polymer

Effect of polymer–filler surface interactions on the phase separation in polymer blends

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Abstract

For the blends of chlorinated polyethylene and copolymer of ethylene with vinyl acetate, the effect of the introducing filler (fumed silica) on the phase behavior of the blends was investigated. It was found that introducing filler in polymer blends depending on its amount lead either to the increase or to the decrease in the temperature of phase separation. At the filler concentration where both components transit into the state of a border layers, the phase separation temperature increases. This effect was explained by the change of the total thermodynamic interaction parameter in the ternary system polymer–polymer–filler. At lower concentration of a filler, the possible effect is the redistribution of the blend components according to their molecular masses between filler surface (in the border layer) and in the bulk that may diminish the phase separation temperature.

Effect of the filler on the phase behavior was explained by the simultaneous action of two mechanisms: by changing the thermodynamics of interaction near the surface due to selective adsorption of one of the components and by the redistribution of components according to their molecular masses between the boundary region (near the surface) and in the matrix.

The measurements of the kinetics of phase separation and calculation of the parameters of the activation energy are in agreement with proposed mechanisms. © 2001 Published by Elsevier Science Ltd.

Keywords: Filled polymer blends; Phase separation; Activation energy of phase separation

1. Introduction

In some of our works, we observed an essential change in the mutual solubility and thermodynamic stability of polymer blends possessing both upper critical solution temperature (UCST) [1] and lower critical solution temperature (LCST) by introducing mineral fillers [2–10]. In particular, it was shown that the introduction of an active filler leads either to increasing or decreasing the temperatures of phase separation [1–4], changing the shape of the cloud point curves depending on the blend composition [1–3], changing the composition of separated phases as compared with the system without filler [7], changing the interaction parameter between two polymers, χ_{AB}, [9,10], etc. The essence of these effects up to now is not quite clear. It may be supposed [11] that as a result of the selective interactions of the blend components with a solid surface (preferential adsorption of one of the components), the surface, or border, layer is formed with composition that differs from the initial composition of the blend. Consider the conventional phase

diagram with LCST (Fig. 1). In the case of preferential adsorption of component B, the formation of the surface layer is equivalent to the shift of the figurative point along the composition axis from the point corresponding to the composition ϑ_B (point a) to point b with composition ϑ_B'. From the other side, the matrix phase will be enriched in component A (point c). If the shape of the border curve does not change in the presence of a solid, by transition through the borderline phase, separation in the surface layer and in the matrix would proceed at different temperatures and the compositions of separated phases in the surface layer and in the matrix will be different. The preferential adsorption of the fractions of lower or higher molecular mass may also contribute to this effect.

It was observed that experimental phase diagrams of some polymer pairs with LCST really are shifted along the composition axis by introducing filler and do change their shape. This means that coexistence of two regions of variable composition (surface layer and matrix) takes place under conditions of the changing thermodynamic interactions between two components in different regions. The reason of this effect may be different in the conformation state of macromolecules of both components at the interface

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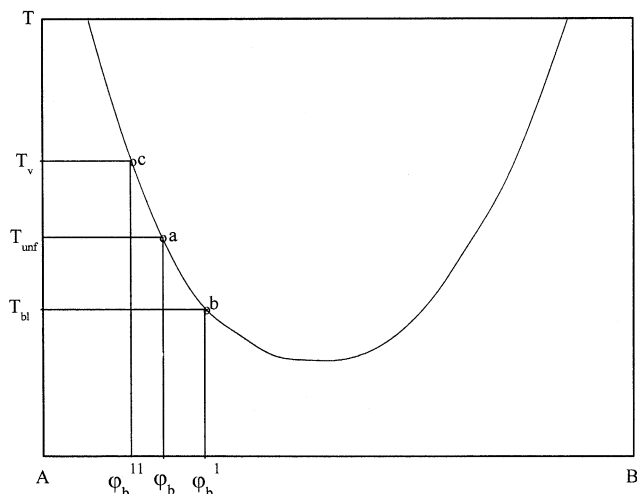 *E-mail address:* lipatov@imchem.kiev.ua (Y.S. Lipatov).

Fig. 1. Conventional phase diagram showing the possibility of the redistribution of composition of the polymer blends between the bulk and surface layers on a solid by selective adsorption of component B and possible change of the temperatures of phase separation near the interface and in the bulk. For explanation, see the text.

with a solid and in the matrix bulk [9]. In the case of selective adsorption, the change in the blend composition in the surface layer and in the bulk also contributes to the conditions of thermodynamic interaction parameter χ_{AB} (taking account of the dependence of this χ parameter on the blend composition). Really, the estimation of parameters χ_{AB} in some blends in the presence of a filler, made by using the inverse gas chromatography [3,9] at the temperatures above glass transition temperatures of both components has shown that its value may diminish as compared with unfilled blends, leading in such a way to the blend compatibilization in the presence of a filler.

From the other point of view, the polymer blend at the interface with solid may be assumed to be a 'quasi-ternary' system of the type: polymer A-polymer B-surface functional groups of a solid [8]. For this case, the compatibilizing effect may be explained by the values of parameters of pair interactions χ_{ij} changing the total interaction parameter of the 'ternary' system χ_{mixture}:

$$\chi_{\text{mixture}} = \chi_{AB}\varphi_A\varphi_B + \chi_{AS}\varphi_A\varphi_S + \chi_{BS}\varphi_B\varphi_S \qquad (1)$$

where A, B and S are polymers A, B and functional groups of the surface and ϑ are their volume fractions. In this case, the free energy of the ternary (filled) system is

$$\Delta G_{S+A+B} = RT(\chi_{SA}\varphi_A\varphi_S + \chi_{SB}\varphi_S\varphi_B + \chi_{AB}\varphi_A\varphi_B) \qquad (2)$$

The results of calculation shows [8] that introduction of functional fillers even for immiscible polymer pairs may lead to the appearance of the miscibility regions, i.e. the composition regions where $\chi_{\text{mixture}} < \chi_{\text{crit}}$ [8]. However, even if such consideration is valid, it cannot have explained the total change in the shape and position of the border curve. When amount of the filler introduced is rather small, it is impossible to assume the interaction of all

molecules of both components with the surface. Such an interaction may take place only in the surface layer at the interface with solid, whereas the greatest part of the blends stays in unperturbed state. Total transition of all macromolecules into the state of a surface layer may be reached only at some critical amount of the solid. This amount should correspond to the thickness of the layer equal to doubled radius of inertia of unperturbed macromolecular coil $(R_\theta^2)^{1/2}$ [12]. Adsorption interaction between solid and polymer in the surface layer essentially diminishes molecular mobility of the chains.

As a result, the kinetic conditions of phase separation become worse and the latter may be uncompleted. This effect may cause so-called nonequilibrium compatibilization, which is determined not by thermodynamic reasons, but by insufficient experimental time needed to reach equilibrium state. This case should be distinguished from true compatibilization due to pure thermodynamic reasons [13].

Up to now, the effect of a filler on the phase behavior of binary polymer blends is investigated in more detail only for the PVA–PMMA blends containing fillers with different chemical nature of their surface. This pair has almost similar nature of the chains and therefore one cannot expect an essential difference in the component adsorption on the filler surface [5]. Therefore, it seems to be important to investigate the blends with different chemical nature of the chains and therefore different affinity to the solid surface. For this purpose, we have chosen the blends of chlorinated polyethylene and ethylene–vinyl acetate copolymer.

These blends were filled with fumed silica containing on its surface the silanol groups. In this case, we can realize the competition for the formation of hydrogen bonds between carbonyl groups of vinyl acetate in copolymer and α-hydrogen atoms of chlorinated polyethylene or carbonyl groups of vinyl acetate in copolymer and silanol groups of fumed silica:

$$\rangle Cl\text{--}C\text{--}H\cdots O{=}C\langle \quad \text{or} \quad \text{--}Si\text{--}OH\cdots O{=}C\langle$$
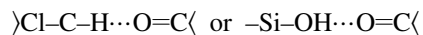
Chlorinated polyethylene may be considered as copolymer consisting of the groups CH_2 and $CHCl$ which should be reflected on the interaction between this polymer and ethylene–vinyl acetate copolymer and between them and a filler surface.

Our main task in this work was to establish the effect of a solid surface on the phase behavior and conditions of phase separation.

2. Experimental

The blends of commercial chlorinated polyethylene with 42.1% of Cl (CPE-42) with ethylene–vinyl acetate copolymer with 45 wt% of vinyl acetate (EVA-45, Levapren, Bayer) and $M_w = 2.56 \times 10^5$, $M_w/M_n = 5.16$ were taken. The component ratios in blends were taken: EVA/CPE 35/65,

40/60 and 50/50. As a solid filler, the fumed silica (aerosil trade mark A-175, production Kalush plant of the Surface Institute of Acad. Sci. of Ukraine) with specific surface 175 m^2/g was used. Cloud point curves were found using light scattering. For this purpose, the films were prepared by immersing the cover glasses into 10% solutions of the blends in tetrahydrofurane with subsequent evaporation of the solvent in vacuum at the room temperature. To prepare filled samples, filler was added to the solutions under intensive agitation for 8 h. The cover glasses were immersed into solution at the end of agitation following the removal of the solvent. In such a way, the samples were prepared with good dispersed filler particles. Fig. 2 shows typical microphotograph of a filled sample. To prevent the thermo-oxidative destruction by heating, the specimens were prepared as sandwiches between two cover glasses. The film thickness was ≈0.2–0.3 mm.

Some blends were opaque as a possible result of the 'Δχ' effect [14] that leads to the appearance of the closed region of incompatibility. The mixtures obtained from such solutions may be two-phased because during evaporation, the system passed through the region of immiscibility. Also, rapid increase in viscosity causes the two-phase structure of the mixture to be frozen, showing in such a way the false UCST [15]. By heating, such films have become transparent and have shown the turbidity (LCST) only afterwards (Fig. 3).

Cloud points were found from the temperature dependence of the light scattering intensity using the known method [16,17]. The heating rate was 2°/min. Cloud points were taken as average from four to five measurements.

The kinetics of phase separation has been studied for the 60/40 blend (w/w) by the transfer of the system from the one-phase state to the unstable region of the phase diagram. For this purpose, the films were stored at the temperature 20°C below the cloud point and then were fast inserted into the thermostated camera heated to different temperatures. After this procedure, the time dependence of the light scattering intensity was measured. The results were treated using the least square method.
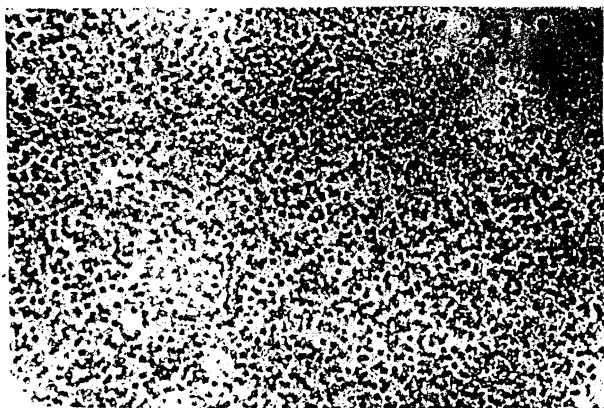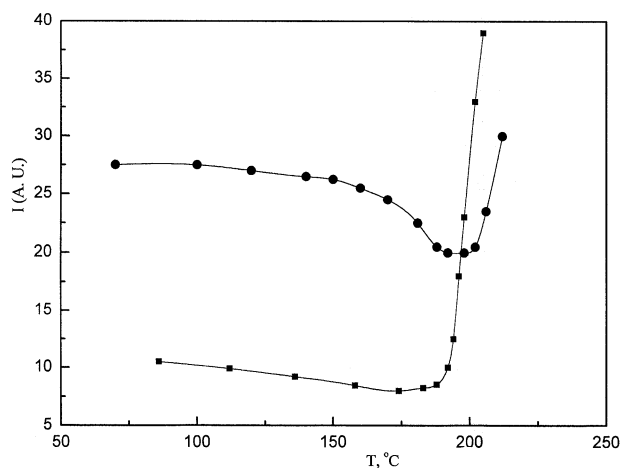

Fig. 3. Dependence of the light scattering intensity on temperature for unfilled (■) and filled with 10% aerosil (●) blend CPE–EVA of composition 60/40.

3. Results and discussion

Fig. 4 shows the cloud point curves for pure and filled blends. It is seen that those are curves typical of the systems with LCST because of the possibility to form hydrogen bonds between both the components and between components and the filler surface. For the blends, a sharp change in the temperatures of phase separation with composition is typical.

The introduction of a filler into the blends under consideration changes the temperatures of phase separation and the shape of cloud point curves. For blends with 10% of aerosil, the temperature of phase separation markedly increases, although the shape of the cloud point curve stays practically symmetric as in the case of unfilled blends. Introduction of 5% filler in blends changes both the shape of the curve and temperatures of phase separation. As is seen from Fig. 4, the introduction of a filler leads to the more gentle sloping shape of the border curve and to sharp decrease in the phase

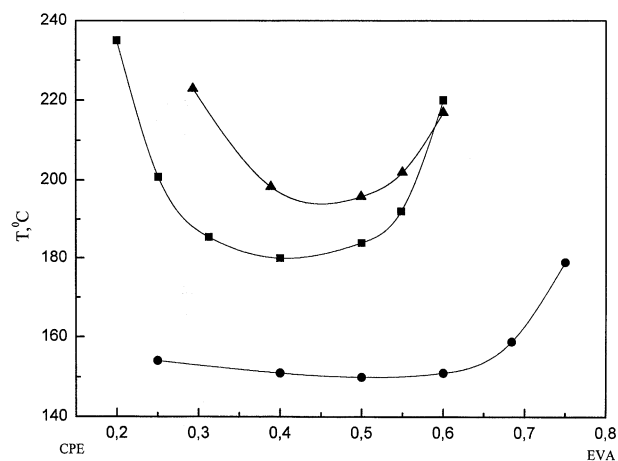Fig. 2. Microphotograph of a blend film filled with 10% of aerosil. × 400.

Fig. 4. Curves of cloud points for unfilled (■) and filled with 10% (▲) and 5% (●) aerosil.

separation temperatures. Thus, for the first time, it was observed that thermodynamic stability of the filled blend may increase or decrease depending on the amount of the filler introduced.

As it was mentioned in Section 1, the changes in the temperatures of the phase separation of polymer blends at the interface with solid are connected with formation of the surface or border layer at the interface with solid where conditions for the interaction of different macromolecules are changed (and correspondingly, the parameter of thermodynamic interaction between two polymers, χ_{AB}, changes as well). Besides, the interaction of each component with the functional groups of a solid also contributes to the total free energy of the system. As a result, filled system consists of two parts — surface layer formed by two component and unperturbed matrix. The compositions of these two parts may be different in the case of selective adsorption of one of the components. The latter effects may be excluded in the case when the whole matrix is under the influence of the field of surface forces, i.e. when it fully transits into the state of the surface border. In such a situation, all the changes in phase behavior should be ascribed to changing the interactions in such quasi-ternary system.

Let us try to consider the systems under investigation from this point of view. For this purpose, we have calculated the thickness of the layers between two filler particles as $\delta = V/(S_{sp}G_f)$, where V is the volume of the blend, S_{sp} is the specific surface of a filler and G_f is the mass of the filler. For the blends loaded with 10% (by weight) of aerosil (specific surface 175 m^2/g), we found the value $\delta \cong 50$ nm. According to [12,18], the critical thickness of the layer between two particles at which all the polymer transits into the state of the surface layer is equal to $\delta \leq 2(R_\theta^2)^{1/2}$, where $(R_\theta^2)^{1/2}$ is the radius of inertia of macromolecules. Calculation of this value for EVA with $M_w = 2.5 \times 10^5$ gives $2(R_\theta^2)1/2 = 30$ *nm*. This value corresponds to the critical thickness of the layer δ. In such a way, we may believe that in our case, all the polymers are in the state of the surface layer, $\delta \cong 2(R_\theta^2)^{1/2}$, where all three types of interactions are operative. From these data, the conclusion may be drawn that the main reason of changing the position and shape of phase diagrams for this blends at the interface with solid is the change of the free energy of the quasi-ternary system. This result is in a good accordance with the data obtained by Reich and Cohen [16] who observed the increase in the temperature of phase separation in thin layers of the PS-poly(vinyl methyl ether) (the system with LCST) at the interface with gold at the film thickness below 1μ. For PVA–PMMA, the same effect was observed at the thickness below some μ [19]. For the latter system, there were observed two temperatures of phase separation: the lower temperature corresponds to the phase separation in the polymer volume, whereas the second, higher temperature, to the surface layer.

For the blend with 5% of filler, the thickness of the layer between two particles is twice as much. In principle, the behavior of such a system may be described using the scheme presented in Fig. 1. However, in this case, we should observe two temperatures of phase separation — for a border layer and for a bulk, both with changed composition (due to selective adsorption) [16,19]. It may be supposed that leveling-off the border curve for 5% loading is connected with other reason. The polymers used in our investigation are very polydispersed. By preparing samples from solution of blends, the adsorption of components takes place that depends on the molecular mass distribution. Usually, adsorption of high molecular mass occurs. But for the semi-dilute solutions, the opposite situation may be true when fractions of lower molecular weights are adsorbed preferentially [20,21]. We prepared our samples from semi-dilute solutions (concentration of about 5%) where overlapping of macromolecular coils takes place. It may be supposed that under such conditions, the preferential adsorption of fraction of lower molecular mass proceeds and the volume of the blend will be enriched in fractions of higher molecular mass. In such a case, by heating the filled system first, we observe the phase separation temperature for the blends of high molecular weight fractions (remember that with increasing molecular masses of components, the phase separation temperature decreases for blends with LCST) [4,17]. The second phase separation temperature for blends of low molecular weight fractions (in the border layer) was not observed experimentally.

The formation of the surface layers should lead to the diminishing molecular mobility of both polymers at the interface [18]. Such effect may lead to the 'nonequilibrium' compatibilization. To prove the existence of this effect, we have studied the kinetics of phase separation in unfilled and filled blends. From the time dependencies of the light scattering intensity, we have calculated the amplification factors (the rate of growth of q-Furier mode of concentration fluctuations $R(q)$, q being the wave number). These measurements have been done at temperatures in the region of unstable states for the blends with component ratio 60/40, corresponding to the apparent composition of the surface layer. Fig. 5 shows typical time dependencies of light scattering intensity. It is seen that at the initial stages, phase separation proceeds according to the spinodal mechanism, namely ln I increases with time in accordance with the theory of spinodal decomposition [22]:

$$I(q,t) = I(q, t = 0)\exp[2R(q)t] \tag{3}$$

Fig. 6 presents the temperature dependencies of ln2$R(q)$ for filled and unfilled blends. It is seen that values $R(q)$ for filled blends are markedly lower as compared with pure blend, i.e. the rates of phase separation really diminish by filler introduction both at 5 and 10% of loading. It is interesting that values of $R(q)$ for systems loaded with 5% of a filler are lower as compared to unfilled blend, but higher if we compare them with the system with 10% of a filler. This fact may support the idea that in a given case, we observe the separation in the blend of more high molecular weight components.
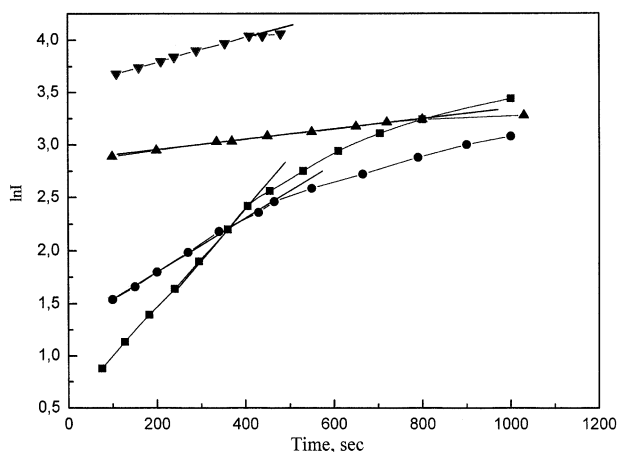
Fig. 5. Dependence of ln I on the time t for unfillled blend of CPE–EVA at the composition 60/40 at 186°C (●) and 203°C (■) and for filled blend (10% of aerosil) at 203°C (▲) and 215°C (▼).

According to the approximate mean field theory [22,23], the value of $R(q)$ at $q = $ const is proportional to the so-called apparent diffusion coefficient D_{app}:

$$D_{app} = D_C(T)(\chi - \chi_S)/\chi_S = D_{app}(T)\varepsilon_T \qquad (4)$$

where the ratio $(\chi - \chi_S)/\chi_S$ is motive power of phase separation, χ_S is the parameter of thermodynamic inter-action between two polymeric components at the spinodal temperature and $D_C(T)$ is the translation diffusion coefficient. Therefore, D_{app} and $R(q)$ are determined by two factors: translation diffusion coefficient $D_C(T)$ and thermo-dynamic motive power, $(\chi - \chi_S)/\chi_S$. The symmetry of the
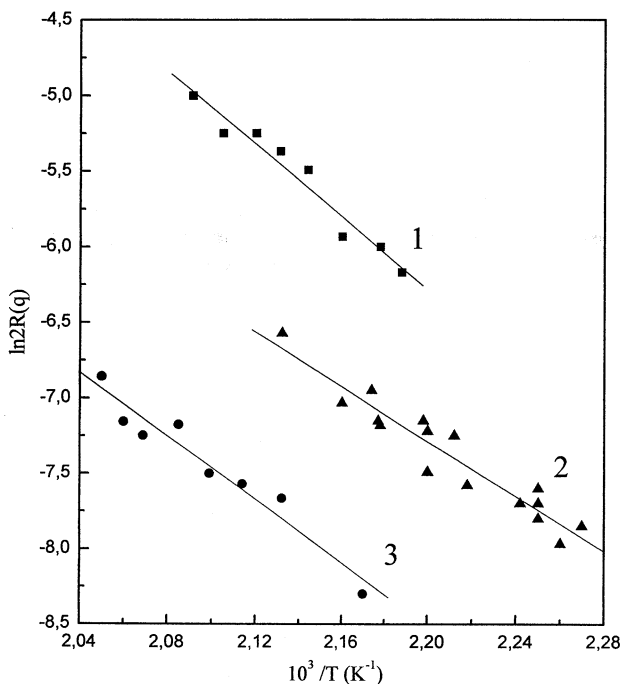

Fig. 6. Dependence of ln2$R(q)$ on 1/T for unfilled (■) and filled 5% (▲) and 10% (●) aerosil for the blend CPE–EVA at the composition 60/40.

cloud point curves for both unfilled ands filled EVA /CPE-42 blends gives the ground to assume that the values of χ_S in both cases are very close and that the temperature depen-dencies of the thermodynamic motive power, $(\chi - \chi_S)/\chi_S$, are similar at small quench depth, $\Delta T = T - T_S$. If it is true, then, according to the Eq. (4), sharp decrease in the rate of phase separation for filled blend, which is characterized by $R(q)$, is connected with essential diminishing of the transla-tion diffusion coefficient $D_C(T)$.

The latter is the result of the restriction of molecular mobility at the interface.

Diminishing mobility and loss of configurational entropy of segments bonded with solid surface should change the activation characteristics of phase separation. Taking $R(q) \approx D_{app}$ at $q = $ const, the temperature dependence of $R(q)$ may be given as

$$R(q) \approx D_{app} = A \exp(-\Delta G/RT) \qquad (5)$$

where ΔG is the Gibbs free energy, R is the gas constant and A is the fore-exponent factor. As $\Delta G = \Delta H - T \Delta S$ where ΔH and ΔS are the enthalpy and entropy of activation correspondingly, Eq. (5) may be written as

$$R(q) = A \exp(-\Delta G/RT) = A \exp(\Delta S/R - \Delta H/RT) \qquad (6)$$

or

$$\ln R(q) = \ln A + \Delta S/R - \Delta H/RT \qquad (7)$$

Fig. 6 shows the experimental dependencies of ln2$R(q) = f(1/T)$ from which the values of ΔH of activation may be calculated. If to accept that the values of A_{filled} and $A_{unfilled}$ are the same for filled and unfilled systems, one can estimate the changes of activation entropy of phase separation in bulk and in the presence of a solid. From values of $R(q)$ at any given temperature T and calculated values ΔH, one can find $\ln A_{filled} + \Delta S_{filled}/R$ and $\ln A_{unfilled} + \Delta S_{unfilled}/R$. Taking $\ln A_{filled} = \ln A_{unfilled}$, the difference between activation entropy $\Delta S_{unfilled} - \Delta S_{filled}$ could be found. Table 1 presents the data on the enthalpy and entropy of activation for various compositions of the blends and amounts of the filler.

Table 1
Enthalpies and entropies of activation of phase separation for various blends of EVA and CPE at different concentrations of a filler

Filler concentration (wt%)	ΔH (kJ/mol)	$(\Delta S_{unfilled} - \Delta S_{filled})$ (J/mol K)
35% EVA		
0	116.5 ± 6.9	–
5	107.9 ± 7.4	23.3 ± 1.12
10	109.7 ± 6.1	29.5 ± 2.1
40% EVA		
0	99.8 ± 8.9	–
5	75.3 ± 6.3	62.2 ± 3.0
10	87.2 ± 9.0	46.1 ± 0.2
50% EVA		
0	136.2 ± 9.3	–
5	117.3 ± 6.7	46.5 ± 0.8
10	120.1 ± 7.4	45.8 ± 4.6

The differences in the enthalpy of activation for two cases may be attributed to the different compositions of the layers at the interface with the filler surface. These layers, as follows from the said above, differ both in the ratio of two components due to selectivity of adsorption and in molecular-mass distribution of both components at the interface and in the bulk. Similar results were demonstrated for unfilled and filled blends of PVA/PMMA [6].

Diminishing activation enthalpy in the presence of a solid may be explained by diminishing the dependence of translation diffusion coefficient $D_C(T)$ on temperature due to restrictions of molecular mobility imposed by the interactions with solid. Simultaneously, the number of possible chain conformations at the interface is also diminished contributing to decrease in entropy [24]. The latter effect should diminish parameter χ_{AB}, i.e. increase the compatibility. The changes of the activation values by filling may be also connected to effects of the redistribution of molecular masses of components between the border layer and matrix.

4. Conclusions

In such a way, introducing filler in a polymer blend with LCST, depending on its amount, leads either to the increase or to the decrease in the temperature of phase separation. At the filler concentration, where both components transit into the state of border layers (are fully under the influence of the surface field forces), the phase separation temperature increases. This effect may be explained by the change of the total thermodynamic interaction parameter in the ternary system polymer–polymer–filler. At lower concentration of a filler, the possible effect is redistribution of the blend components according to their molecular masses between filler surface (in the border layer) and in the bulk that may diminish the phase separation temperature.

In these cases, both effects are operative changing interactions in the boundary layer and changing the molecular mass distribution of components between two regions of a blend matrix — between surface region and the bulk.

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