Polymers for Advanced Technologies
Volume 8, pp. 261–264

Influence of Competition Between Binary Pairwise Interactions on the Phase Behavior in Ternary Blends

Guangxian Li* and Tang Ping
Department of Plastics Engineering, Sichuan Union University, Chengdu, Sichuan 610065, China

ABSTRACT

There are three binary pairs in a ternary blend and competition exists among these pairwise interactions owing to the asymmetry of the interaction energies between these binary pairs, which will determine the overall phase behavior of the blend. The influence of molecular weight of the components on the asymmetry of the interactions was discussed based on a ternary copolymer blend poly(styrene-co-acrylonitile)/poly(styrene-co-methylmethacrylate/poly(methyl methacrylate-co-acrylonitile) (SAN/SMMA/MAN). It has been demonstrated that the asymmetry of the interactions between different binary polymer pairs is driven not only by the difference of interaction parameters, i.e. the so-called $\Delta\chi$ effect, but also by the difference of chain length between different components in the mixture. If the two effects are coincident with each other, the asymmetry of the interactions will be intensified, promoting phase separation. On the other hand, the compatibility of the system may be improved remarkably as the two factors are in opposite directions. It implies that a miscible ternary blend may be available simply by exchanging the order of the molecular weight between the different components against the asymmetry direction caused by their corresponding interaction parameters, which is easier to do in many experimental conditions. © 1997 by John Wiley & Sons, Ltd.

Polym. Adv. Technol. **8**, 261–264 (1997)
No. of Figures: 6 No. of Tables: 0 No. of Refs: 7

KEYWORDS: asymmetry effect; competitive interactions; ternary blends; copolymer; miscibility

* Correspondence to: G. Li.

INTRODUCTION

In a binary polymer blend (designated components 1 and 2), there is only one binary interaction pair (1–2), and miscibility in the system is judged by the criterion $\chi_{12} \leqslant \chi_{12\,\text{crit}}$, where $\chi_{\text{crit}} = 0.5\ (N_1^{-0.5} + N_2^{-0.5})^2$ and N_i is the degree of polymerization of component *i*. There are three such binary pairs (1–2, 1–3 and 2–3) in a ternary polymer blend (designated 1, 2 and 3), and the interaction between any two of the components will be influenced by the third one, which has the opportunity to interact with other components as well. In fact, these pairwise interactions are competitive and the phase behavior in the mixture will depend upon the net effect of these competitive intractions. Conditions for the miscibility in a ternary blend are that at east two of these binary pairs are miscible ($\chi_{ij} \leqslant \chi_{ij\,\text{crit}}$), and that these competitive interactions should not be strong, that is, the difference of interaction energies between these binary pairs is small.

The competition of interactions between the components in the mixture was often considered to be driven by the difference of the interaction parameters between the components. Zeman and Patterson [1] were the first to demonstrate in their study of polymer solutions that the phase behavior in ternary systems was determined mainly by the asymmetry in the polymer–solvent interactions, the so-called $\Delta\chi$ effect ($\Delta\chi = \chi_{12} - \chi_{13}$), which has been illustrated for a number of systems [2–6]. However, until now, little work on the influence of the difference of molecular weights between different components on the asymmetry of the polymer–polymer interactions has been reported [7]. It is not well recognized so far that the original application of the mean-field theory to describe the $\Delta\chi$ effect is based on the precondition that the molecular weights of components are equal,

CCC 1042–7147/97/040261–04 $17.50

Received 20 March 1996
Revised 13 June 1996

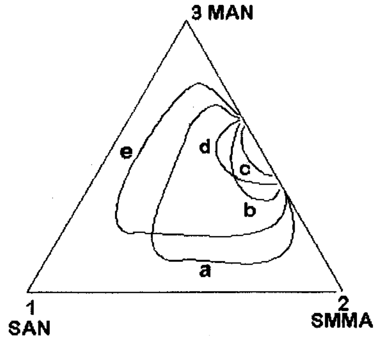

FIGURE 1. Influence $\Delta\chi$ effect on the spinodal curves: (a) SAN (s 65 vol%) $\chi_{12}=-0.0037$, $\chi_{13}=-0.0118$, $\Delta\chi=0.0081$; (b) SAN (s 70%) $\chi_{12}=-0.0117$, $\chi_{13}=-0.0156$, $\Delta\chi=0.0039$; (c) SAN (s 75 vol%) $\chi_{12}=-0.0156$, $\chi_{13}=-0.0154$, $\Delta\chi=0.0002$; (d) SAN (s 80 vol%) $\chi_{12}=-0.0154$, $\chi_{13}=-0.00110$, $\Delta\chi=0.0110$; (e) SAN (s 85 vol%) $\chi_{12}=-0.0110$, $\chi_{13}=-0.0025$, $\Delta\chi=0.0085$.

which is hard to meet in most application cases. It needs to be modified in order to reflect contributions of molecular weight difference between the components to the asymmetry of the system. The competition of the pairwise interactions in the mixture is closely related not only to the difference between interaction parameters but also to the difference of the chain lengh between the components.

THEORETICAL APPROACH

According to the Gibbs free energy of mixing and spinodal conditions of Flory–Huggins mean-field theory, the spinodal equation for a three-component mixture is as follows [3, 4]:

$$\begin{aligned}N_1\Phi_1+N_2\Phi_2+N_3\Phi_3+[N_1N_2(\chi_1+\chi_2)\Phi_1\Phi_2\\+N_2N_3(\chi_2+\chi_3)\Phi_2\Phi_3+N_1N_3(\chi_1+\chi_3)\Phi_1\Phi_3]\\+4N_1N_2N_3(\chi_1\chi_2+\chi_1\chi_3+\chi_2\chi_3)\Phi_1\Phi_2\Phi_3=0\end{aligned} \tag{1}$$

where N_i and Φ_i quantify the degree of polymerization and volume fraction of component i respectively, and χ_i is related to the binary interaction parameters by the following expression:

$$\chi_1=(\chi_{12}+\chi_{13}-\chi_{23})/2 \tag{2}$$

and the other χ_is are obtained by cyclic interchange of subcripts.

If the level of component 1 to interact with component 2 may be qualified by the difference between their critical and binary interaction parameters, i.e. $\chi'_{12}=\chi_{12\,\mathrm{crit}}-\chi_{12}$ $(\chi_{12\,\mathrm{crit}}\geqslant\chi_{12})$, then the competition of component 2 with 3 for component 1, in other words, the asymmetry in interactions between binary pair 1–2 and 1–3 can be expressed as follows:

$$\begin{aligned}\Delta\chi'&=\chi'_{12}-\chi'_{13}=(\chi_{12\,\mathrm{crit}}-\chi_{12})-(\chi_{13\,\mathrm{crit}}-\chi_{13})\\&=\chi_{12\,\mathrm{crit}}-\chi_{13\,\mathrm{crit}}+\chi_{13}-\chi_{12}\\&=\Delta\chi_{\mathrm{crit}}+\Delta\chi\end{aligned} \tag{3}$$

The two terms of $\Delta\chi_{\mathrm{crit}}$ and $\Delta\chi$ on the right side of the equation represent contributions of molecular weights and interaction parameters to the asymmetry in the interactions respectively. When all the molecular weights of the components are equal, $\Delta\chi_{\mathrm{crit}}=0$, and $\Delta\chi'=\Delta\chi$, eq. (3) becomes the original one defined by Zeman and Patterson [1]. This shows that the use of $\Delta\chi$ as a measure of asymmetry of interactions is valid only under certain special conditions. According to eq. (3), $\Delta\chi'$ is a function of both molecular weights and interaction parameters of components, so the competitive interactions in the mixture may be weakened by adjusting the $\Delta\chi_{\mathrm{crit}}$ against the $\Delta\chi$, and making a miscible ternary blend available.

The various conditions of asymmetry effect on the phase behavior are discussed in the present paper by using a ternary copolymer blend of poly(styrene-co-acrylonitrile) poly(styrene-co-methyl-methacrylate)/poly(methylmethacrylate-co-acrylonitrile (SAN/SMMA/MAN). For a binary blend composed of copolymers with a common segment, A_XB_{1-X}/C_YB_{1-Y}, where X and Y are composition volume fractions, the expression for the blend interaction parameter is as follows:

$$\chi_{\mathrm{blend}}=X^2\chi_{\mathrm{AB}}+XY(\chi_{\mathrm{AC}}-\chi_{\mathrm{AB}}-\chi_{\mathrm{BC}})+Y^2\chi_{\mathrm{BC}} \tag{4}$$

where χ_{ij} refers to the interaction parameter between segments i and j. In this article, the binary interaction parameters were estimated by the experiments to be $\chi_{\mathrm{SAN}}=0.83$, $\chi_{\mathrm{SMMA}}=0.03$ and $\chi_{\mathrm{MAN}}=0.46$ [3].

RESULTS AND DISCUSSION

In order to obtain a miscible ternary blend, the asymmetry of the interactions between the different binary polymer pairs has to be considered. Otherwise, even if all three binary pairs meet the requirement $\chi_{ij}\leqslant\chi_{\mathrm{crit}}$, phase separation may still occur in the mixture [6]. There are four types of the influence of $\Delta\chi'$ effect on the phase behavior of the blends.

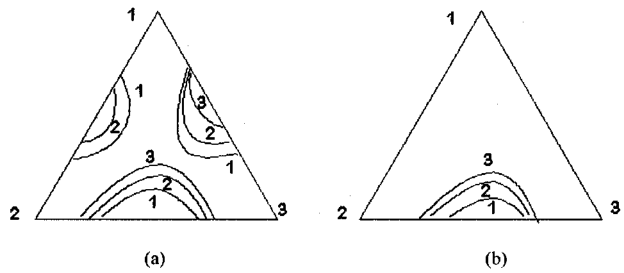

FIGURE 2. The influence of the asymmetry of molecular weights on the spinodal diagrams: $\chi_{12}=\chi_{13}=\chi_{23}=0.01$, $\Delta\chi=0$. (a) Curve 1–$N_1=N_2=N_3=250$, $\Delta\chi'=0$; curve 2–$N_1=200$, $N_2=250$, $N_3=300$, $\Delta\chi'=0.00072$; curve 3–$N_1=150$, $N_2=250$, $N_3=250$, $\Delta\chi'=0.00137$. (b) Curve 1–$N_1=150$, $N_2=200$, $N_3=250$, $\Delta\chi'=0.0011$; curve 2–$N_1=100$, $N_2=200$, $N_3=300$, $\Delta\chi'=0.0023$; curve 3–$N_1=80$, $N_2=200$, $N_3=320$, $\Delta\chi'=0.00259$. Note: when $N_1=N_2=N_3=250$, the system is miscible in the overall composition regions, spinodal disappeared.)

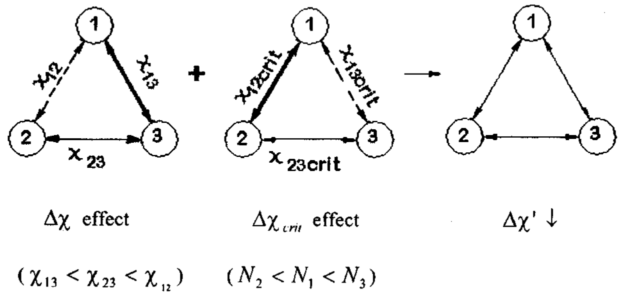

FIGURE 3. The opposite of the direction of $\Delta\chi$ and $\Delta\chi_{\text{crit}}$ causes the asymmetry to decrease ($\Delta\chi'\downarrow$): —— strong; —— moderate; ···· weak binary interactions.

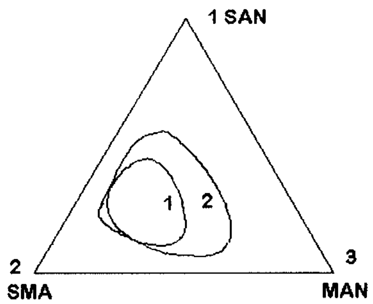

FIGURE 4. Spinodal curves for the ternary blend SAN/SMMA/MAN: χ_{12}=0.0084, χ_{13}=−0.0148, χ_{23}=0.0069. Curve 1−N_1=170, N_2=250, N_3=310, $\Delta\chi'$=0.0221; curve 2−N_1=250, N_2=170, N_3=210, $\Delta\chi'$=0.0240.

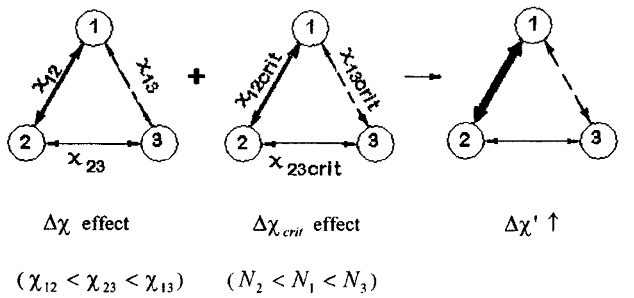

FIGURE 5. The same direction of $\Delta\chi$ and $\Delta\chi_{\text{crit}}$ causes the asymmetry to increase ($\Delta\chi'\uparrow$): —— strong; —— moderate; ···· weak binary interactions.

All the Molecular Weights of the Components in a Ternary Blend are Equal

On this condition, $\Delta\chi_{\text{crit}}=0$, and $\Delta\chi'=\Delta\chi$, it becomes the original case that the phase behavior will be determined by the asymmetry of the interaction parameters, i.e. $\Delta\chi$ effect, which is illustrated in Fig. 1 [3]. It shows that the spinodal region increases with an increase of the $\Delta\chi$ values.

All the Interaction Parameters of Components are Equal

On this condition, $\Delta\chi=0$, and $\Delta\chi'=\Delta\chi_{\text{crit}}$, the phase behavior of the blends will be controlled by the asymmetry of the molecular weights between the different components. Figure 2(a) shows that as the molecular weights of three components are equal, the spinodal regions are symmetrical (as shown in curve 1), and they will be changed as the difference between the component molecular weights increases ($\Delta\chi'\uparrow$). Figure 2(b) indicates that a miscible blend can be altered into an immiscible one and the immiscible regions will expand with an increase of the assymmetry ($\Delta\chi'$) of the molecular weights between the components.

Both the Molecular Weights and the Binary Interaction Parameters of the Three Components are Not Equal ($\Delta\chi\neq0$, $\Delta\chi_{\text{crit}}\neq0$)

This is usual in the polymer blends, and there are two cases under this condition. First, the effects of $\Delta\chi_{\text{crit}}$ and $\Delta\chi$ offset each other as shown in Fig. 3. The interactions between the 1–3 pair are stronger than that of the 1–2 pair, according to values of their interaction parameters (in $\Delta\chi$ effect). On the other hand, judged by the molecular weight asymmetry, the interactions of the 1–2 pair are more energetically favorable than that of the 1–3 pair (in the $\Delta\chi_{\text{crit}}$ term). Therefore, the combination will reduce the value of $\Delta\chi'$, improving the overall asymmetry in the system, and promote the miscibility of the blends. Figure 4 shows that the spinodal region (curve 1) becomes

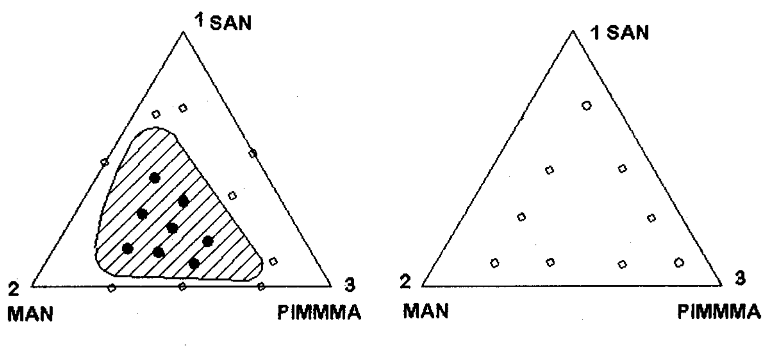

FIGURE 6. SAN/MAN/PIMMMA blend spinodal phase diagram: χ_{12}=0.00260, χ_{13}=−0.0480, χ_{23}=0.00470, $\Delta\chi$=0.0508. (a) N_1=521, N_2=310, N_3=56, $\Delta\chi'$=0.0614; (b) N_1=521, N_2=56, N_3=310, $\Delta\chi'$=0.04, spinodal collapsed. ● = Immiscible blend, ○ = miscible blend.

smaller as the direction of the asymmetry in the molecular weights is changed (reordering N_1, N_2 and N_3 as 170, 250 and 210), which causes $\Delta\chi'$ to decrease.

Second, the effects of $\Delta\chi_{crit}$ and $\Delta\chi$ are coincident with each other as shown in Fig. 5. Since both the interaction parameters and the molecular weights are favorable to the interactions between the 1–2 pair and unfavorable for that of the 1–3 pair, the combination will intensify the overall asymmetry in the system, thereby promoting phase separation. The spinodal regions expand accordingly as shown in Fig. 4 (curve 2).

The above analysis and calculation with the experimental data suggest that the miscibility in ternary polymer blends can be controlled not only by changing the interaction parameters and their asymmetry, but also by simply adjusting the molecular weights of the components and their asymmetry against the asymmetry of the corresponding interaction parameters. The latter is easier to do in many applications. The above phenomena have been observed experimentally in ternary polymer blend of SAN/MAN/PIMMMA [poly(*N*-phenylitaconimide-methylmethacrylate] [6] as shown in Fig. 6, and further work using other ternary blends is being undertaken in the laboratory.

The Molecular Weights of the Components and the Binary Interaction Parameters of the Components are Equal

For this condition, $\Delta\chi_{crit}=0$, $\Delta\chi=0$, then $\Delta\chi'=0$ and it becomes a completely symmetrical system. A study on this will be reported later.

Acknowledgment

Financial support from the National Natural Science Foundation of China is gratefully acknowledged.

REFERENCES

1. L. Zeman and D. Patterson, *Macromolecules, 5,* 513 (1972).
2. G. ten Brinke, G. Karasz, F. E. Karasz and W. J. Macknight, *Macromolecules, 16,* 1827 (1983).
3. J. M. G. Cowie, G. Li, R. Ferguson and I. J. McEwen, *J. Polym. Sci. B: Polym. Phys., 30* 1351 (1992).
4. A. C. Su and J. R. Fried, *Polym. Eng. Sci., 27,* 1657 (1987).
5. H. Zhang, D. E. Bhagwagar, M. M. Coleman, P. C. Painter and J. F. Graf, *Polymer, 35(25),* 5379 (1994).
6. G. R. Brannock and D. R. Paul, *Macromolecules, 23,* 5240 (1990).
7. J. M. G. Cowie, G. Li and I. J. McEwen, *Polymer, 35(25),* 5517 (1994).