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Compatibilizing effect of a filler in binary polymer mixtures

A.E. Nesterov, Y.S. Lipatov*

Institute of Macromolecular Chemistry, National Academy of Sciences, Kiev 253660, Ukraine

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Abstract

The thermodynamics of mixing of two miscible or immiscible polymers with a solid has been considered. It is shown theoretically that the introduction of a specific filler in binary polymer mixtures increases the thermodynamic stability of the ternary system. The compatibilizing effect of the filler depends on the change in free energy of mixing between the two polymers, the effect being more pronounced for immiscible systems. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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Earlier [1–5] it was shown that the introduction of a mineral filler into a binary polymer mixture may lead to an increase or a decrease of the compatibility between the two polymers. Two cases of compatibilization have been considered [5]—an equilibrium compatibilization when after the filler introduction the thermodynamic stability of the system increases, and a non-equilibrium case when due to interaction of both components with the filler surface, the molecular mobility of the macromolecules diminishes preventing the phase separation in the system. From this point of view it is important to consider theoretically the thermodynamics of interactions in the ternary system: polymer A + polymer B + filler S.

In some studies [6–14] it was shown that the introduction of a third component into the binary immiscible mixture of two polymers, where the third polymer is miscible with each component of binary mixture, may lead either to full miscibility of the ternary system or to the appearance of miscibility windows. For the case of different thermodynamic interaction parameters of the third polymer with components of the immiscible mixture, the asymmetry of the phase diagrams is observed [11,12]. In addition, for the immiscible mixtures of polyolefins with polyacrylates and polymethacrylates it was discovered that a mineral filler (like silica) also may serve as compatibilizator [14]. In the latter case the compatibilizing effect of a mineral filler is supposed to be determined by the specific interaction of a filler surfaces with each component of the mixture. These problems are of a great importance for understanding the adhesion of binary polymer mixtures to solids [15]. Simple thermodynamic consideration shows that the adhesion of a binary mixture to a solid will be promoted in cases when the mixture is formed by immiscible components.

The compatibilization effect of two immiscible polymers by adding the third polymer component may be described in the framework of the Flory–Huggins theory [16] extended for describing ternary mixtures. The change in the free energy of mixing three components (per unit volume) is expressed as

$$\frac{\Delta G_{\mathrm{mix}}}{V} = RT\left[\left(\frac{\varphi_A \ln \varphi_A}{V_A} + \frac{\varphi_B \ln \varphi_B}{V_B} + \frac{\varphi_C \ln \varphi_C}{V_C}\right) + \chi_{AB}\varphi_A\varphi_B + \chi_{AC}\varphi_A\varphi_C + \chi_{BC}\varphi_B\varphi_C\right] \quad (1)$$

where V is the mixture volume, V_i is the molar volume of a component i, χ_{ij} is the interaction parameter between components i and j, that determines the sign and value of the heat of mixing and φ_i is the volume fraction of component i. For polymer mixtures the combinatorial entropy contribution may be neglected as their miscibility is driven by enthalpic force. Therefore, supposing that parameters χ_{ij} do not depend on the composition, Eq. (1) may be presented as

$$\Delta G_{\mathrm{mix}} = RTV(\chi_{AB}\varphi_A\varphi_B + \chi_{AC}\varphi_A\varphi_C + \chi_{BC}\varphi_B\varphi_C) \quad (2)$$

where the terms in brackets may be expressed through the thermodynamic interaction parameter for the ternary mixture

$$\chi_{A+B+C} \cong \chi_{AB}\varphi_A\varphi_B + \chi_{AC}\varphi_A\varphi_C + \chi_{BC}\varphi_B\varphi_C \quad (3)$$

A positive value of the parameter χ_{A+B+C} corresponds to an

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* Corresponding author.

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immiscible system whereas a negative value is indicative of miscibility.

Eq. (3) may be used for describing surface interactions an the filled system consisting of two components A and B and a filler S. In such a system three types of pair interaction exist: the adsorption interactions of each component with the surface and interaction between two polymer components.

The heats of adsorption for polymeric systems may be both negative and positive [17]. For the purpose of the present consideration we accept the change of enthalpy by adsorption of a polymer onto solid $\Delta H < 0$. If both polymeric components of the blend are strongly adsorbed onto the filler surface we may accept that the interaction parameters of a polymer A and B with the functional groups on surface S are negative (χ_{SA} and χ_{SB}). In this case, as is seen from Eq. (3), for both miscible and immiscible polymer pairs the introduction of a filler that strongly interacts with polymers A and B will decrease the value χ_{A+B+S}, i.e. enhance the thermodynamic stability of the system. If the free energy of any binary system is $\Delta G_{ij} = RT\chi_{ij}\varphi_i\varphi_j$, the free energy of the filled system may be written as

$$\begin{aligned}\Delta G_{S+A+B} &= RT(\chi_{SA}\varphi_S\varphi_A + \chi_{SB}\varphi_S\varphi_B + \chi_{AB}\varphi_A\varphi_B)\\ &= \Delta G_{SA} + \Delta G_{SB} + \Delta G_{AB} \qquad (4)\end{aligned}$$

where φ_S refers to the concentration of functional groups on the surface of a solid, these groups interacting with corresponding functional groups of the polymers. Although the heat of adsorption may be both positive and negative, we consider only the case when $\Delta H < 0$.

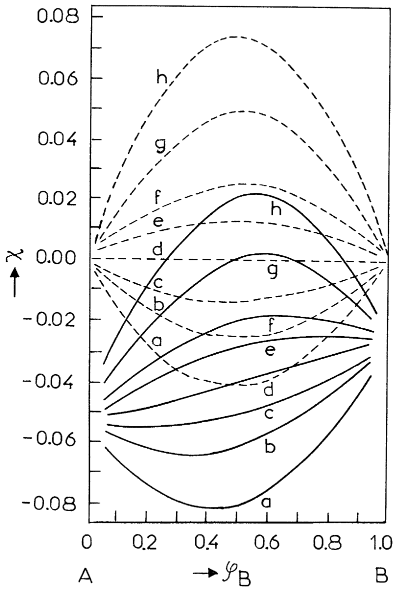

Fig. 1. Concentration dependence of the parameter of thermodynamic interaction χ for binary mixture polymer A + polymer B (χ_{AB}) (dotted lines) and for ternary system polymer A + polymer B + filler surface S (solid lines) at various χ_{AB}: (a) − 0.2; (b) − 0.1; (c) − 0.05; (d) 0; (e) + 0.05; (f) + 0.1; (g) + 0.2; (h) + 0.3. By calculations of the interaction parameter χ_{A+B+S} the following values have been used: $\chi_{SA} = -0.6$, $\chi_{SB} = -0.3$, $\varphi_S = 0.1$ (see the text).

For miscible polymer pairs ($\chi_{AB} < 0$) $-\Delta G_{S+A+B} < -\Delta G_{AB}$. If the polymer pair is immiscible ($\chi_{AB} > 0$), the sign of ΔG_{S+A+B} will depend on the value of χ_{AB}; in particular, at $|(\Delta G_{SA} + \Delta G_{SB})| < \Delta G_{AB}$, on the value of $\Delta G_{S+A+B} > 0$ and vice versa, i.e. at $|(\Delta G_{SA} + \Delta G_{SB})| > \Delta G_{AB}$, the value ΔG_{S+A+B} is negative and the blend is more stable thermodynamically.

Earlier it was shown [18,19] that the introduction of a filler surface compatible with the polymer mixture changes the position and the shape of the curve of the phase separation. This was explained by the selective adsorption of one of the mixture's components when the adsorption interaction of one component is stronger than the other [19]. As an example consider the case when $\chi_{SA} = -0.6$ and $\chi_{SB} = -0.3$ (this implies a massive favourable interaction with filler surfaces) and changing χ_{AB} from negative to positive values; from Eq. (3) the concentration dependencies of the parameter χ_{S+A+B} for the ternary mixture polymer A + polymer B + filler S have been calculated at $\varphi_S = 0.1$ (Fig. 1). It is seen that when $\chi_{AB} < 0$, parameters χ_{S+A+B} are negative and higher in magnitude compared with the binary mixture. The concentration dependence of the parameter is concave downwards to the concentration axis and is non-symmetric. If $\chi_{AB} > 0$ at any values of this parameter the concentration dependence of χ_{S+A+B} is convex and its sign depends on χ_{AB}: with increasing χ_{AB} in the region of intermediate compositions, χ_{S+A+B} becomes positive, the region of positive values broadening with increasing χ_{AB}.

It is worth noting that the difference $\chi_{S+A+B} - \chi_{AB}$ is greater for immiscible polymer pairs, i.e. for them the adsorption should be higher compared with miscible pairs in accordance with experimental data on adsorption of miscible and immiscible pairs from solution [20].

Thus, the results of theoretical analysis show that even for incompatible polymer pairs the introduction of a filler may lead either to the appearance of compatibility or, at least, to improving compatibility. That means that the filler plays the role of an active compatibilizator for binary polymer

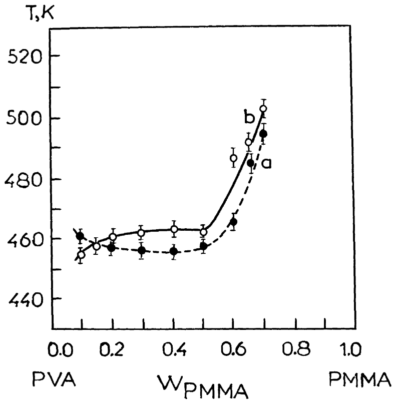

Fig. 2. Cloud point curves for the PVA/PMMA blend without filler (●) and with 10% by weight of fumed silica A-175 (○) with specific area 175 $m^2\,g^{-1}$[22]. According to ref. [23] the concentration of free hydroxyl groups for A-175 is ≈ 2.5 mmol m^{-2}.

mixtures. As is seen from Eq. (4), with increasing filler content, the compatibilizing effect is enhanced. These conclusions are in agreement with experimental data for the blends of poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVA) reinforced with fumed silica. For this system the parameter of segmental adsorption of PVA on the filler surface is almost two times greater compared with PMMA [19].Introducing fumed silica leads to increasing of the temperature of phase separation and to the change in the shape of the cloud point curve (Fig. 2). in addition, increasing the filler concentration increases the temperature of phase separation [21]. Another confirmation of the theoretical result is the diminishing the thermodynamic interaction parameter for the blend with increasing filler content [1–5]. It should be noted that all the cases considered relate to the equilibrium compatibilization [5].

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