Chemical Engineering Science 71 (2012) 18–31

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

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

Effect of viscous dissipation on acousto-spinodal decomposition of compressible polymer solutions: Early stage analysis

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ARTICLE INFO

Article history:
Received 14 October 2011
Received in revised form
11 November 2011
Accepted 14 November 2011
Available online 29 November 2011

Keywords:
Viscous dissipation
Compressible polymer solutions
Acoustic wave
Pressure-induced phase separation
Spinodal decomposition
Diffusion

ABSTRACT

A compressible Newtonian–Cahn–Hilliard fluid mixture in conjunction with the Sanchez–Lacombe equation of state is used to develop a one-dimensional linear model that describes acousto-spinodal decomposition by pressure-induced phase separation in compressible polymer solutions. The integrated model extends previous work (Rasouli and Rey, 2011) on inviscid acousto-spinodal decomposition of compressible polymer solution. Acousto-spinodal decomposition by pressure-induced phase separation couples density wave phenomena with mass transfer driven by spinodal decomposition process. For dissipative acousto-spinodal decomposition the relevant parameters are the ratio of diffusion speed to density wave speed Mach number (*Ma*) and the Reynolds number (*Re*). Under diffusion limitation (low *Ma*) polymer concentration gradients act as a sound source in a wave equation that feeds back into the polymer concentration balance equation, producing oscillatory spinodal decomposition. Phase diagrams in terms of Mach and Reynolds numbers show that under low viscosity, oscillatory growth is independent of viscous dissipation and only arises under low *Ma* number. On the other hand, under high viscosity effects, oscillatory spinodal decomposition may be generated by increasing *Re* or by decreasing *Ma*. The viscous attenuation of spinodal decomposition kinetics and the amplitude of density waves are characterized. Total structure factor calculations are qualitatively consistent with experiments at low wave vectors. Acousto-spinodal decomposition is a novel process that offers new processing and characterization routes for polymer solutions and melts.

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1. Introduction

Phase separation processes are relevant to the synthesis, processing, and characterization of polymer solutions based-materials (Folie and Radosz, 1995). Phase separation (PS) in polymer solutions can occur by spinodal decomposition (SD) or nucleation and growth (NG) (Zhang and Kiran, 2005). Equilibrium in polymer solutions include thermal (constant temperature), chemical (chemical potentials' equality), and mechanical (pressure equality) equilibrium (Ghiass and Rey, 2008, 2009a, 2009b; Rasouli and Rey, 2011). Therefore instability and consequently spinodal decomposition can be proceeded by adding solvent (solvent-induced spinodal decomposition—SD-SIPS), thermal quenches (temperature-induced spinodal decomposition—SD-TIPS), polymerization (polymerization-induced phase separation—SD-POIPS), and pressure quenches (pressure-induced spinodal decomposition—SD-PIPS) (Zhang and Kiran, 2005; Oh and Rey, 2000, 2001; Chan and Rey, 1995, 1997). The use of thermodynamic instabilities to tailor polymer microstructures is the basis of many well known separation processes (Chan and Tran, 2005; Sanchez and Balazs, 1989; Sanchez, 1983, 1991; Kim et al., 2002). On the other hand many polymer processing routes require thermal and pressure quenches, either to recover solvent or to achieve thermo-mechanical states compatible with product formation, generating pressure-induced phase separation via spinodal decomposition (Liu and Kiran, 2001; Zhang and Kiran, 2005). The production of polyethylene by solution polymerization at high pressure involves such steps and hence includes SD-PIPS (Folie and Radosz, 1995; Liu and Kiran, 2001). This paper is restricted to the analysis and simulation of pressure-induced spinodal decomposition of compressible polyethylene solutions.

For these materials at a fixed temperature T, the total Helmholtz free energy per unit mass $\hat{A}$ (Ghiass and Rey, 2008):

$$\hat{A} = \int_V \rho[\hat{A}_h(\rho,\omega) + \kappa/2(\nabla\omega)^2]dV \tag{1}$$

is the sum of the homogeneous $\hat{A}_h = \hat{A}_h(\rho,\omega)$ contribution and gradient contribution $\hat{A}_g = \kappa/2(\nabla\omega)^2$; ρ is density and ω is the polymer mass fraction and $\nabla\omega$ its gradients. Performing a 1-D variation δA with respect to concentration ω and density ρ one obtains (Ghiass and Rey, 2009a, 2009b)

$$\frac{1}{\rho}\frac{d}{dx}\left(\rho\frac{d\omega}{dx}\right) = \frac{\partial\hat{A}_h}{\partial\omega} - (\overline{\mu}_p - \overline{\mu}_s),$$

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doi:10.1016/j.ces.2011.11.025

$$\rho^2 \frac{\partial \hat{A}_h}{\partial \rho} - P_0 = -\kappa\rho\left(\frac{d\omega}{dx}\right), \tag{2a, b}$$

where in the chemical equilibrium equation the term $(\overline{\mu}_p - \overline{\mu}_s)$ is the equilibrium polymer and solvent chemical potential and in the force balance equation $P = \rho^2 \partial \hat{A}_h(T,\rho,\omega)/\partial\rho$ is the pressure and P_0 is the external pressure. The chemical and mechanical equilibrium are then coupled through density ρ, concentration ω, and concentration gradient $d\omega/dx$. Using Baker's formula, the interfacial tension for a phase separated polymer solution is the integral of the excess pressure (Ghiass and Rey, 2009a, 2009b):

$$\gamma = \int_{-\infty}^{+\infty} \kappa\rho\left(\frac{d\omega}{dx}\right)^2 dx = \int_{-\infty}^{+\infty} (P_0 - P)dx. \tag{3}$$

The kinetics of SD in compressible solutions, even in the early linear regime stage, exhibits significant deviations from incompressible solutions through the couplings between concentration and density. In the linear early stage regime SD under variable density, assuming negligible viscosity, it was shown that concentration gradients act as a sound source in the density wave equation (Rasouli and Rey, 2011):

$$\frac{\partial^2 \rho'}{\partial t^2} = f\frac{\partial^2 \rho'}{\partial x^2} + \underbrace{g\frac{\partial^2 \omega'}{\partial x^2}}_{\text{sound source}} \tag{4}$$

giving rise to attenuated acoustic waves under sufficiently slow diffusion that are coupled to the growing concentration fluctuations; prime variables denote perturbations, "f" is the square of the sound speed, and "g" is a function of the thermodynamic and transport parameters. Hence pressure-induced spinodal decomposition in compressible solutions is termed acousto-spinodal decomposition. As it is known, viscous attenuation of sound propagation in a single compressible fluid modifies the density wave equation to

$$\frac{\partial^2 \rho'}{\partial t^2} = f\frac{\partial^2 \rho}{\partial x^2} + \underbrace{k\frac{\partial}{\partial t}\frac{\partial^2 \rho'}{\partial x^2}}_{\text{viscous attenuation}}, \tag{5}$$

where k contains the viscosity parameter. Hence we can expect that the kinetics of the SD-PIPS process in the linear regime considered in the present paper couples the polymer mass fraction dynamics with an equation that shares the sound source and viscous attenuation indicated in Eqs. (4) and (5). Furthermore as shown below since the chemical potential $\mu(\rho,\omega) = \partial \hat{A}_h(\rho,\omega)/\partial\omega$ is a function of density, the density wave viscous attenuation (Eq. (5)) feeds back into the SD process creating additional couplings between acoustic and spinodal modes. Finally, since acoustic modes are longitudinal, the generated flow kinematics is a periodic compression and expansion, and hence extensional rheology is part of the process.

In our previous work, the equilibrium thermodynamic phase diagram and interfacial tension of solution using Modified Sanchez–Lacombe (MSL) equation of state (EOS) are characterized using polyethylene in n-hexane solution as model system(Ghiass and Rey, 2008, 2009a, 2009b). In our latest work (Rasouli and Rey, 2011), we investigated the kinetics of 1-D pressure-induced phase separation via SD for inviscid compressible binary solutions and characterized the unique couplings between density waves and concentration fluctuations. In the present paper we characterize viscous dissipation effects on 1-D pressure-induced phase separation (PIPS) by spinodal decomposition, in the early stage. In the present paper we use the thermodynamic parameters and phase diagram of previous work (Rasouli and Rey, 2011) and extend the inviscid kinetics presented in that paper by incorporating viscous dissipation effects. The presentation sequence, basic equations, and methodology used in the present paper and Appendices are based on Rasouli and Rey (2011). The specific objectives of this paper are:

1. Develop an integrated pressure-induced acousto-spinodal decomposition model for the early stage of phase separation in Newtonian compressible viscous solution assuming isothermal conditions, using mass, momentum, diffusion balance equations, and the Sanchez–Lacombe EOS.
2. Characterize the effect of viscous dissipation and generated extensional flow due to density change on the nature and

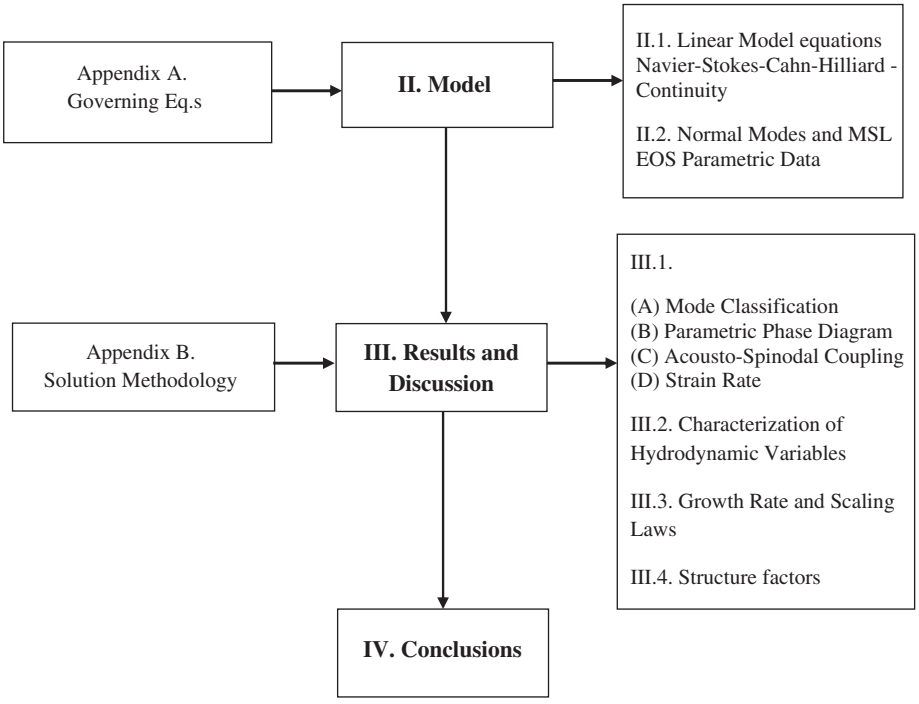

Fig. 1. Organization of the paper (MSL: Modified Sanchez–Lacombe EOS).

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