European Polymer Journal 49 (2013) 2721–2729

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

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

Filler effects on the phase separation behavior of poly (methyl methacrylate)/poly (styrene-co-acrylonitrile) binary polymer blends

Miao Du [a], Qiang Wu [b], Min Zuo [a,*], Qiang Zheng [a]

[a] *Key Laboratory of Macromolecule Synthesis and Functionalization, Ministry of Education, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China*

[b] *College of Engineering, Zhejiang A-F University, Hangzhou 311300, China*

ARTICLE INFO

Article history:
Received 9 December 2012
Received in revised form 13 April 2013
Accepted 9 June 2013
Available online 17 June 2013

Keywords:
Fumed silica particles
Phase separation
Spinodal decomposition
Nucleation and growth

ABSTRACT

The phase separation behaviors of poly (methyl methacrylate) (PMMA)/ poly (styrene-co-acrylonitrile) (SAN) blends with and without fumed silica (SiO_2) have been investigated using time-resolved small-angle light scattering and dynamic rheological measurements. It is found that the effect of SiO_2 on the phase separation behavior of PMMA/SAN blend obviously depends on the composition of the blend matrix. The addition of SiO_2 causes the cloud point (T_c) and binodal temperature (T_b) to slightly increase for 60/40 PMMA/SAN, and sharply decrease for 30/70 PMMA/SAN. However, the introduction of SiO_2 just causes a small increase of the spinodal temperatures (T_s) for PMMA/SAN with all compositions. Hence, the metastable region of 30/70 PMMA/SAN filled with 5 wt% SiO_2 is expanded in large amplitude by the fillers, while the same region of 60/40 filled PMMA/SAN hardly changes. The selective absorption of PMMA on the surface of SiO_2 results in the difference between the composition of surface layer and that of polymer matrix, especially for 30/70 PMMA/SAN filled with 5 wt% SiO_2. For such system, the phase separation of the surface layer occurs according to an SD mechanism at relatively low annealing temperatures. The SiO_2 particles then act as nuclei, inducing the phase separation of the matrix according to NG mechanism.

1. Introduction

The incorporation of fillers into polymeric systems, such as homopolymers, blends, or block copolymers, to form composite materials has been studied and industrialized for decades. It is opening pathways for engineering flexible composites that exhibit advantageous electrical, optical, mechanical, flammable or gas permeable properties [1–20]. Although polymer composites have been used in a large scale, there is little understanding of how the fillers influence the phase stability and kinetics of phase separation for binary polymer blends. It is of practical importance because the properties of ternary polymer composites strongly depend on their morphology and structure.

It is found that the introduction of fillers changes the phase stability and affects the kinetics of phase separation of polymer blends due to the interactions of polymer components with the fillers. The thermodynamic interaction parameter (χ_{AB}) between two polymeric components (A/B type) may either be increased or decreased by the addition of fillers [21–26]. The change depends on the nature of the interactions between the polymeric components and filler surface. As a result, the phase separation temperatures either increase or decrease for binary polymer mixtures with a lower critical solution temperature (LCST) or upper critical solution temperature (UCST) [22–28].

Usually, for an A/B-type binary polymer blend filled with spherical nanoparticles, the phase separation

---

* Corresponding author. Tel./fax: +86 571 87953075.
E-mail address: kezuomin@zju.edu.cn (M. Zuo).

0014-3057/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.eurpolymj.2013.06.006

behavior curve is determined by considering the mixture composition, nanoparticle radius. The homopolymer degree of polymerization (N), which the particles are attracted to one of the two components (e.g., when nanoparticles are coated by A-type ligands), is also considered. The particle radius eventually becomes comparable to the gyration radius (R_g) of the polymer chain. Once this occurs, the added particles begin to influence the configurational entropy of the polymer matrix chains. For a conventional phase diagram at an LCST, the addition of nanoparticles leads to an increase in $\chi_{AB}N$ for blends with high fractions of A. In contrast, $\chi_{AB}N$ decreases for blends with low fractions of A. These phenomena accordingly cause the phase separation temperature to increase for the former and decrease for the latter [6]. Hence, the spinodal curve shifts toward the lower volume fraction of polymer A. Nesterov and Lipatov reported that the cloud point (T_c) of a poly(vinyl acetate) (PVA)/poly (methyl methacrylate) (PMMA) blend with a high PVA fraction was diminished by the addition of SiO_2 particles (preferential adsorption of PVA). On the other hand, T_c increased for a blend with a low PVA fraction [29].

Lipatov considered the effects of an interface on the dynamics and thermodynamics of phase separation in filled polymer blends [30]. He also gave a pertinent theoretical description on the premise of a spinodal decomposition mechanism. However, experimental data on the position of spinodals and binodals in filled blends are sparse. To date, estimating phase behavior in metastable regions has not yet been accomplished.

A PMMA/styrene–acrylonitrile (SAN) copolymer blend exhibits a typical LCST phase separation upon heat treatments. Huang investigated the phase behavior of a PMMA/SAN blend filled with silica particles (SiO_2) with an average diameter of about 6 μm by rheological measurements [28]. They found that the addition of SiO_2 leads to an overall increase in the phase separation temperature of the matrix. The rationale given was that the filler enhanced the phase stability of the PMMA/SAN mixtures. Moreover, differences between blends with PMMA as the minor and major components were also noted [31,32]. These differences were believed to have arisen from the selective interactions of the blend components with a solid surface (preferential adsorption of one of the components).

In the present study, the influence of SiO_2 particles with an average diameter of 50 nm on the phase behavior of PMMA/SAN blends was investigated. Dynamic rheological measurements and time-resolved small-angle light scattering (SALS) were performed. The addition of SiO_2 was found to slightly increase T_c of PMMA/SAN with a *near-critical* composition, such as 60/40 (*w*/*w*) PMMA/SAN. However, T_c decreased with an *off-critical* composition, such as 30/70 PMMA/SAN. To assess the differences between the phase separation mechanisms of blends with *near-critical* and *off-critical* compositions, the kinetics of the phase separation in the PMMA/SAN blends were investigated by SALS. Via dynamic rheological measurements, the metastable and unstable regions of these systems were determined for the first time. This determination enabled the study of the phase behavior of the metastable region.

2. Experimental section

2.1. Materials and sample preparation

Commercial PMMA (IH830, $\overline{M_n} = 4.7 \times 10^4$ g/mol, $\overline{M_w}/\overline{M_n} = 1.82$) was purchased from LG Chemical, Ltd., Korea. SAN (PN-127H; AN = 28 wt%, $\overline{M_n} = 6.5 \times 10^4$ g/mol, $\overline{M_w}/\overline{M_n} = 1.91$) was from the Chimei Corporation, Taiwan. Fumed silica (SiO_2) with a specific surface area of 250 m^2/g and an average particle size of 50 nm were obtained from the Degussa Corporation, Germany. The particles were modified with octamethyl cyclotetrasiloxane (D4). The interfacial tension (γ) between PMMA and D4 (γ_1), as well as between SAN and D4 (γ_2) were 3.0 and 6.2 dyn/cm, respectively, according to our previous tests [33]. Hence, the PMMA chains were selectively adsorbed on the surface of SiO_2 in the PMMA/SAN/SiO_2 mixtures. A similar result was reported by Steinmann et al. [34]. In the present study, monomer radius $r_0 = 0.5$ nm, and the degree of polymerization of PMMA and SAN was $N_{PMMA} = N_{SAN} \approx 470$. Hence, $r_0N^{1/2} \approx 10$ nm, which corresponded to the size grade of the SiO_2 particles.

PMMA and SAN at different weigh rations were dissolved in methyl ethyl ketone ($CH_3C(O)C_2H_5$) at a weight fraction of 5% to form the uniform mixture solutions and then the solutions were cast on the cover slips. After the solvent evaporated at an ambient environment, the samples were further dried at 85, 100, 115 °C respectively in a vacuum oven for at least 72 h to remove any residual solvent. SiO_2 particles were directly introduced into the polymer solutions and the filler loadings of all nanocomposite samples were set as 3 wt%, 5 wt%, and 7 wt%, respectively. The resulting suspension was refluxed for 24 h. Then the ternary nanocomposite films were prepared just as the above-mentioned method. The sample films with the thickness of 20–25 μm for SALS testing are uniform and transparent.

The blend and nanocomposite films with another thickness of 90 μm were also obtained by the methods mentioned above; however, the concentration of the polymer solution was 15% by weight and the solution was cast on the surface of glass plates. These films were folded up and compression molded into disc form having a diameter of 25 mm and thickness of 1.2 mm at 10 MPa below 140 °C for rheological measurements.

2.2. Time-resolved small-angle light scattering (SALS)

The SALS apparatus was the same as that used in our previous studies [11,12], and the principle of this system was detailed in the literature. In our study, SALS was employed to investigate the kinetics of phase separation and to determine the T_c curves for both filled and unfilled blends. It was also appropriate for the filled systems because there existed no fogging phenomenon for the nanocomposite samples with low loading SiO_2.

According to our previous works [11,12,35], T_c for the PMMA/SAN blends could not be obtained by linear extrapolation to zero at different heating rates. Hence, T_c was measured at a heating rate of 0.1 °C/min and obtained as the average value of three to four parallel determinations.