

Effect of Nanoclay on the Phase Separation Behavior of Poly(methyl methacrylate)/Poly(vinyl acetate) Binary Polymer Blends*

Ji-shi Zhao, Min Zuo**, Chao-ying Lin and Qiang Zheng

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

Abstract The effect of nanoclay on the phase-separation behavior of poly(methyl methacrylate)/poly(vinyl acetate) (PMMA/PVAc) blends has been mainly investigated by small-angle laser light scattering. It is found that the effect of clay on the thermodynamics and kinetics of phase-separation for PMMA/PVAc blends seems inconsistent. The kinetics phase-separation rate decreases, while the thermodynamics parameters, cloud points T_c and delay time t_D of isothermal phase-separation also decrease, and the variation amplitude depends on the matrix composition. The affinity of clay to PMMA results in the composition difference between the border layer and the polymer matrix and further causes the concentration fluctuation at the early stage of phase separation to reduce T_c and t_D . On the other hand, the decrease of phase-separation rate is caused by the mechanical barrier effect of clay on the macromolecular diffusion of blend matrix. Hence, such seemingly counterintuitive results on the thermodynamics and kinetics of phase-separation are attributed to different dominant factors.

Keywords: Nanocomposites; PMMA/PVAc blend; Clay; Phase separation behavior; Morphology.

INTRODUCTION

It is well known that most polymer materials widely used in academic research and industrial application are often multi-component/multi-phase blends or composites and their properties mainly depend on their phase structure and morphology^[1]. Hence, it is of great importance to control the formation and evolution of the morphology and structure of polymer alloys for the desired performance. Generally, the incorporation of nano-filler into polymer blends may further improve their modulus, impact strength, heat resistance, conductivity or flammability. Besides the performance improvement of polymer materials, the effect of nano-filler on the miscibility/compatibility and the morphology evolution of polymer blends would be also significant. While the influence of a wide range of nano-fillers on the morphology of immiscible polymer blends has been explored, the effect of their presence in partially miscible blends is not yet fully understood. Hence, the sufficient understanding of the effect of filler on the thermodynamic phase-separation behavior for binary polymer blends, especially for polymer blends with critical phase behaviors, such as lower critical solution temperature (LCST) blends and upper critical solution temperature (UCST) blends, would help us predict and optimize the permanent stability, and then the mechanical properties of filled binary polymer systems.

In the last two decades, some researches related to the effect of filler on the miscibility and phase-separation behavior of binary polymer blends have been carried out. With the incorporation of filler into polymeric matrix,

* This work was financially supported by the National Natural Science Foundation of China (Nos. 51003093 and 51273173), the Program for Zhejiang Provincial Innovative Research Teams (No. 2009R50004) and the Research Foundation of Education Bureau of Zhejiang Province (No. Y200908238).

** Corresponding author: Min Zuo (左敏), E-mail: kezuomin@zju.edu.cn

Received December 18, 2013; Revised January 15, 2014; Accepted January 16, 2014

doi: 10.1007/s10118-014-1527-5

the phase behavior may be quite different from that of the binary blend without filler. In Goharpey's research^[2], it was found that the addition of hydrophilic nano-silica (SiO_2) caused the increase of the phase separation temperature for polystyrene/poly(vinyl methyl ether) (PS/PVME) blend, assisted the free energy reduction and the stability of the homogeneous phase, and also slowed down the phase separation dynamics. However, Xia^[3] found that the incorporation of multi-walled carbon nanotubes shifted the phase separation temperature of low density polyethylene (LDPE)/PS to lower temperatures and accelerated the rate of phase separation. Obviously, the above-mentioned two findings were just totally opposite. What's more, Moldenaers^[4] noted that the influence of thermally reduced graphene sheets on the phase separation temperature of poly(α -methyl styrene-co-acrylonitrile)/poly(methyl methacrylate) (α -MSAN/PMMA) was nonmonotonous and relevant with the composition. Furthermore, Lipatov^[5] investigated the effect of fumed silica on the phase separation of chlorinated polyethylene/ethylene-vinyl acetate (CPE/EVA) copolymer blends. He found that the increase or decrease of their phase separation temperature mainly depended on the amount of the filler introduced. In short, the phase behaviors of such matrices became more complicated. The introduction of filler into the blends might change their phase-separation temperature (increase or decrease)^[2, 3], the interaction parameters between two components^[5, 6] and even the shape of their cloud point curve^[7, 8].

Polymer-layered silicate nanocomposites have attracted a great deal of attention due to their academic and industrial importance. Over the last decade, many different commercial thermoplastic polymers have been used for the preparation of nanocomposites with either pure or organically-modified clay. They have shown dramatic improvements in mechanical, thermal and barrier properties with a small amount of layered silicates. The researchers mainly focused their attention on the mechanical and thermal properties of such nanocomposites^[9–12]. Up to now, little effort has been made to investigate the effect of layered silicate on the structure, morphology and properties of polymer blends with critical phase behavior. Prior works by Krishnamoorti^[13, 14] reported that the phase behavior of PS/PVME blends is nearly unaffected by organically modified layered silicate, because there is no preferred interaction among layered silicate with the two matrix components and the interactions are both weak. Nevertheless, these findings might be invalid for other partially miscible polymer blends, which can be ascribed to the fact that the interaction among layered silicate and the polymer components is much different in these systems.

Here, the high specific surface area associated with clay particles may enhance the chances of adsorption of macromolecular chains onto their surface. The PMMA/PVAc blend is partially miscible with LCST. In such system, two matrix components may have nearly strong interaction with clay because this pair has almost similar nature of the chains. The existence of strong interaction may lead to different effects of clay on the phase separation behavior for PMMA/PVAc blends from that for PS/PVME blends. However, few studies about the influence of clay on the phase separation of PMMA/PVAc systems have been carried out until now. The aim of this paper is to systematically investigate the effect of clay on the morphology and thermodynamic phase behavior of PMMA/PVAc blends by the combination of small angle laser light scattering (SALLS) and phase contrast microscopy (PCM).

EXPERIMENTAL

Materials

Poly(methyl methacrylate) (PMMA) (IF850, $M_w = 8.6 \times 10^4$, $M_w/M_n = 2.04$, LG Co. Ltd, South Korea) and poly(vinyl acetate) (PVAc) (189480, $M_w = 9.9 \times 10^4$, $M_w/M_n = 2.56$, Aldrich Co. Ltd, USA) were both commercial products and used as received. Montmorillonite clay (N-605, Nanocor Co. Ltd, USA) used in our study was surface modified with 25 wt%–30 wt% methyl dihydroxyethyl hydrogenated tallow ammonium and its lateral dimension is about 5 μm .

Sample Preparation for SALLS

PMMA and PVAc were dried for 6 h at 60 °C and the clay was also dried for 24 h in a vacuum oven to remove any moisture prior to use. For two-component systems, PMMA and PVAc at different weight ratios were

dissolved in chloroform (CHCl_3) at 3 wt% to form a clear and uniform solution under constant mechanical agitation at room temperature for 12 h. For three-component systems, a solution with clay in CHCl_3 was sonicated before PMMA and PVAc at 3 wt% were dissolved into the suspension. The system was then sonicated to achieve the uniform dispersion of clay in the polymer blend solution. Subsequently, the mixture was cast onto the surface of cover glasses at 38 °C. After the solvent evaporated at an ambient environment, the samples were further dried at 50, 60, 75 and 85 °C, respectively in a vacuum oven for at least 96 h to remove residual solvent. The thickness of the sample film was measured to be about 10–20 μm with uniform and transparent appearance, characteristic of single-phase structure.

Time-Resolved Small-Angle Laser Light Scattering (SALLS)

The SALLS apparatus was the same as that used in our previous studies^[15–17] and its detailed principle was available in other literatures^[18]. In the non-isothermal experiments, the samples were first heated to 90 °C on a hot stage, and then heated up at different heating rates of 0.1, 0.25, 0.5, 1, 3 and 5 $\text{K}\cdot\text{min}^{-1}$ until the late stage of phase separation of the samples. In the isothermal annealing experiments, the hot stage was first heated up to the required temperatures and kept for 3 min. Then the samples were put on the hot stage and the real-time relationships among intensity, time, temperature and scattering angle were obtained from the online detecting scattering patterns. The accuracy of temperature control was about (± 0.1) K.

Phase Contrast Microscopy (PCM)

Phase contrast microscopy (B1-PH, Motic, China Group Co. Ltd) was employed to detect the fine morphology of phase-separated blends and nanocomposites. The images were recorded by means of a CCD digital camera (Nikon-4500, Nikon, Japan) and imported into the computer memory for subsequent analysis. The samples were kept at 170 °C for different times. All the morphological images were recorded in real time online.

Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM, JEM 1200EX, Japan) was used to detect the morphological evolution of binary and ternary systems. The dispersion and location of clay could be also obtained.

X-ray Diffraction (XRD)

An X-ray diffractometer (D/Max-2550pc, Rigaku) was used to determine the gallery distance of silicate layers of the clay at 40 kV, 250 mA. The scanning rate was 5 ($^\circ$)/min. The d -spacing could be calculated according to Bragg's law ($\lambda = 2d\sin\theta$, $\lambda = 0.154059$ nm).

RESULTS AND DISCUSSION

Effect of Nanoclay on the Cloud Points of PMMA/PVAc Blends

The cloud points (T_c) of PMMA/PVAc blends and PMMA/PVAc/clay nanocomposites were determined by SALLS upon heating at a given rate. The dependence of the cloud point on heating rate for PMMA/PVAc blends and PMMA/PVAc/clay nanocomposites with two matrix compositions is shown in Fig. 1. It can be found that T_c s for binary blends and ternary nanocomposites both depend intensely on the heating rate and move towards higher temperatures as the heating rate increases, due to the delayed effect of macromolecular segment mobility. Furthermore, T_c and heating rate obviously deviate from the linear relationship and the equilibrium phase separation temperature can be hardly obtained from the simple linear extrapolation. The introduction of nano-clay hardly influences the nonlinear and nonequilibrium phase-separation characteristics of PMMA/PVAc blend matrix, similar to those of other polymer blends in our previous study, such as PMMA/ α -MSAN^[19], PS/PVME^[20] and poly(*N*-methyl methacrylimide)/poly(vinylidene fluoride) (PMMI/PVDF)^[21]. On the other hand, the presence of clay causes the decrease of T_c s for PMMA/PVAc blend matrices with two compositions and the drop of T_c for PMMA/PVAc (20/80/1) nanocomposite is more visible, even about 30 K.

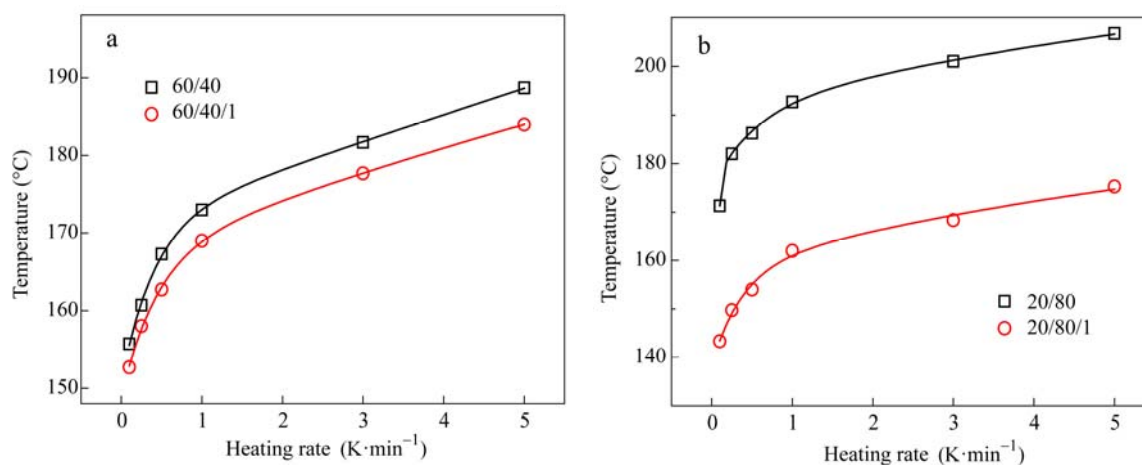


Fig. 1 Dependence of cloud points on heating rate for (a) PMMA/PVAc (60/40) blends and PMMA/PVAc/clay (60/40/1) nanocomposites and (b) PMMA/PVAc (20/80) blends and PMMA/PVAc/clay (20/80/1) nanocomposites

Here, 0.25 K·min⁻¹ was selected as a model heating rate to obtain the phase diagrams of binary and ternary systems. Figure 2 shows the dependence of cloud points on PMMA content for unfilled and clay filled PMMA/PVAc systems. It should be noted that T_c s aren't given for unfilled and filled PMMA/PVAc (80/20) systems because their T_c s are higher than their decomposition temperatures. Obviously, the incorporation of clay does not change the characteristics of LCST phase behavior for their blend matrix, but it causes the T_c s curves of blend matrix to shift towards lower temperatures. Their decrease trend of T_c is different from that for PMMA/SAN/clay systems in our previous study^[22], indicating that the presence of clay reduces the miscible region of PMMA/PVAc blend matrix, rather than enlarges such region. Furthermore, the decrease amplitude of T_c significantly depends on the composition of blend matrix. It can be found that the incorporation of clay causes the sharp reduction of T_c s for PMMA/PVAc blend with a high PVAc fraction and just a slight decrease for the blend with a low PVAc fraction. Hence, the phase diagram changes. It was reported by Lipatov^[7] that for the same blend matrix, the presence of fumed silica also caused the shift of cloud point curve towards the lower temperature and the especially sharp decline of T_c for the blend matrix with a predominant content of either PMMA or PVAc. Such dependence of T_c variation on the composition of blend matrix may be attributed to the formation of a border layer on the filler surface.

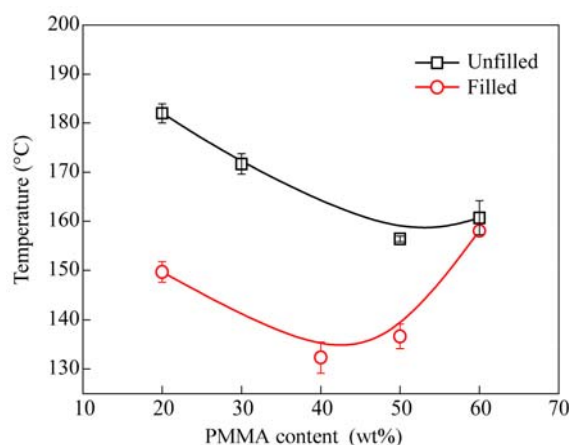


Fig. 2 Dependence of cloud points on PMMA content for PMMA/PVAc blends and PMMA/PVAc/clay nanocomposites at the heating rate of 0.25 K·min⁻¹

Although PMMA and PVAc have similar nature of the chains, different interactions between PMMA and PVAc with clay may also result in a border layer, whose composition of polymer blend is different from that in bulk matrix. Here, with the introduction of 1 wt% clay into PMMA/PVAc blend, both components can hardly transit into the state of border layers, which are fully under the influence of the surface field forces. In other words, the filled systems consist of two parts, surface layer formed by two components and unperturbed matrix. According to the literatures^[23–26], the interfacial tensions among PMMA, PVAc and clay at different temperatures can be obtained based on the harmonic mean equation, as shown in Table 1. And then the wetting coefficient, ω_a can be evaluated to predict the location of clay according to Young's equation. It can be found that at all investigated three temperatures, the used organically-modified clay tends to be located in PMMA phase. Namely, it has more affinity to PMMA than PVAc and its surface layer is PMMA-rich. When PMMA is the dominant component, such as PMMA/PVAc (60/40) system, the surface layer composition is close to that of the bulk, which just causes a small decrease of T_c in the filled system. When PVAc is the majority, there are large discrepancies between the composition of the surface layer and that of the bulk. Hence, the decline of T_c for filled system may be caused by the redistribution of the blend components in the border layer and the bulk. Furthermore, the dispersed clay may also become the nuclei for a new phase which initiates phase separation to lower the overall phase separation temperature.

Table 1. Interfacial tension and wetting coefficients according to harmonic mean equation

Temperature (°C)	Interfacial tension ($\text{mN}\cdot\text{m}^{-1}$)			Wetting coefficient, ω_a	Location prediction
	$\gamma_{\text{PMMA-clay}}$	$\gamma_{\text{PVAc-clay}}$	$\gamma_{\text{PMMA-PVAc}}$		
170	0.295	0.863	0.331	-1.716	PMMA
180	0.271	0.805	0.319	-1.674	PMMA
190	0.247	0.748	0.307	-1.632	PMMA

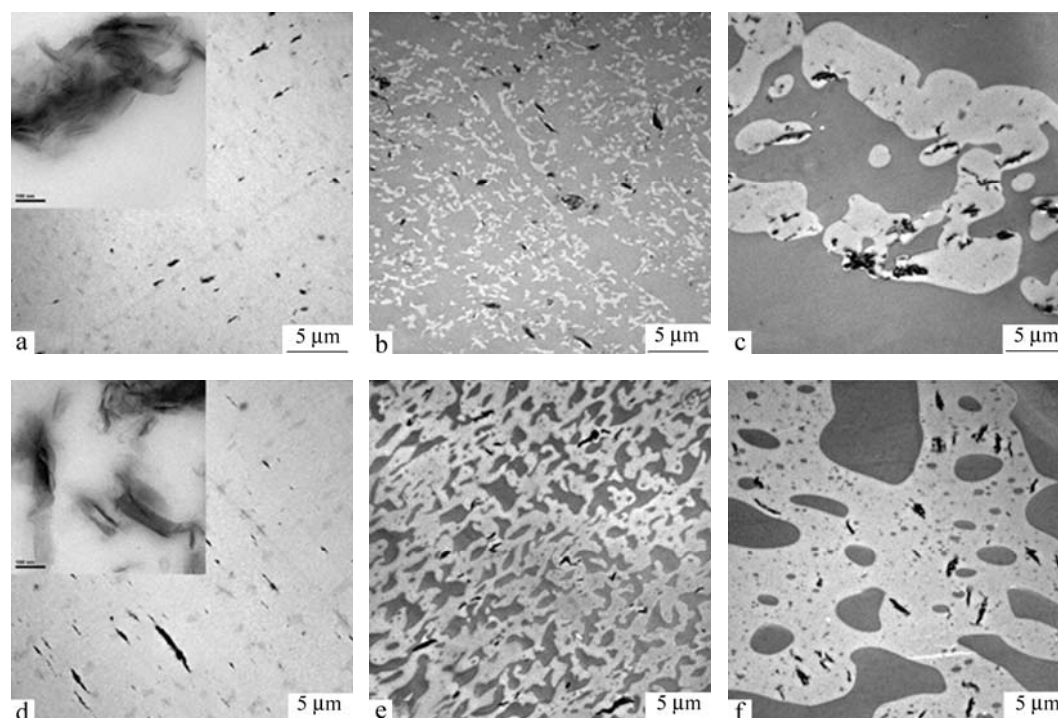


Fig. 3 TEM micrographs of PMMA/PVAc/clay nanocomposites: (a) 20/80/1 without annealing, (b) 20/80/1 annealed at 170 °C for 150 s, (c) 20/80/1 annealed at 170 °C for 3000 s, (d) 60/40/1 without annealing, (e) 60/40/1 annealed at 170 °C for 360 s, (f) 60/40/1 annealed at 170 °C for 3000 s

Figures 3(a) and 3(d) show the TEM micrographs of 20/80/1 and 60/40/1 PMMA/PVAc/clay nanocomposites without annealing. It can be noted that the introduction of clay hardly destroys the homogeneity of polymer blends. Both of these two nanocomposites have the intercalated structure of clay. The exfoliated clay can be hardly found in our nanocomposites and there exist some aggregated clays in the nanocomposites. Figures 3(b), 3(e) and 3(c), 3(f) show the TEM micrographs of 20/80/1 and 60/40/1 PMMA/PVAc/clay nanocomposites at the early and late stages of phase separation, respectively. With the proceeding of phase separation, the clay gradually tends to move to the PMMA-rich domain (bright region). And especially at the late stage of phase separation, the clay is almost located in the PMMA-rich domain with the domain coarsening. It is obvious that the used clay has more affinity to PMMA than to PVAc, which is consistent with our calculation results listed in Table 1.

XRD has been used extensively for the study of silicate dispersion in polymer matrixes and in the small-angle region XRD is used to determine the intercalation of polymer chains in the nano-clay galleries. Figure 4 shows the X-ray diffraction patterns of virgin clay and 1 wt% clay filled PMMA/PVAc nanocomposites. It can be found that the clay dispersions in the homogenous blend matrix are almost independent on the compositions of polymer matrices. Owing to small contribution of intercalation diffraction with the addition of a small amount of clay (1 wt%) into polymeric matrix, just a very weak peak at low diffraction angle of $2\theta = 2.5^\circ$ can be observed for two nanocomposites. According to the Bragg's equation, the d -spacing can be calculated from θ values. It is noted that d -spacing values of nanocomposites are both larger than that of virgin clay, indicating some intercalation of clay in PMMA/PVAc matrix. Such results can be also confirmed by the TEM observations, as shown in the inlays of Figs. 3(a) and 3(d). The diffraction peaks at $2\theta = 5.2^\circ$ may be the contribution of some aggregated clay.

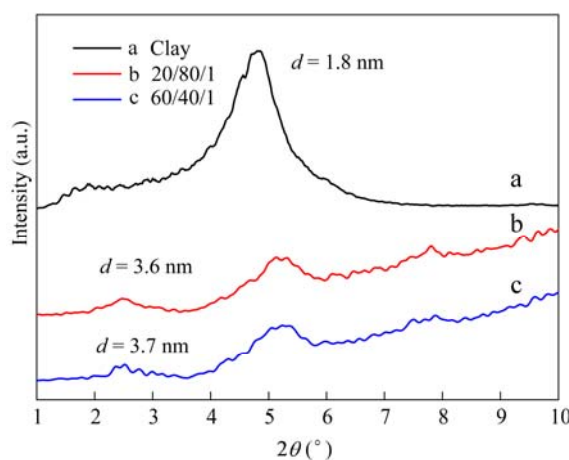


Fig. 4 X-ray diffraction patterns of virgin clay and 1 wt% clay filled PMMA/PVAc nanocomposites

Effect of Clay on the Phase Behavior of PMMA/PVAc Matrix During Isothermal Phase Separation

The linear theory of Cahn-Hilliard^[27, 28] can be used to describe the scattering intensity evolution at the early stage of phase separation for binary polymer blends. For ternary nanocomposites, the theory is still applicable to describe the phase-separation behavior at the early stage of spinodal decomposition. Considering the thermal fluctuation of stable binary polymer blends, Cook^[29] modified the Cahn-Hilliard function into

$$I(q, t) = I_s(q, 0) + [I_m(q, t_m) - I_s(q, 0)] \cdot \exp[2R(q)t] \quad (1)$$

where $I_s(q, 0)$ is the scattering intensity of the stable system and $q = (4\pi/\lambda)\sin(\theta/2)$ is the wavenumber of the spatial composition fluctuation, in which λ is the corresponding wavelength and θ is the scattering angle. The relaxation rate or amplification factor, $R(q)$, is further related by

$$R(q) = -Mq^2 \left(\frac{\partial^2 f_m}{\partial \phi^2} + 2kq^2 \right) \quad (2)$$

in which M is the mobility coefficient of molecules, ϕ is the volume fraction, k is the energy gradient energy coefficient and f_m is the mean field free energy of mixing. Equation (2) includes the apparent diffusion coefficient, D_{app} , which describes the uphill diffusion during SD:

$$D_{app} = -M \frac{\partial^2 f_m}{\partial \phi^2} \quad (3)$$

Hence, $R(q)$ and D_{app} values can be determined from the slope of plots of $\ln[(I(q,t)-I_s(q,0))/(I_m(q,t_m)-I_s(q,0))]$ versus t and the interception of plot of $R(q)/q^2$ versus q^2 , respectively. Then, the effect of clay on the kinetics at the early stage of isothermal phase separation can be detected clearly.

Figure 5 shows the semilogarithmic plots of normalized scattering intensity I_N versus time during isothermal annealing process under various temperatures for unfilled and filled PMMA/PVAc (60/40) systems. Here, the delay time t_D is defined as the time when the sample begins to phase separate after reaching the given annealing temperature. Namely, t_D is just the time when I_N begins to increase remarkably, as shown in Fig. 5. It is noted that the delay time t_D strongly depends on the annealing temperature and decreases with the increase of annealing temperature. The dependence of t_D on the annealing temperature for unfilled and filled PMMA/PVAc (60/40) systems is given in Fig. 6. Here, it can be found obviously from Fig. 6 that t_D s for the filled system are shorter than those for the unfilled system, indicating that the incorporation of clay makes the concentration fluctuation of PMMA/PVAc blend at the early stage of SD occur more easily. In other words, the presence of clay decreases the phase stability of PMMA/PVAc blend matrix. Such results are just consistent with our cloud point results. The selective adsorption of PMMA on the clay may result in the redistribution of the blend components in the border layer and the bulk. Such composition difference may further cause the concentration fluctuation at the early stage of SD, which can have an obvious effect on their equilibrium phase separation temperature and kinetics^[30–32].

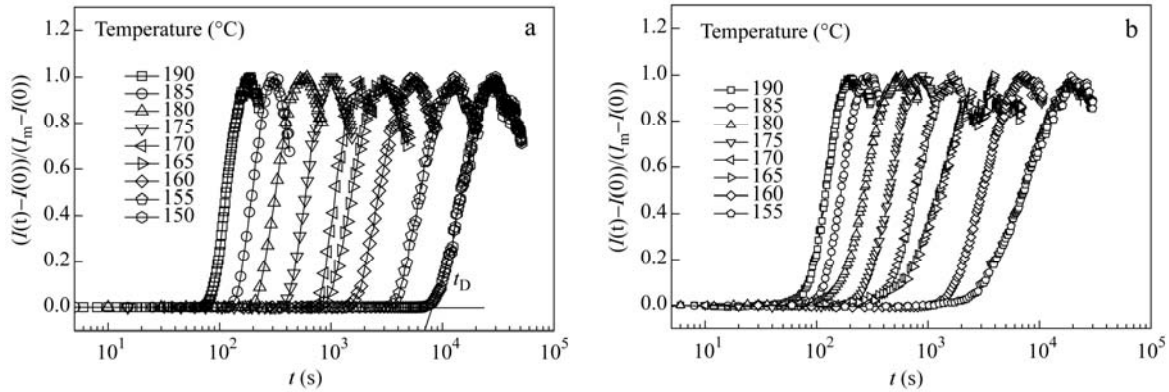


Fig. 5 Time evolution of normalized scattering intensity for (a) PMMA/PVAc (60/40) blends and (b) PMMA/PVAc/clay (60/40/1) nanocomposites under different annealing temperatures

The presence of clay affects the thermodynamics of PMMA/PVAc blends (including T_c and t_D). It can be also noted from Fig. 5 that the slopes of I_N for unfilled and filled systems are different, indicating that their kinetics of phase separation is also distinct. Hence, the influence of clay on the kinetics of phase separation should be explored further. Figure 7 demonstrates the plots of D_{app} for the unfilled and filled PMMA/PVAc systems. For unfilled and filled systems, all the D_{app} values nearly increase exponentially with the temperature in the given temperature region, similar with our previously reported PMMA/ α -MSAN and PMMA/SAN/clay systems^[19, 22]. Hence, the equilibrium spinodal temperature can be hardly obtained from the simple linear

extrapolation of D_{app} , which is quite different from the previous results^[33, 34]. It is also found that the D_{app} values for the unfilled blends are obviously higher than those for the filled nanocomposites, indicating that the uphill diffusion at the early stage of SD for filled system is markedly retarded by the clay.

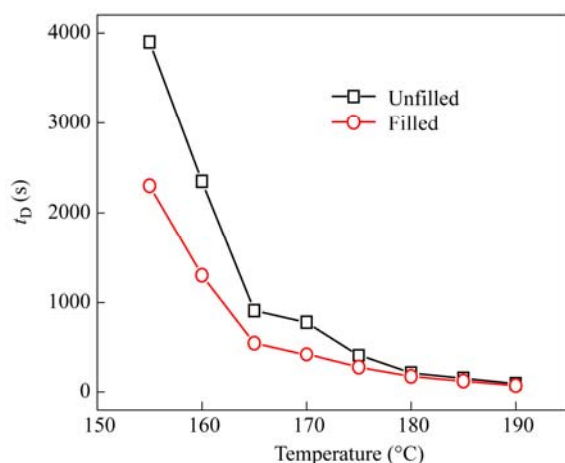


Fig. 6 Temperature dependence of delay time t_D of phase separation for unfilled and filled PMMA/PVAc (60/40) systems

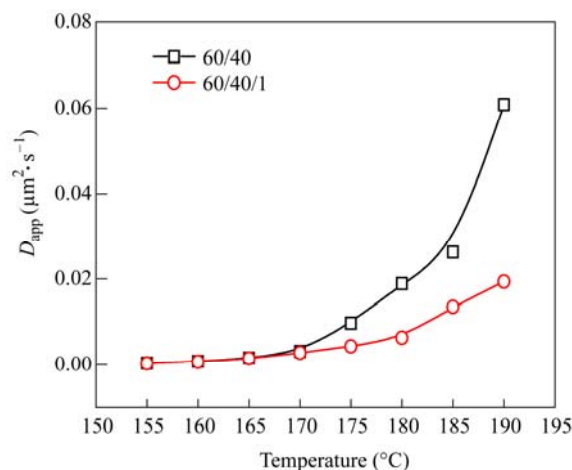


Fig. 7 Temperature dependence of D_{app} for PMMA/PVAc (60/40) blends and PMMA/PVAc/clay (60/40/1) nanocomposites

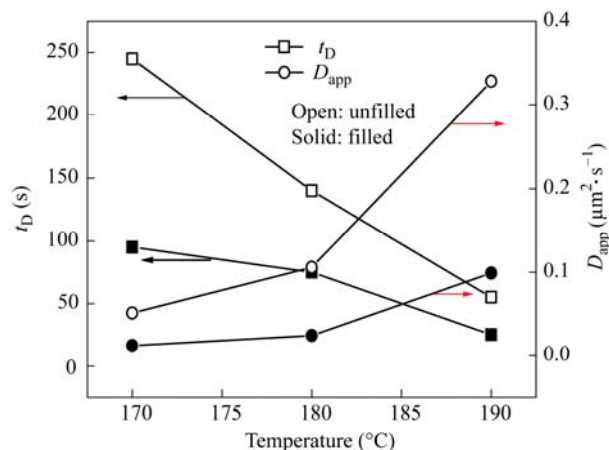


Fig. 8 Temperature dependence of the delay time t_D and D_{app} for unfilled and filled PMMA/PVAc (20/80) systems

In general, for thermal-induced phase separation systems, their phase separation rate strongly depends on the annealing depth $\Delta T = T - T_s$ in the external temperature field and always increases with ΔT ^[35–37]. The equilibrium spinodal temperature T_s is hardly obtained from the linear extrapolation and therefore the cloud point at the lowest heating rate T_{cl} is approximatively thought as T_s . It can be known from Fig. 1 that T_{cl} s of filled systems are lower than those of unfilled systems. Hence, at the same isothermal annealing temperatures, ΔT_s of filled systems are obviously larger than those of unfilled systems and the phase separation rates of filled systems should be higher. Here, the obtained results of D_{app} seem contradictory with the results from T_c and t_D . However, the cloud point T_c and delay time t_D are both the manifestation of thermodynamics of phase separation and depend on their critical concentration fluctuation, while phase separation rate and D_{app} should reflect the kinetics of phase separation, mainly decided by the diffusional movement ability of segments. The effect of clay on the thermodynamics of phase separation for PMMA/PVAc blends has been discussed in the former section and may result from the composition redistribution of PMMA/PVAc blends owing to the affinity of PMMA to clay.

However, the kinetics difference of phase separation for unfilled and filled systems may be attributed to the mechanical barrier effect of clay on the molecular mobility of polymer blend matrix chains. Hence, different dominant factors lead to this seemingly counterintuitive phenomenon.

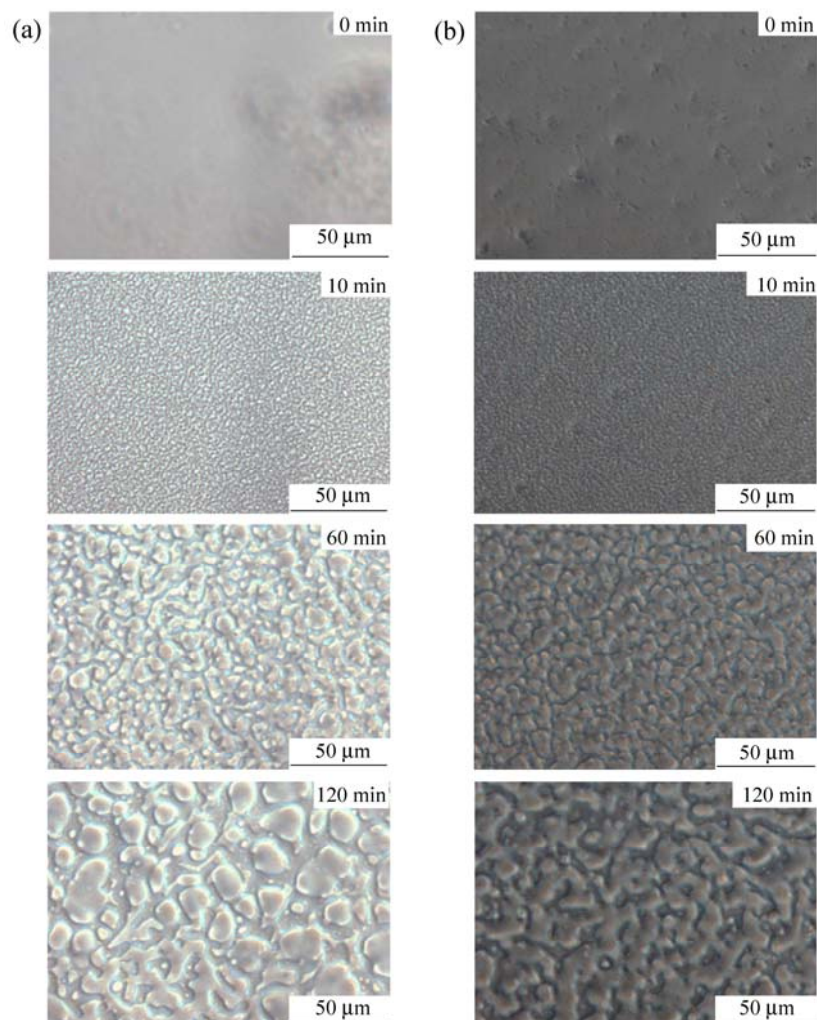


Fig. 9 Morphology evolution of (a) PMMA/PVAc (60/40) blends and (b) PMMA/PVAc/clay (60/40/1) nanocomposites isothermally annealed at 170 °C for different times

For PMMA/PVAc (60/40) system, the introduction of clay just slightly lowers the cloud point. But for filled PMMA/PVAc (20/80) nanocomposite, the T_c is about 30 K lower than that for the unfilled blend. Here, the isothermal phase separation behavior of unfilled and filled PMMA/PVAc (20/80) systems should be investigated further to obtain the influence of clay on the phase-separation kinetics for polymer blend matrix. Figure 8 shows the temperature dependence of the delay time t_D and D_{app} for unfilled and filled PMMA/PVAc (20/80) systems. The introduction of clay also reduces t_D and D_{app} of PMMA/PVAc (20/80) blend matrix. The variation trend is similar with that for PMMA/PVAc (60/40) system, but the reduction amplitudes of t_D for PMMA/PVAc (20/80) system at the same annealing temperatures are much more obvious than those for PMMA/PVAc (60/40) system. Such result is just consistent with the variation of T_c . For PMMA/PVAc (20/80) system, the great composition difference in the border layer and bulk is mainly attributed to the selective adsorption of PMMA on the clay. In the metastable region, the surface layers on the clay may act as the nuclei for a new phase, inducing the phase separation according to spinodal mechanism. On the other hand, the annealing depth ΔT for unfilled

PMMA/PVAc (20/80) system may be about 30 K smaller than that for filled system at the same annealing temperature, but the kinetics parameter, D_{app} of unfilled system is still higher than that of filled system, hardly affected by ΔT . It also verifies that the kinetics parameter is mainly controlled by the macromolecular diffusion of polymer blend matrix. The large annealing depth ΔT of filled PMMA/PVAc (20/80) system induced by the incorporation of clay just causes the distinct shortening of the delay time. The influence of clay on the thermodynamics and kinetics parameters for PMMA/PVAc system with different compositions keeps the similar variation trend.

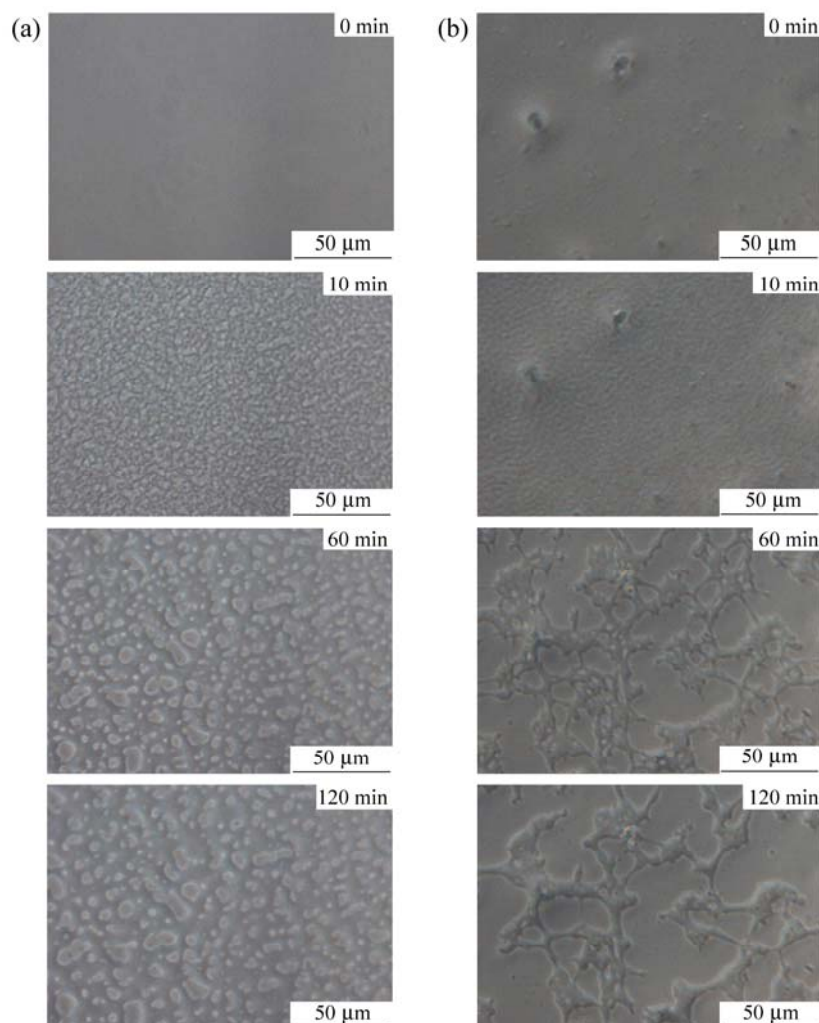


Fig. 10 Morphology evolution of (a) PMMA/PVAc (20/80) blends and (b) PMMA/PVAc/clay (20/80/1) nanocomposites isothermally annealed at 170 °C for different times

In order to understand the morphology evolution of isothermal phase separation, PCM has been used to observe this process visually. Figures 9 and 10 show the morphology evolution of unfilled and filled PMMA/PVAc systems isothermally annealed at 170 °C for different time. At the early stage of phase separation, all the investigated systems show the cocontinuous morphology, characteristic of SD phase separation. For unfilled and filled PMMA/PVAc (60/40) systems, their morphology at the early stage of phase separation is similar, but at the late stage the domain sizes of unfilled system are bigger than those of filled system, indicating that the existence of clay may also retard the domain coarsening at the late stage. On the other hand, for unfilled and filled PMMA/PVAc (20/80) systems, there are significant differences in their morphology evolution at the

late stage. Under the same annealing conditions, the morphology of unfilled PMMA/PVAc (20/80) changes from the cocontinuous structure to the insular structure, while the filled system still shows the cocontinuous morphology. Owing to the affinity of clay to PMMA, the clay may move to the PMMA-rich region at the late stage of SD and then cause the viscosity increase of PMMA-rich phase^[38, 39]. Hence, the PMMA-rich region with high viscosity in the filled system is hard to change from a continuous phase to an island phase.

CONCLUSIONS

The effect of clay on the morphology and phase separation behavior of PMMA/PVAc blends has been investigated. The incorporation of clay leads to the decline of two thermodynamics parameters, the cloud points T_c and the delay time of phase separation t_D , for polymer blend matrix and their decrease amplitude is remarkably dependent on the composition of PMMA/PVAc, indicating that the clay may destroy the phase stability at the early stage. For PMMA/PVAc systems filled with 1 wt% clay, the affinity of clay to PMMA may cause the redistribution of the blend components in the border layer and the bulk. For filled PMMA/PVAc (60/40) system, just small amplitude decrease of T_c and t_D is observed because the border layer composition is close to that of unfilled blend. In filled PMMA/PVAc (20/80) system, their obvious decrease of the two thermodynamics parameters may be attributed to the large discrepancies between the composition of the surface layer and that of the matrix, which may cause the concentration fluctuation at the early stage of phase separation to occur at lower T_c and shorten t_D , or make the clay act as the nuclei for a new phase. However, the effect of clay on the kinetics parameter D_{app} of phase separation for both two compositions is just opposite and the decrease of D_{app} is attributed to the mechanical barrier effect of clay on the molecular mobility of polymer blend matrix chains. Hence, different dominant factors may lead to these seemingly counterintuitive results.

REFERENCES

- 1 Olabisi, O., Robeson, L.M. and Shaw, M.T., "Polymer-Polymer Miscibility", Academic Press, New York, 1979, p. 89
- 2 Gharachorlou, A. and Goharpey, F., *Macromolecules*, 2008, 41(9): 3276
- 3 Xia, Q.M., "The preparation and properties of CNT/LDPE/PS conductive composites", Thesis, Donghua University, 2007
- 4 Vleminkx, G., Bose, S., Leys, J., Vermant, J., Wubbenhorst, M., Abdala, A.A., Macosko, C. and Moldenaers, P., *ACS Appl. Mater. Interfaces*, 2011, 3(8): 3172
- 5 Lipatov, Y.S., Nesterov, A.E., Ignatova, T.D. and Nesterov, D.A., *Polymer*, 2002, 43(3): 875
- 6 Nesterov, A.E. and Lipatov, Y.S., *Polymer*, 1999, 40(5): 1347
- 7 Nesterov, A.E., Lipatov, Y.S., Horichko, V.V. and Gritsenko, O.T., *Polymer*, 1992, 33(3): 619
- 8 Du, M., Wu, Q., Zuo, M. and Zheng, Q., *Eur. Polym. J.*, 2013, 49(9): 2721
- 9 Burgaz, E., *Polymer*, 2011, 52(22): 5118
- 10 Ray, S.S., *Ind. Eng. Chem*, 2006, 12(6): 811
- 11 Manias, E., Touny, A., Wu, L., Strawhecker, K., Lu, B. and Chung, T.C., *Chem. Mater.*, 2001, 13(10): 3516
- 12 Moniruzzaman, M. and Winey, K.I., *Macromolecules*, 2006, 39(16): 5194
- 13 Yurekli, K., Karim, A., Amis, E.J. and Krishnamoorti, R., *Macromolecules*, 2003, 36(19): 7256
- 14 Yurekli, K., Karim, A., Amis, E.J., and Krishnamoorti, R., *Macromolecules*, 2004, 37(2): 507
- 15 Peng, M. and Zheng, Q., *Chinese J. Polym. Sci.*, 2000, 18(6): 565
- 16 Zheng, Q., Peng, M., Song, Y.H. and Zhao, T.J., *Macromolecules*, 2001, 34(24): 8483
- 17 Zuo, M., Peng, M. and Zheng, Q., *Polymer*, 2005, 46(24): 11085
- 18 Hashimoto, T., Kumaki, J. and Kawai, H., *Macromolecules*, 1983, 16(4): 641
- 19 Zuo, M., Peng, M. and Zheng, Q., *J. Polym. Sci. Part B: Polym. Phys.*, 2006, 44(11): 1547
- 20 Zuo, M., Shangguan, Y.G. and Zheng, Q., *Polym. Int.*, 2010, 59(6): 787
- 21 Hu, H.X., Shangguan, Y.G., Zuo, M. and Zheng, Q., *J. Polym. Sci. Part B: Polym. Phys.*, 2008, 46(18): 1923

- 22 Pang, D.Z., Zuo, M., Zhao, J.S. and Zheng, Q., *Chinese J. Polym. Sci.*, 2013, 31(11): 1470
- 23 Lewin, M., Mey-Marom, A. and Frank, R., *Polym. Adv. Technol.*, 2005, 16(6): 429
- 24 Gomari, S., Ghasemi, I., Karrabi, M. and Azizi, H., *J. Polym. Res.*, 2012, 19(1): 1
- 25 Wu, S., *J. Polym. Sci. Polym. Symp.*, 1971, 34: 19
- 26 Krevelen, D.W.V. and Nijenhuis, K.T., "Properties of Polymer", Science Press, Beijing, 2010
- 27 Cahn, J.W. and Hilliard, J.E., *J. Chem. Phys.*, 1958, 28(2): 258
- 28 Cahn, J.W., *J. Chem. Phys.*, 1965, 42(1): 93
- 29 Cook, H.E., *Acta. Metall.*, 1970, 18(3): 297
- 30 Jinnai, H., Hasegawa, H., Hashimoto, T. and Han, C.C., *J. Chem. Phys.*, 1993, 99(6): 4845
- 31 Pincus, P., *J. Chem. Phys.*, 1981, 75(4): 1996
- 32 de Gennes, P.G., *J. Chem. Phys.*, 1980, 72(9): 4756
- 33 Snyder, H.L., Meakin, P. and Reich, S., *Macromolecules*, 1983, 16(5): 757
- 34 Yang, H., Shibayama, M., Stein, R.S., Shimizu, N. and Hashimoto, T., *Macromolecules*, 1986, 19(6): 1667
- 35 Kyu, T. and Saldanha, J.M., *Macromolecules*, 1988, 21(4): 1021
- 36 Hu, H.Q., Li, J.Y., Zhang, C.G. and Han, C.C., *Polymer*, 2010, 51(20): 4619
- 37 Tomura, H., Saito, H. and Inoue, T., *Macromolecules*, 1992, 25(5): 1611
- 38 Wang, M., Yu, J.H., Hsieh, A.J. and Rutledge, G.C., *Polymer*, 2010, 51(26): 6295
- 39 Dhibar, A.K., Mallick, S., Rath, T. and Khatua, B.B., *J. Appl. Polym. Sci.*, 2009, 113(5): 3012