

SOME ASPECTS OF MORPHOLOGIES AND INTERFACES IN COPOLYMER / HOMOPOLYMER BLENDS*

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ABSTRACT

Based on a series of morphological studies of blends of homopolymer (Homo) and a variety of block and graft copolymers (Cop), the nature of phase separation, interface, emulsification and inner morphology of copolymer-dispersed phase etc. in the blends are discussed. In the cases of Cop AB/Homo A/Homo B systems, in which one homopolymer forms matrix, it is observed that the dispersed homopolymer phase is exclusively associated with Cop AB, i.e. no Homo A-Homo B interface exists. This phenomenon is believed to be caused by minimizing the interfacial energy of the systems. Meanwhile, preferential solubilization or anchoring of the like chains of copolymer into homopolymer matrix leads to stabilization of the dispersed phase in the matrix. In addition, regular variation of the inner morphology of the dispersed copolymer phase with the composition and molecular parameters of the component polymers is observed. When the two components have comparable proportions, alternating concentric shells are the most common feature which is associated with minimizing the interfacial energy in the Cop/Homo systems.

INTRODUCTION

The "microphases" produced in the process of phase separation in block copolymers are not the true phases defined by Gibbs^[1]. Since there is a chemical connection between the two unlike block chains located in the two phases respectively, the phases can not be separated mechanically and the size of each phase is determined by the length and conformations of the chains. These peculiarities, which are very interesting in theoretical considerations and the related properties of the thermoplastic elastomers made of block copolymers, have made the study of the phase separation in block copolymers a very popular and fruitful subject during the past twenty years. Achievements in this field have in turn promoted research of phase separation in polymer blends comprising a copolymer and corresponding homopolymers (Cop/Homo). An important characteristic of this kind of blends is the conditional miscibility between chains of one type block of copolymer, say A, which are called bound A, and chains of homopolymer A, which are called free A, although they are identical in chemistry and therefore, at first glance, are expected to be solubilized each other without limitation. It has been known that the entropy loss of chain conformation in mixing of the free and bound chains is responsible for the limited solubilization. Because of the presence of microphase separation, limited miscibility between copolymer and the related homopolymers and the non-equilibrium nature of the blends, the morphologies of copolymer/homopolymer blends are usually very diverse and complicated.

As far as the formation of complicated morphologies in Cop/Homo blends is concerned, the

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explanation presented by Eastmond et al.^[2,3] is significant. Based on a series of morphological research of the blends comprising A_2BA_2 -type copolymers (ABCPs), they pointed out that the complicated morphologies were caused by macrophase separation between the homopolymer and copolymer and microphase separation in the copolymer. Although this conclusion was drawn based on ABCP/Homo systems, it is generally true for Cop/Homo blends comprising different kinds of copolymers. In interpreting the formation of stable disperse copolymer-rich phase in homopolymer matrix, differing from Eastmond, Riess et al.^[4] emphasized the role of emulsification of high-molecular-weight copolymer to the dispersed particles of low-molecular-weight copolymer. In addition, Argon, Cohen et al.^[5-7] recently presented some morphological results associated with the study on crazing in Cop/Homo systems. In recent years, by studying Cop/Homo blends including a variety of copolymers, i.e. simple graft copolymer^[8], multi-branch graft copolymer^[9], ABCP^[10], diblock, triblock and four-arm block copolymers^[11], Jiang et al. presented a series of morphological data of Cop/Homo systems and put forward that the chain architecture of a copolymer has a substantial effect on its miscibility with homopolymers^[12]. Based on the results mentioned above and especially some of our unpublished data, in this paper, the morphological features of Cop/Homo systems including interfacial behaviour, emulsification and the internal morphology of the dispersed copolymer phase will be discussed.

EXPERIMENTAL

The following copolymer samples are involved in the discussion of this paper: Graft copolymer (PB-g-PS) with polybutadiene (PB) backbone and polystyrene (PS) branches^[8], A_2BA_2 type copolymer having polycarbonate as A chain and PS as B chain (ABCP)^[10]; multibranch graft copolymer (PI-g-PS) with polyisoprene (PI) backbone and PS branches^[9]; diblock, triblock and four-arm star-type block copolymers of styrene and isoprene (PI-b-PS)^[11]. The preparation, purification and characterization of the samples were described in the corresponding cited papers. The procedures for making the Cop/Homo blends and observation of the blend morphologies with an electronic microscope were mentioned in these papers as well.

RESULTS AND DISCUSSION

Interfaces in Cop/Homo Blends

Generally speaking, in a ternary blend comprising copolymer AB, homopolymer A and B, three types of interfaces, i.e. Cop-Homo A, Cop-Homo B and Homo A-Homo B may exist besides that associated with microphase separation. The morphological results of two kinds of ternary blends studied in our laboratory have been reported, i.e. the blends of multibranch graft copolymer PI-g-PS with Homo PS and PI^[9]; diblock or triblock or four-arm block copolymers of PI and PS and the homopolymers^[11]. In all the cases, the Homo PS is the major component (77 wt %) with very high molecular weight forming matrix and the weight ratio of the copolymer to PI is about 3 to 1. We have noticed that in all the blends showing macrophase separation between the copolymer and homopolymers, PI and PS, only two types of interfaces i.e. Cop-Homo A and Cop-Homo B were found. A typical result is shown in Fig. 1. Since the sample film for this study was stained by OsO_4 followed by microtoming, OsO_4 was not able to penetrate into the center part of the PI particules during the limited staining period and then Homo PI regions only show black outer shells. A remarkable feature of these blends is that PI phase is always associated with and surrounded by the

copolymer phase having distinct microphase separation. In all the micrographs we obtained for the two kinds of blends, there is no exception to this phenomenon. In addition, from the micrographs reported by Gebizlioglu et al.¹⁷⁾ for the blends of multi-arm PI-b-PS and homopolymers of PI and PS, the same feature could be found. Obviously, the repulsive interaction between PI and PS segments makes the interface between PI and PS possess high interfacial energy. Therefore, replacement of this interface by PI-Cop would apparently decrease the energy. This is the driving force for PI phase to be separated from Homo PS phase and to accompany the copolymer phase. Under usual conditions for the blend preparation, this driving force might be sufficient to overcome the energy barrier of molecular transport for realizing segregation and proximity of PI to the copolymer phase.



Fig. 1 Electron micrograph of blend PI-g-PS/PI/HPS (weight composition 17/6/77), molecular weight (kg/mol): PI and PS blocks in the copolymer 53.9 and 52.4; PI 6.5 and HPS 457

It is widely accepted that in ternary blends of homopolymers A and B and a small proportion of copolymer AB, block chains of the copolymer preferentially extend and mix into the corresponding homopolymer regions. This is the basis for compatibilization of copolymer AB for blends of homopolymers A and B. However, since block chains and the same-type of homopolymer chains are indistinguishable by transmission electronic microscopy, this argument has not been confirmed by TEM observation. It is interesting that in our recent study of the morphologies of Cop/Homo A/Homo B ternary blends, in which suitable compositions were adapted so that PI and PS phases were completely separated by the copolymer phase, the morphological observations provided evidence for the preferential solubilization of a block in the same type homopolymer region. We noticed that within the dispersed phase in high-molecular-weight PS matrix as shown in Fig.2, PI phase is surrounded by a bright ring (denoted by the arrow) which is obviously a shell composed of PS chains. Since Homo PS chains are not able to penetrate to the central part of the dispersed particles, this bright shell must be composed of the PS blocks of the copolymer. This implies that the PI chains connected with those PS blocks enriched around the PI domains are located in the outer-shell area of the PI phase. Obviously, this spatial arrangement of the block chains is favourable

for minimizing the number of the unlike contact pairs and interfacial energy. This kind of PS bright ring surrounding PI phase immersed in the copolymer phase can be extensively observed in the ternary blends we studied. In addition, in some of the micrographs reported by Argon, Cohen et al. such as Fig. 28 of ref. [5], while a bright ring surrounding the PB phase could be clearly seen, the microphase morphology of the copolymer near the interfacial area was found to be altered forming a few lamellar layers from the intrinsic wavy-rod microdomains for minimizing the interfacial energy.



Fig. 2 Morphology of the dispersed phase of blend PI-g-PS/PI/HPS (weight composition 17/6/77) at higher magnification.

Molecular weight (kg/mol): PI and PS blocks in the copolymer 53.9 and 30.1; PI 6.5, HPS 457

Although the experimental results just mentioned presented a proof for the phenomenon of preferential mixing of block chains with the same type of homopolymer chains i.e., so-called anchoring of block chains, EM observations are not able to provide detail information about the chain conformation and segment distribution of the free and bound chains around the interfacial area. In studying the miscibility of a homopolymer in the domains of the same type copolymer blocks, based on the experimental results, a gradient-density model^[13] was proposed i.e., maintaining a constant total reduced density of the segments in the whole domains solubilized with homopolymer chains, the blocks form a distribution of segment density decreasing from the phase boundary to the center of the domains while the segment density of homopolymer decreases from the center to the boundary. Using this model, for the case of block copolymer with lamellar structure, statistical expectation gives that miscibility between copolymer and homopolymer is generally in better agreement with experimental results in literature than Meier's theory^[14], in which homogeneous segment density of both homo and block chains in the block domains with solubilized homopolymers was assumed. Recently, using this gradient density model to the case of block copolymer with spherical morphology, we succeeded in expecting its miscibility with homopolymer^[15]. This advance made us believe that in incompatible Cop/Homo systems, in the interfacial area between the copolymer and homopolymer, both bound and free chains may assume a gradient density distribution rather than homogeneous one for minimizing the conformation entropy loss.

Emulsification

In exploring the nature of morphologies in Cop/Homo systems, Riess et al.^[4] emphasized the role of emulsification of high-molecular-weight block copolymer. They studied ternary blends of homo PS and two PI-*b*-PS block copolymers with different molecular weights. The common feature of the blends they found was dispersion of copolymer particles having the structure of alternating concentric shells in PS matrix. Since the average size of the dispersed particles decreased with the ratio of the amount of high-molecular-weight block copolymer (E) to that of low-molecular-weight copolymer (D), Riess et al. suggested that Cop E played the role of an emulsifier for the dispersed particles composed of Cop D. However, in our recent work on the Cop/Homo blends which deals with a variety of copolymers^[8-11], stable dispersion of copolymer phase in the size of the order of micrometer with internal structures was a common feature for the immiscible blends. Usually, the dispersion is very stable and no segregation of the dispersed particles was observed under the ordinary conditions of solvent evaporation for making the blends. Eastmond et al.^[2-3] reported that segregation of the dispersed phase of copolymer-rich phase in homopolymer matrix forming two macroscopic layers could only be observed when the mixture was sealed and allowed to stand for a few weeks after phase separation occurred under the ordinary conditions of solvent casting. Therefore, it seems that the presence of high-molecular-weight copolymer is not necessary for the formation and stabilization dispersion of copolymer in homopolymer matrix. In fact, as we discussed above, in the interfaces between copolymer particles and homopolymer matrix, the block chains of the same type as the homopolymer would extend and anchor to the homopolymer phase. Therefore, it is that these block chains located at the most outer part of the particles emulsify and stabilize the dispersed phase (Fig.3).

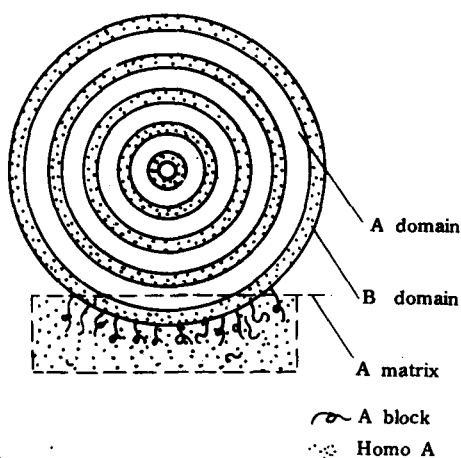


Fig. 3 A schematic representation of dispersed copolymer phase with alternating concentric layer structure and its stabilization by anchoring of the like chains into homopolymer matrix

Recently, according to the results of SAXS studies, Hadziioannou et al.^[16] reported that in blends of two block copolymers with similar composition and microstructure but different molecular weights, like blocks from the two copolymers were solubilized each other and formed their common domains. On the other hand, Jiang et al.^[17] found that two block copolymers having similar chemical composition did not solubilize with each other when their molecular weights were considerably different. These results are helpful for making proper explanation for the main

morphological facts presented by Riess et al., i.e., in the blends of two block copolymers (E and D) with one homopolymer, the dispersed phase with the internal structure of concentric shells is probably constituted by the miscible two copolymers with microphase separation. Another experimental result presented by Riess et al. that the size of the dispersed phase decreases with increasing the ratio of the amount of E to D also seems understandable without assuming emulsification—Cop/Homo compatibility generally increases with the average molecular weight of the copolymer, therefore, increasing the value of E/D will lead to finer and more stable dispersion. Contrast with other ternary blends studied by Riess et al. showing only one type of dispersed phase, Fig. 11 in ref. [4] clearly presents two different morphologies of the dispersed phase i.e. spherical microdomains of PI blocks and macrodomains with internal concentric-shell structure of block copolymer. Riess et al. concluded that this special feature is caused by “incomplete emulsification” of Cop E to Cop D. We notice that since the microstructures of the two block copolymers in the blends are quite different, i.e., 1,4-unit contents are 55% in Cop E while more than 90% in Cop D and the difference in the molecular weights of Cop D and E is considerable, the two block copolymers are expected to be immiscible. Therefore, in the blend, Cop E, which has higher molecular weight of PS block, would be solubilized with the homopolymer showing only discrete PI microdomains in the matrix while Cop D would be separated from the matrix forming macroscopic copolymer-rich phase. Clearly, this explanation for the nature of the morphology shown in Fig. 11 of ref. [4] does not support the argument about emulsification^[4].

Internal morphologies of dispersed copolymer phase

In most of Cop/Homo blends studied by Eastmond et al.^[2,3] Riess et al.^[4], Argon and Cohen et al.^[5-7], copolymers were minor components and formed the dispersed phase with internal microphase separation. A great number of data reported show that the copolymer can keep its

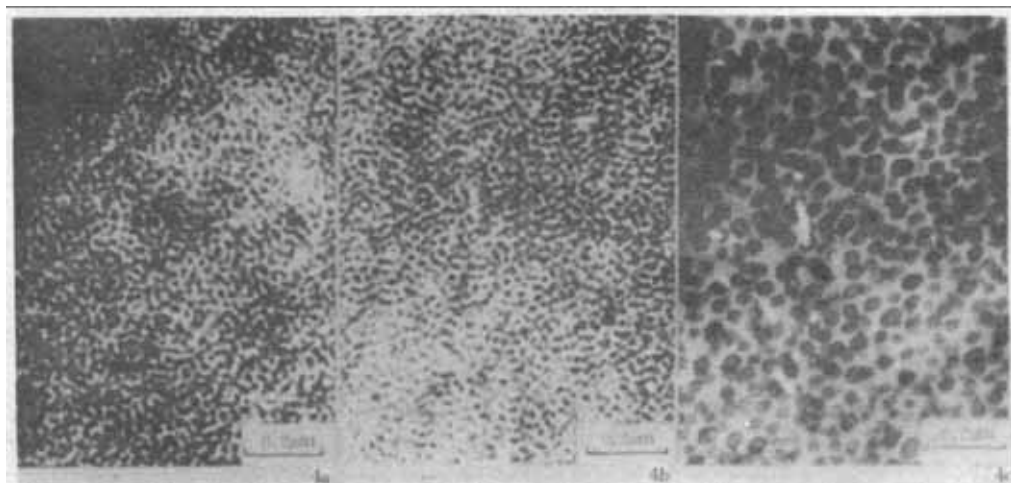


Fig. 4a Morphology of copolymer phase in blend of PI-g-PS/HPS (weight composition 23/77), molecular weights (kg/Mol): PI 53.9, PS 30.1 and HPS 457

Fig. 4b Morphology of copolymer phase in blend of PI-g-PS/PI/HPS (weight composition 17/6/77), Molecular weights (kg/Mol): PI and PS blocks 53.9 and 30.1, PI 53.9, HPS 457

Fig. 4c Morphology of copolymer phase in blend of PI-g-PS/PI/HPS (weight composition 17/6/77), molecular weights (kg/Mol): PI and PS blocks 53.9 and 30.1, PI 6.5, HPS 457

intrinsic morphology in the dispersed phase when the copolymer is not solubilized with the homopolymer. In the blends comprising multibranch copolymer of PI-g-PS and high molecular weight PS (HPS) we studied, the characteristic spherical morphology of the copolymer was kept in the copolymer dispersed phase (Fig.4a). This intrinsic morphology maintains in ternary blend of Cop/HPS/PI, in which the molecular weight of PI is high enough so insoluble with PI microdomains (Fig.4b). When PI with much lower molecular weight is added, the characteristic morphology still keeps in the dispersed phase but with apparent size increment of PI microdomains (Fig.4C). It seems interesting to compare this result with that reported by Gebizlioglu et al.^[7] dealing with multi-arm Cop/PS/PI blends. Since the molecular weight of PI in the latter case is very low (3000), it was expected to be greatly solubilized with PI blocks in the copolymer. Gebizlioglu et al. observed the variation of the characteristic morphology of the copolymer-dispersed phase with the weight ratio of PI to the copolymer, i.e., wavy-rod structure changed to a feature with coexistence of wavy rod and concentric shell first and then to the pure concentric shell structure as more PI homopolymer was added.

The alternating concentric shell morphology is very common in dispersed copolymer-rich phase in immiscible Cop/Homo systems. It is generally accepted that a copolymer having characteristic lamellar morphology may form concentric shell structure in its spherical dispersed copolymer phase. With regard to the transition from the planar lamellar structure to concentric shell structure, in our opinion, minimizing the interfacial energy is probably still the driving force for the process. For a Cop/Homo system with a certain volume fraction of the copolymer-dispersed phase, obviously, spherical morphology gives minimum interfacial area and the interfacial energy will depend on the chemical composition in the interfacial region. Apparently, the dispersed phase of the copolymer AB will present the minimum interfacial energy with homopolymer matrix A if the most outer shell of the phase is totally composed of A blocks. Now that block A forms the most outer shell, block B is expected to form the most but one shell. Continuation of this process leads to the formation of alternating concentric layer morphology which occurs mostly when the two blocks of a copolymer have comparable proportions. This process may not proceed fully during solvent-casting resulting in a particular morphology having only a few well-developed alternating layers near the interface area but irregular microdomain structure in the inner part of the dispersed copolymer phase^[18].

CONCLUSIONS

1. In the solvent-casting Cop AB/Homo A/Homo B blends, copolymer phase always accompanies homopolymer phases, so in general, only two types of interfaces i.e. Cop-Homo A and Cop-Homo B could be found. This is realized by meeting the demand of minimizing the interfacial energy of the blend systems.
2. In immiscible Cop-Homo systems with Cop as a minor component, preferential mixing of the like chains of the copolymer with the homopolymer in the matrix leads to stable dispersion of the copolymer phase. The presence of copolymer with higher molecular weight as an emulsifier of the system is not necessary.
3. In Cop AB/Homo A/Homo B ternary blends, copolymer in the dispersed phase may keep its characteristic morphology if it is completely immiscible with the homopolymers. However, a regular variation of the morphology of the dispersed copolymer phase with the amount the homopolymer

added could be observed if the homopolymer is partially solubilized in the corresponding domains of the copolymer. In the case of the dispersed phase having comparable amounts of the two components, the alternating concentric shell structure is a very common feature which is associated with the demand of minimizing the total interfacial energy of the systems.

Keywords:

Polymer blends; Morphology; Interface; Emulsification

REFERENCES

- [1] The Collected Works of J. Willard Gibbs, Vol 1, Longmans, 1928.
- [2] Eastmond, G. and Phillips, D., *Polymer* **1979**, *20*, 1501.
- [3] Eastmond, G. and Phillips, D., "Polymer Alloys" (Eds. D. Klempner and K. Krisch) Plenum Press, New York (1977) p. 141.
- [4] Riess, G.; Schliengen, M. and Marti, S., *J. Macromol. Sci. -Phys.* **1984**, *17*, 355.
- [5] Argon, A.; Cohen, R.; Gebizlioglu, O. and Schwier, C., *Adv. Polym. Sci.*, **1983**, *52/53*, 275.
- [6] Gebizlioglu, O.; Argon, A. and Cohen, R., *Polymer*, **1985**, *26*, 519.
- [7] Gebizlioglu, O.; Argon, A. and Cohen, R., *Polymer* **1985**, *26*, 529.
- [8] Jiang, M.; Huang, X. and Yu, T., *Polymer*, **1983**, *24*, 1257.
- [9] Jiang, M.; Cao, X. and Yu, T., *Polymer*, **1986**, *27*, 1917.
- [10] Jiang, M.; Huang, X. and Yu, T., *Polymer*, **1985**, *26*, 1186.
- [11] Jiang, M.; Cao, X. and Yu, T., *Polymer*, **1986**, *27*, 1923.
- [12] 江 明, 高分子材料科学与工程 (*Polym. Material Sci. Eng*) **1987**, *3*, (2) 7.
- [13] Xie, H.; Liu, Y.; Jiang, M. and Yu, T., *Polymer* **1986**, *27*, 1928.
- [14] Meier, D., *Polym. Preprints*, **1977**, *18*(1), 340.
- [15] Xie, H.; Liu, Y.; Jiang, M. and Yu, T., *Makromol. Chem. Rapid Commun.* **1988**, *9*, 79.
- [16] Hadzioannou, G. and Skoulios, A., *Macromolecules* **1982**, *15*, 267.
- [17] Jiang, M.; Xie, J. and Yu, T., *Polymer* **1983**, *23*, 1557.
- [18] Phillips, D., Ph.D. Thesis, Liverpool University **1978**.