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Evolution of concentration fluctuation during phase separation in polymer blends with viscoelastic asymmetry

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ABSTRACT

A systematic rheological method is suggested to study the kinetics of concentration fluctuation during phase separation. It is based on the idea that the storage modulus of a phase separating polymer blend is composed of modulus due to the growing domains (interfacial contribution) and due to the thermally induced local composition fluctuations inside the domains (components' contribution). The two part contributions to the blend modulus varied with frequency. A crossover frequency was determined, below and above which the elastic modulus is dominated by the interfacial contribution and by the components' contribution, respectively. At frequency much above the crossover frequency, the variation of storage modulus is due to the change of local compositions, which can be calculated according to the relationship between the blend composition and the dynamic modulus in miscible state. In addition, the steady state values of local compositions can be considered as the thermodynamic equilibrium compositions at the annealed temperature, which help us to construct phase diagram. Moreover, the interfacial contribution at frequency lower than the crossover frequency could be isolated by subtracting the components' contribution from the blend's modulus. The characteristic length of domains were got through YZZ model with the equilibrium interfacial tension, which is comparable to the results from transmission electron microscopy (TEM). Furthermore, from the evolution of local compositions and the growth way of the characteristic length of domains, the crossover time from the intermediate stage to the late stage of spinodal decomposition can be specified. This method is tested on poly (methyl methacrylate)/poly (styrene-co-acrylonitrile) (PMMA/SAN) blend, and would be applicable in other polymer blends with viscoelastic asymmetry.

1. Introduction

Blending is an effective way to tune material properties for practical application. The level of miscibility is dependent on the mixing entropy and enthalpy [1]. Components with different molecular weight and interaction parameters can form either miscible or immiscible blends. Liquid–liquid phase separation is a fundamental phenomenon in partially miscible blends which can result in multi-phase/scale structure. Two types of phase separation mechanisms often occur upon variation in temperature. When the blend is quenched into the metastable region of the phase diagram, the phase separation occurs via nucleation and growth (NG) mechanism, during which the minor component usually forms droplets in the matrix of the major component and form the sea-island morphology. When the blend is quenched into the unstable region, the phase separation occurs instantaneously by spinodal decomposition (SD), leading to the co-continuous morphology [2,3].

Kinetics of SD in A/B blend has been explored extensively in the seventies and eighties of last century by experimental and analytical approaches [4–10]. Three stages [11] have been proposed to characterize the mechanism of SD, as manifested in Fig. 1. In the early stage, thermal concentration fluctuation caused by the thermodynamic instability makes the amplitude of concentration fluctuations $\delta\phi(t)$ increase with time and can be described by the Cahn-Hilliard-Cook linearized theory [12–14], while only very small or no increase in the wavelength of concentration fluctuation $\Lambda(t)$ [15]. In the intermediate stage, both the amplitude $\delta\phi(t)$ and the wavelength $\Lambda(t)$ of concentration fluctuation increase in a nonlinear way. A-rich and B-rich domains are formed and the interface between domains can be specified. The concentration of components in different domains (e.g. ϕ_A and ϕ_B) change

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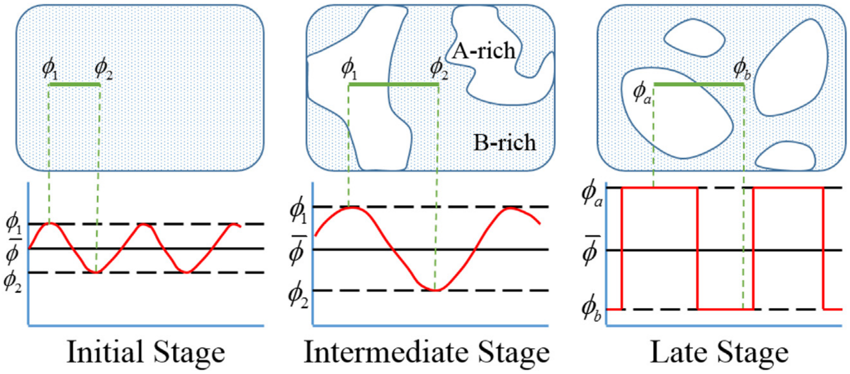

Fig. 1. Schematics of concentration fluctuation during phase separation.

successively. In the late stage, the amplitude of concentration fluctuations $\delta\phi(t)$ reaches a steady value. Driven by the interfacial tension, the wavelength of the concentration fluctuation $\Lambda(t)$ still grows with time through the coarsening in domains. In fact, the evolution of amplitude and wavelength of concentration fluctuation are difficult to be quantified simultaneously in the real space. Morphological observation using optical microscopy could only give the evolution of wavelength from domain sizes and usually works in the late stage due to the spatial resolution. Therefore, efforts have been paid to solve this problem in reciprocal space using scattering techniques, such as time-resolved small angle light-scattering (SALS) [6,15,16], small angle neutron scattering (SANS) [17,18] and small-angle X-ray scattering (SAXS) [19]. Time-resolved SANS and SAXS are more useful as they can approach a much smaller length scale than SALS. In these methods, the growing global structure of the self-assembling structure can be scaled with a single time-dependent length parameter, the domain spacing is inversely proportional to the characteristic wavenumber at the scattering peak. Moreover, Jinnai et al. [17] have suggested to decompose the time-resolved scattering intensity $S(q,t)$ into the scattering intensity from the growing domains $I_T(q,t)$ and from the thermally induced local composition fluctuations inside the domains $I_T(q,t)$. The time evolution of the composition difference between the two coexisting domains could be determined from $I_T(q,t)$ according to the prediction of the scattering theory based upon the random-phase approximation.

Another powerful tool to investigate phase separation is rheology. The measured macroscopic rheological functions of materials are affected by both thermodynamics and kinetics factors. From a theoretical point of view, the viscoelastic properties due to concentration fluctuations were initially investigated by Fredrickson et al. [20] in dynamically symmetric polymer blends, and have been extended to dynamically asymmetric blends recently [21]. Ajji et al. [22] proposed a scaling analysis for binary homopolymer blends based on the mean-field theory, and the result is comparable to that from small-angle neutron scattering (SANS). However, the works on concentration fluctuation are restricted in the homogeneous region near the phase separation temperature. On the other hand, a lot of works including simulations and experiments were carried out to investigate the mechanism and the morphology of phase separation from viscoelastic properties [9,23–30]. In frequency sweep, a shoulder is found at low frequency during phase separation for off-critical blends, where the pronounced elastic properties in terminal regime is attributed to the formation of droplet-matrix structure. In such a case, linear viscoelastic properties are often fitted by the emulsion model to get the interfacial tension or other structural information such as the domain size and its distribution [31]. For near-critical blends in which phase separation leads to a co-continuous structure, the storage modulus shows a power law behavior at low frequency, where the terminal region can be directly associated with the interfacial tension and characteristic length of domains [28]. Another frequently used way is the isothermal time sweep. Different observations and suitable interpretations were made from temporal evolutions of dynamic moduli in the literatures. For the SD process, the storage modulus G′ decreases continuously [25,32], while in the NG process, G′ could either decrease [27] or increase [25] continuously depending on the magnitude of frequency. There can be an initial increase in the elastic modulus of both NG and SD due to the concentration fluctuations [27]. In view of these reports, the basic problem of phase separation has been revealed by rheology, while a thorough rheological analysis of concentration fluctuation is still a challenge because of the coupled effects of the amplitude and wavelength of concentration fluctuation on the viscoelastic properties, where the former influence is always ignored in the literatures. The influence of fluctuation amplitude can be neglected only in a system with strictly viscoelastic symmetry. In this work, we will show how to decouple the effect of the fluctuation amplitude and wavelength in viscoelastic properties, and reveal how the evolution of concentration fluctuation can be resolved by rheology.

2. Experimental section

2.1. Materials and processes

Commercial grade of poly(methyl methacrylate) (PMMA, IF850, Mw = 15.9 × 10^4 g/mol, Mw/Mn = 1.64, Tg = 96 °C) and poly(styrene-co-acrylonitrile) (SAN, 81HF, Mw = 14.1 × 10^4 g/mol, Mw/Mn = 2.08, Tg = 105 °C, containing 28.4 wt % acrylonitrile) were both supplied by LG Chemical Ltd. and used as received. Previous study has shown that PMMA/SAN blends have a LCST-type phase diagram with the critical temperature about 155 °C at critical composition 70/30 [33].

PMMA and SAN were dried in a vacuum oven at 80 °C for 2 days before mixing. A series of blends with compositions from 10/90 to 90/10 have been prepared by melt mixing in an XSS-300 torque rheometer (Shanghai Kechuang Rubber & Plastic Equipment Co, China) under 50 rpm at 150 °C for 20 min. The mixing temperature was set in the one-phase regime of phase diagram to ensure blends maintaining a homogeneous state. The samples were then compressed into sheets with 1 mm in thickness at 150 °C under 10 MPa for rheological testing.