (1) the ethylene + EMA system, (2) the ethylene + MA system, and (3) the ethylene + MA + EMA system. These data were correlated with the SL EoS. Furthermore, the SL EoS was applied to predict the phase equilibria of ethylene + MA + EMA ternary system.

2. Experimental

2.1. Materials

All chemicals used in this study are listed in Table 1. The co-monomer weight composition ratio reported by the supplier was ethylene/MA to be 79/21 (92/8 mol%). The number average, weight average, and Z-average molar mass of the EMA were measured in this work by size exclusion chromatography (SEC) with a differential refractive index detector and were determined to be $\overline{M}n$ (25 kg/mol), $\overline{M}w$ (180 kg/mol), and $\overline{M}z$ (831 kg/mol). Tetrahydrofuran (purity > 99.8 mass%, stabilizer free, Wako Chemicals) was used as SEC eluent and polystyrene molecular weight standards were used for calibration of the SEC. All chemicals were used as received. Melting point temperature (T_m) of EMA was measured with DSC (Seiko Instruments Inc., DSC6100) according to JIS K7121. The temperature at the top of peak is adapted as the T_m and is shown in Table 1.

2.2. Apparatus and procedure

2.2.1. Gravimetric method apparatus (gas solubility in polymer)

The solubility of ethylene into the molten EMA was measured with a gravimetric method [21] using a magnetic suspension balance. Estimated uncertainties of temperature and pressure measurements were ±0.05 K, and ±0.002 MPa, respectively. Estimated uncertainty of the solubility is less than 14.8% without considering swelling error and 15.0% with assuming 5% swelling error.

2.2.2. Synthetic method apparatus

An apparatus based on the synthetic method was applied for which details of measuring the bubble point (BP) and cloud point (CP) pressures have been described in Sato et al. [17,20]. Estimated uncertainties of temperature, BP, and CP were ±0.05 K, ±0.056 MPa, ±0.061 MPa, respectively. A sample of known composition was prepared gravimetrically. Estimated uncertainty of weight fraction of ethylene was less than 0.0005. In the measurement of the EMA + MA + ethylene ternary system, the EMA weight composition of EMA/MA solution was held constant at 10 wt%.

3. Correlation and prediction model

In this work, the experimental data were correlated using the Sanchez-Lacombe equation of state (SL EoS) [4,5].

$$\tilde{P} = -\tilde{\rho}^2 - \tilde{T}[\ln(1-\tilde{\rho}) + (1-1/r)\tilde{\rho}] \quad (1)$$

$$\tilde{P} = P/P^*, \ \tilde{\rho} = \rho/\rho^*, \ \tilde{T} = T/T^*, r = MP^*/RT^*\rho^* \quad (2)$$

The values of characteristic parameters, P^*, ρ^*, and T^* of the SL

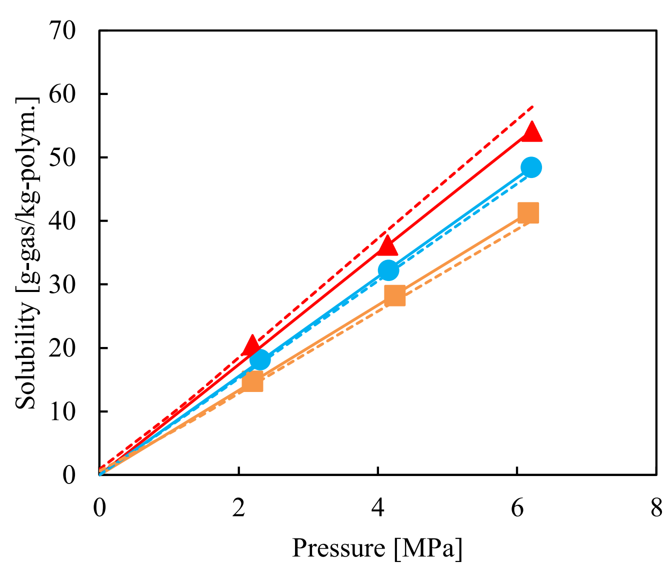

Fig. 1. Experimental and correlation results of the solubility of ethylene (1) in molten poly (ethylene-co-methyl acrylate) (3). Symbols: 373.15 K (triangle), 393.15 K (circle), 413.15 K (square); Lines: correlation with temperature dependent (solid line) and temperature independent (dashed line) interaction parameters.