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Morphology Development through an Interfacial Reaction in Ternary Immiscible Polymer Blends

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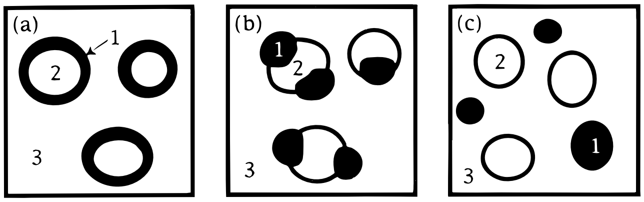
ABSTRACT: We studied the morphology development of ternary immiscible blends through an interfacial reaction between components. This phenomenon was observed in two ternary blend systems; one is composed of polyamide(6) (PA6), polycarbonate (PC), and poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] (SEBS), and the other is composed of PA6, PC, and polystyrene (PS), where PA6 forms the continuous matrix in both blend systems. Maleinated SEBS (SEBS-gMA) or maleinated PS (PS-gMA) is incorporated with its unmodified polymer (un-SEBS and un-PS, respectively) at various ratios into the blends of PA6/PC. The blends of PA6/PC/un-SEBS and PA6/PC/un-PS show a similar phase formation in which the two dispersed polymers are stuck together in a PA6 matrix. The use of the maleinated polymers instead of their unmodified polymers in the blends of PA6/PC changes the phase formation drastically. The maleinated polymers react with amine end groups of PA6 at the interface during the melt mixing. Through this interfacial reaction, the domains of the maleinated polymers are dispersed in the PA6 matrix at about 100 nm in diameter, and at the same time the maleinated polymers encapsulate the PC domains. This means that the interfacial reaction induces the change of the formation of the domains composed of two dispersed phases. That is, the interfacial reaction changes the formation from “stack formation”, where the two dispersed polymers are stuck together, to “capsule formation”, where the PC domains are encapsulated by the other phase. Moreover, when both the unmodified and its maleinated polymers are incorporated together in a variety of ratios, the encapsulation by SEBS onto the PC domains gradually becomes incomplete as the ratio of the unmodified SEBS increases, whereas the encapsulation by PS of the PC is complete even when un-PS and PS-gMA are incorporated together. We discuss this morphology development in terms of the change of interfacial tensions between PA6 and maleinated polymers through the interfacial reaction. We assumed that the reduction of interfacial tension through the interfacial reaction is the driving force for this morphology development.

Introduction

Polymer alloys and blends constitute over 30 wt % of polymer consumption with an annual growth rate of about 9% that has remained constant for last 10 years and is four times the growth rate of the total plastic industry.[1] Their role will continue to increase. The great majority of useful blends are immiscible, and their outstanding performance stems from their multiphase morphologies. Hence, the control and the prediction of morphologies are of great importance for the optimization of desired properties. In binary immiscible blends, it is experimentally established and commonly recognized that the size and distribution of the dispersed particles are the result of a competitive process between breakup and coalescence.[2,3] Interfacial tension, the shear rate of mixing, and the viscosity ratio of the blend components are key parameters governing the degree of dispersion. In ternary immiscible blends where two minor phases are dispersed in a continuous matrix, not only the dispersed particle sizes but also the formation of the two dispersed phases in the matrix are important factors affecting their performance. For a ternary blend system consisting of polymers **1**, **2**, and **3**, where polymer **3** is the continuous matrix, three phase formations are expected as shown schematically in Figure 1: (a) “capsule formation” of **2** encapsulated by **1**, (b) “stack formation” of **1** and **2** stuck together, and (c) “isolated formation” of **1** and **2** dispersed separately. It has been known that the morphology development of nonreactive ternary immiscible blends are mostly governed by the balance of interfacial tensions between each component.[4]



'Capsuel formation' 'Stack formation' 'Isolated formation'

Figure 1. Schematic description of phase formations to appear in ternary immiscible polymer blends composed of **1**, **2**, and **3**: (a) “capsule formation” of **2** encapsulated by **1**; (b) “stack formation” of **1** and **2** stuck together; (c) “isolated formation” of **1** and **2** dispersed separately.

Introducing the chemical reaction between components during melt blending is an effective path for the modification of blend morphologies. This reactive processing improves the interfacial adhesion and then improves the mechanical properties of blends through chemical coupling of the phases and the reduction of the particle size. The effect of this process has been demonstrated in terms of the improvement of impact strength[5,6] and in terms of *in situ* compatibilization.[7,8] Previously, we reported the compatibilizing effect of a triblock copolymer of poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] functionalized with maleic anhydride onto the poly(ethylene-*co*-butylene) mid block (SEBS-gMA) in blends of polyamide(6) (PA6) and polycarbonate (PC).[9,10] We found that the *in situ* chemical reaction at the interface between PA6 and SEBS-gMA induces the

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change of the phase formation of the blends where PA6 forms the continuous phase.[9] The PA6/PC blends with unmodified SEBS (un-SEBS) exhibited the "stack formation" where un-SEBS and PC are stuck together as illustrated in Figure 1b, while the blends with SEBS-gMA show the "capsule formation" of SEBS onto the PC domains as illustrated in Figure 1a. This indicates that the interfacial reaction between the PA6 matrix and SEBS induces the change of the formation of the domains composed by SEBS and PC. Through this phase formation, SEBS works as a compatibilizer to improve the interfacial adhesion between PA6 and PC, and then, the remarkable improvement of mechanical properties can be achieved.[10]

Although many works are related to the reaction-induced morphology development, the previous works studied the phenomena where the resulting heterogeneous structures are achieved through a polymerization of components in an initially miscible mixture. High-impact polystyrene (HIPS) and acrylonitrile–butadiene–styrene (ABS) are well-known polymer alloys obtained through a polymerization of styrene monomers and through a copolymerization of styrene and acrylonitrile monomers, respectively, in the presence of polybutadiene rubber.[11] So too the blends of thermoset/thermoplastic[12] and of thermoset/rubber[13] exhibited a reaction-induced phase separation through the curing of thermoset resins. Those phase separation schemes are interpreted on the basis of the spinodal decomposition, which is induced by the molecular weight increase of thermoset resins in the curing process. Basic studies regarding the dynamics of the phase separation process induced by the polymerization of a system have also been carried out.[14] The morphology development found in the PA6/PC/SEBS blend system is, however, different from the above cases. That is, the blend system is inhomogeneous in the initial state and the local reaction at an interface triggers the morphological change.

In this paper, we investigate in detail the interfacial situation of SEBS contacting the PA6 phase and the PC phase using transmission electron microscopy (TEM). In addition, polystyrene (PS) is incorporated into the PA6/PC blends as an alternative for SEBS, and morphology development by the interfacial reaction between PA6 and a maleinated PS (PS-gMA) is demonstrated. The interfacial situation between PA6 and PS-gMA is different from that between PA6 and SEBS-gMA due to the different reaction sites for SEBS-gMA and PS-gMA. Comparing the results obtained from the both blend systems, we discuss the mechanism of this morphology development precisely.

Experimental Section

Materials. All of the materials except for the polystyrene functionalized with maleic anhydride (MA) were supplied from commercial sources. PA6 is a hydrolytic poly(ϵ-caprolactam) for which the product name is A1030BRF. It was supplied by Unichika Co., Ltd., with an number average molecular weight of 22 500 and melting flow rate of 4.3. The concentration of the amine end group was determined at 5.0×10^{-5} mol/g by the titration. Bisphenol-A polycarbonate (PC) was supplied by Teijin Chemical Co. Ltd. for which the product name is Panlite L-1250Y. SEBS has polystyrene end blocks and a hydrogenated butadiene midblock resembling an ethylene–butylene copolymer. The SEBS functionalized with 2 wt % MA onto the hydrocarbon chains, which is designated SEBS-gMA, is Kraton 1901 supplied by Shell. The molecular weight is 85 000 and the styrene content is 29 wt %. Unmodified SEBS (un-SEBS) is Kraton 1652 of which the molecular weight and styrene content are the same as those for Kraton 1901. Polystyrene (PS) was obtained from Wako Chemical Co., Ltd., and the number-average molecular weight is 170 000.

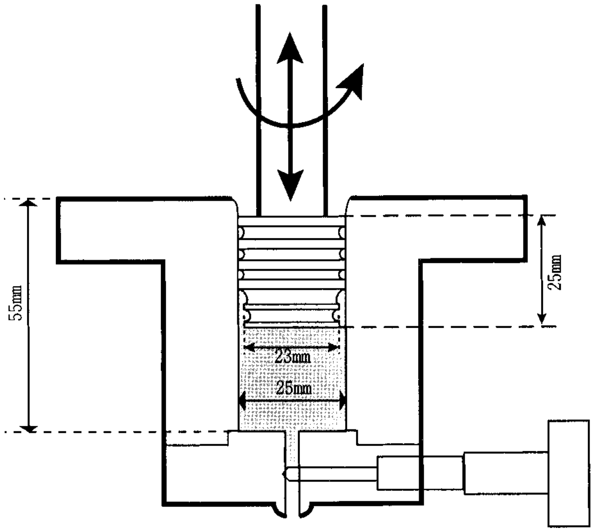

Figure 2. Schematic illustration of the miniature mixer used in this study.

The Functionalization of PS with Maleic Anhydride. The functionalization with MA onto the α-carbon of polystyrene main chain was carried out according to the method reported by Okawara *et al.*[15] A 2.0 g sample of polystyrene containing 0.019 mol of styrene units and 0.02 mol of MA (2.0 g) were dissolved in 60 mL of benzene. After complete dissolution, 0.02 mol of benzoyl peroxide (BPO) dissolved in 10 mL of benzene was added into the solution, and the solution was refluxed at 80 °C for 8 h under a nitrogen atmosphere. The reaction mixture was poured out into 1 L of methanol to extract the unreacted MA and BPO. The precipitate was collected and dried *in vacuo* at 60 °C. Then the polymer was purified by precipitation from methylene chloride solution into methanol. The concentration of MA grafted onto PS was determined to be 1.7 wt % by a titration with a 0.1 N toluene/methanol (1:1) solution of sodium methoxide.

Blending Procedure. All of the polymers were dried at 80 °C for at least 12 h in a vacuum oven to remove sorbed water before processing. The blend samples were prepared using the miniature mixer developed in our laboratory.[9] Figure 2 shows the illustration of the rotor and the chamber of this mixer. Miniature mixers have been frequently used for the blending of polymers available in limited quantities to simulate industrial blending. Sundararaji et al. reported that the morphology development in the miniature mixer was quantitatively similar to that for the industrial extruders.[16] We specially designed the rotor to create an extentional flow in a melt to obtain homogeneous morphologies. All of the ingredients, of which the total amount was 10 g, were fed into the mixing chamber and were mixed at 260 °C for 10 min at a rotation speed of 80 rpm. The diameter of the rotor is 23 mm, and the maximum shear rate is 48 s^{-1}. The torque level during the mixing reaches a steady state within 5 min; hence, mixing for 10 min should be enough to achieve an equilibrated morphology. Then the rotor was lowered and the mixed sample was pushed out into the preheated mold to obtain a sheet 3 mm in thickness.

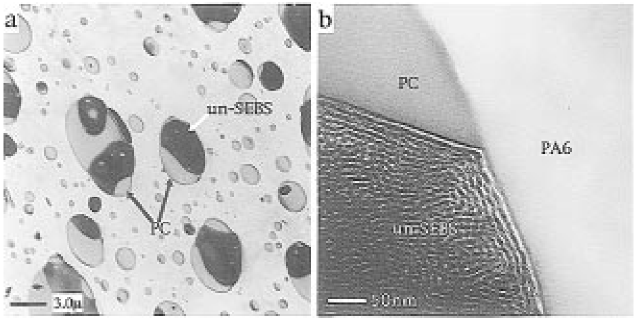

Figure 3. (a) TEM photograph showing the phase formation appearing in the PA6/PC/un-SEBS 68/23/9 blend. (b) A higher magnification view of part a focusing on the interfacial situation of SEBS contacting PA6 and PC. The PS blocks in SEBS are mostly stained with RuO_4 and appear dark.

Transmission Electron Microscopy. Morphological studies were carried out by transmission electron microscopy (TEM). Specimens for TEM observation were prepared by cryomicrotoming of the molded samples at −110 °C using a diamond knife. The cutting direction was perpendicular to the flow direction of the molded sheets. Afterward the specimens were exposed to the vapor of ruthenium tetraoxide (RuO_4) for 10 min. A Zeiss CEM 902, equipped with an electron energy filter to perform energy-filtering transmission electron microscopy (EFTEM), was used at an accelerating voltage of 80 kV. Zero-loss filtered ($\Delta E = 0$ eV) images were recorded on the imaging plate (IP) system, FDL5000, Fuji Photofilm Film Co., Ltd., and processing of the obtained images to achieve optimized contrast was carried out with the IP-processor of this system. A detailed description of this microscope[17,18] and the application of EFTEM to polymeric materials[9,19,20] appeared elsewhere.

The Concept of Neumann's Triangle. We introduced the concept of Neumann's triangle[21] to discuss the interfacial tension balance in ternary polymer blends. Small pieces of a polymer (0.5 mm × 0.5 mm) were sandwiched between two other polymer films and were annealed at 260 °C for 10 min in a hot stage, Limkam TH-600RH, under a nitrogen atmosphere. Afterward the cross sections of the sandwiched films were observed under a microscope to evaluate the shape and the location of the sandwiched pieces between the two polymers.

Results and Discussion

Interfacial Situation of SEBS in the Blend of PA6/PC. Figure 3a is a TEM photograph showing the phase formation of the PA6/PC/un-SEBS 68/23/9 blend. SEBS is a microphase-separated thermoplastic elastomer where the PS blocks at the both ends are associated in rigid domains that form a lattice in the flexible poly(ethylene-*co*-butylene) (PEB) matrix.[22] Having this microdomain structure, SEBS can be identified in this blend system by the use of RuO_4 as a staining agent for PS domains.[9] The dispersed domains in this blend are composed of PC and SEBS stuck together in the PA6 matrix. Figure 3b is the higher magnification view focused on the interfaces between PA6 and SEBS and between PC and SEBS. This reveals that at both interfaces the PS layers of SEBS cover both polymers. This means that both PA6 and PC have better compatibility with PS blocks than with PEB blocks in SEBS.

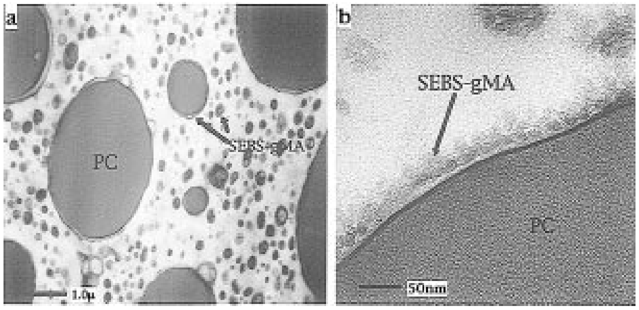

Figure 4. (a) TEM photograph showing the phase formation appearing in the PA6/PC/SEBS-gMA 68/23/9 blend. (b) A higher magnification view of part a focusing on the boundary between PA6 and PC to show the interfacial situation of SEBS-gMA.

When SEBS-gMA is introduced instead of un-SEBS into the blend of PA6/PC, MA grafted to SEBS reacts with the amine end groups of PA6, and as a result, a fine dispersion of SEBS in the PA6 matrix can be achieved and at the same time SEBS encapsulates the PC domains as shown in Figure 4a. In the binary blends of PA6/SEBS, the use of SEBS-gMA has a dramatic effect on the reduction of the domain size.[5,6] This effect can be achieved by steric hindrance against coalescence of SEBS drops during melt mixing caused by an interfacial reaction between PA6 and SEBS-gMA.[23] The size of the SEBS domain in the ternary blends of PA6/PC/SEBS-gMA is approximately 100 nm which is comparable with the size obtained in the binary blends of PA6/SEBS-gMA.[9] Focusing on the domains composed by SEBS and PC together in the PA6/PC/SEBS blend system, one can mention that the interfacial reaction between PA6 and SEBS-gMA induces a change in the formation of the domains composed of PC and SEBS. That is, the formation is changed from the "stack formation", where PC and SEBS are stuck together, to the "capsule formation", where PC is encapsulated by SEBS. Figure 4b represents the interfacial situation of SEBS-gMA existing between a PC domain and the PA6 matrix in the PA6/PC/SEBS-gMA 68/23/9 blend. As in the blend of PA6/PC/un-SEBS, the PS layer in SEBS lies at the interface between SEBS and the PC domain, and the thickness of this layer is about 6 nm, which is comparable to the case of the PA6/PC/un-SEBS blends. On the other hand, due to the interfacial reaction between PA6 and SEBS-gMA, the interfacial situation between PA6 and SEBS is absolutely changed. Namely, the interface between PA6 and SEBS is diffused and no clear layer of PS, as could be seen in the blends of PA6/PC/un-SEBS, can be identified. The site of the reaction on SEBS is the PEB mid-block; hence, the PEB blocks should face toward the PA6 matrix through the reaction. All of the above evidence suggests that the change of the phase formation from the "stack formation" to the "capsule formation" through the interfacial reaction is caused by the change of the interfacial situation between PA6 and SEBS. As shown in Figure 5, when both SEBS-gMA and un-SEBS are incorporated together into the blend of PA6/PC 68/23 where the total amount of added SEBS is held at 10 wt % and the ratio of un-SEBS to SEBS-gMA is varied, the encapsulation by SEBS of the PC domains becomes gradually incomplete as the ratio of un-SEBS increases. Moreover, the thickness of the SEBS phase on the domain boundary increases, accompanied by incomplete encapsulation. This implies to us that the ability of SEBS to displace the PA6 matrix from the surface of PC is improved with an increased interfacial reactivity. In other words, the wettability of SEBS on the PC surface in a PA6 atmosphere is improved. In the blends of PA6/PC with a combination of SEBS-gMA and un-SEBS, the domains of dispersed SEBS in the PA6

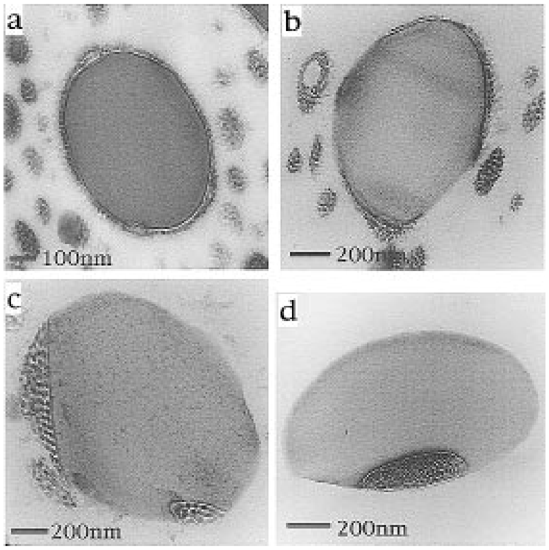

Figure 5. TEM photographs representing the formation of domains composed by PC and SEBS in the PA6 matrix. The total fraction of SEBS is held at 10 wt %, and the ratio of SEBS-gMA to un-SEBS is varied in the blend of PA6/PC 68/23. The ratios of SEBS-gMA to un-SEBS are (a) 10/0, (b) 6/4, (c) 4/6, and (d) 0/10.

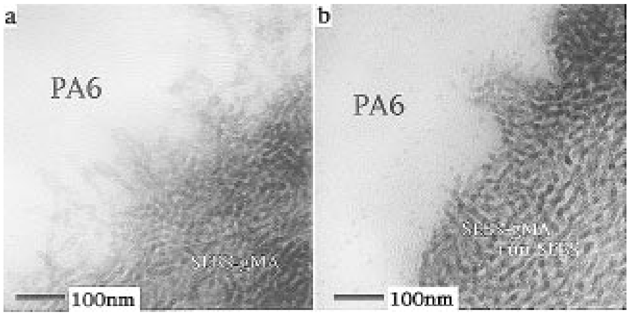

Figure 6. TEM photographs showing the interfaces of laminated films of (a) PA6/SEBS-gMA/PA6 and of (b) PA6/(SEBS-gMA+un-SEBS)/PA6. RuO_4 is introduced to visualize the SEBS microdomain structure.

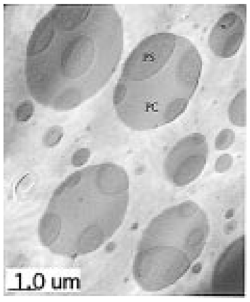

Figure 7. TEM photograph showing the phase formation of PA6/PC/un-PS 68/23/9 blend.

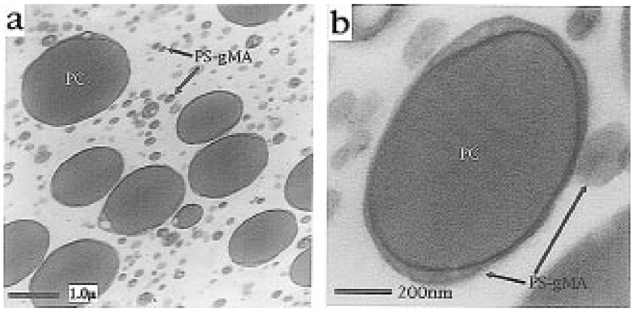

Figure 8. (a) TEM photographs showing the morphology of PA6/PC/PS-gMA 68/23/9. (b) A higher magnification view of part a showing a PC domain encapsulated by PA-gMA.

matrix are enlarged as found in the blends of PA6 with a combination of SEBS-gMA and un-SEBS.[5,6] This indicates that both SEBSs are involved in one phase. Hence, the interfacial reactivity can be controlled by varying the ratio of un-SEBS to SEBS-gMA. To confirm this, the laminations of PA6 and SEBS were annealed at 260 °C for 10 min, and then the cross sections were observed by TEM. A 10 wt % solution of SEBS dissolved in methylene chloride was spin-coated on a PA6 film, and then it was laminated with an another PA6 film after evaporation of the solvent. Figure 6a is a TEM photograph showing the interfacial situation between PA6 and SEBS-gMA alone, indicating that the boundary between PA6 and SEBS is significantly rough and SEBS diffuses deeper into the PA6. On the other hand, the boundary between PA6 and the mixture of SEBS-gMA/un-SEBS 50/50 is not so as rough as the lamination of PA6 and SEBS-gMA alone, as shown in Figure 6b. These two photographs obviously present different interfacial situations, insisting that un-SEBS and SEBS-gMA are mixed homogeneously and that the interfacial reactivity can be controlled by varying the ratio of un-SEBS to SEBS-gMA.

Reaction-Induced Phase Formation in the Blends of PA6/PC/PS. Regarding the fact that the PS layers in SEBS domains are in contact with both the PA6 phase and the PC phase in the blends of PA6/PC/un-SEBS as shown in Figure 3b, it can be predicted that the blends of PA6/PC/un-PS also will show the same phase formation as that of PA6/PC/un-SEBS for the reason that the morphology development of nonreactive ternary immiscible blends are mostly governed by the balance of interfacial tensions between the respective polymers.[4] In fact, as shown in Figure 7, the blend of PA6/PC/un-PS 68/23/9 exhibits the "stack formation" where PC and PS are stuck together in the PA6 matrix. The change of the phase formation induced by an interfacial reaction as found in the PA6/PC/SEBS blend system is also achieved when PS-gMA is introduced into the blend of PA6/PC. The morphology of the PA6/PC/PS-gMA 68/23/9 blend at different magnifications is shown in Figure 8. There are two kinds of domains in terms of the domain size existing in the PA6 matrix as seen in the blends of PA6/PC/SEBS-gMA (Figure 8a). The larger one corresponds to PC domains, and the smaller one corresponds to PS-gMA domains. The size of the PS-gMA domains dispersed in PA6 matrix is comparable with the size of PS-gMA domains in the binary blends of PA6/PS-gMA as reported by Jo *et al.*[24] and also is comparable with the size of SEBS-gMA domains dispersed in the PA6/PC/SEBS-gMA blends. This indicates that the interfacial reaction between PA6 and PS-gMA occurs effectively in the blends of PA6/PC/PS-gMA during the melt mixing. Complete encapsulation by PS-gMA of the PC domains also occurs as shown in Figure 8b. This means that the morphology development through the interfacial reaction as seen in the PA6/PC/SEBS blend system is also achieved in the PA6/PC/PS blend system. Figure 9 shows the morphologies of the PA6/PC 68/23 blends incorporating both PS-gMA and un-PS at two different ratios, where the total composition of PS is held at 10 wt %. As in the case of PA6/PC/SEBS blends, the increase of the ratio of unmodified PS enlarges the PS domains dispersed in the PA6 matrix. This means that un-PS and PS-gMA are involved in the same domains, and the interfacial reactivity can be controlled by varying the ratio of PS-gMA to un-PS. However, the complete encapsulation by PS of the PC domains can be achieved even when the ratio of un-PS to PS-gMA is 7/3 (Figure 9a). Only

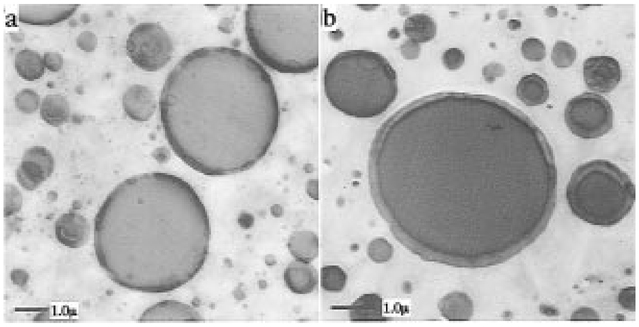

Figure 9. TEM photographs showing the morphologies of PA6/PC 68/23 blends with a combination of un-PS and PS-gMA. The total fraction of PS is held at 10 wt %. The ratios of un-PS to PS-gMA are (a) 3/7 and (b) 7/3.

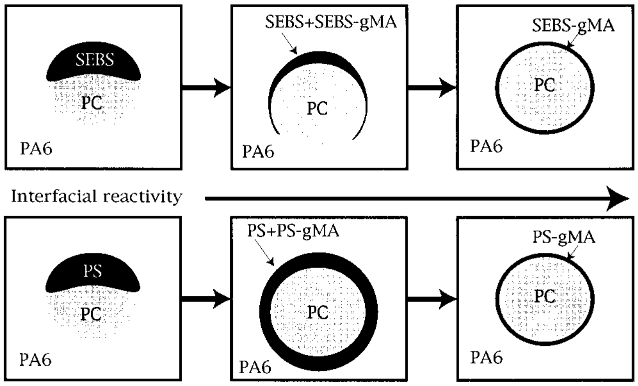

Figure 10. Schematic illustrations to explain the tendency of morphology development by varying the ratio of the unmodified polymer to its maleinated polymer: (a) morphology development in the PA6/PC/SEBS blend system; (b) morphology development in the PA6/PC/PS blend system.

the thickness of the PS phase encapsulating the PC decreases as the ratio of PS-gMA to un-PS increases (Figure 9b). This morphological trend is different from that obtained when the combination of SEBS-gMA and un-SEBS is introduced to the blends of PA6/PC. Figure 10 illustrates the morphology development obtained in the blend systems of PA6/PC/SEBS (Figure 10a) and of PA6/PC/PS (Figure 10b) by varying the ratio of the maleinated polymer to its unmodified one. In the blend system of PA6/PC/SEBS, the encapsulation by SEBS of the PC domains gradually becomes complete as the ratio of SEBS-gMA to un-SEBS increases, and complete encapsulation can be achieved only by the use of SEBS-gMA alone, whereas in the blends of PA6/PC/PS, the complete encapsulation by PS of PC can be obtained even when both PS and PS-gMA are used. This suggests that low interfacial reactivity is enough to give complete encapsulation in the PA6/PC/PS blend system, whereas, in the PA6/PC/SEBS blend system, higher interfacial reactivity is required to achieve the complete encapsulation.

The Reduction of the Interfacial Tension by an Interfacial Reaction. As mentioned earlier, the morphological variation through the interfacial reaction is assumed to be caused by the change of the interfacial situation between PA6 and the maleinated polymers. The most important parameter characterizing the interface in immiscible blends is the interfacial tension. It is well-known that block and graft copolymers are efficient additives for the reduction of polymer/polymer interfacial tension. A premade block copolymer added into a blend, comprising blocks that are miscible with one of the homopolymers in the blends, prefers to span at the interface between the homopolymers and reduces the interfacial tension to 40−70%.[25,26] The use of the *in situ* formation of block or graft copolymers by coupling of reactive groups on each of the homopolymers is an alternative method for the simple addition of graft or block polymers into blends. Fleischer *et al.* reported that interfacial modification with end-functionalized interfacial agents reduces the interfacial tension by up to 70% through the interpolymer end-complexation.[27] They used carboxy-terminated polybutadiene (PBD-COOH) and amine-terminated poly(dimethylsiloxane) (PDMS-NH_2) as the interfacial agents for reducing the interfacial tension for the PBD/PDMS blend system. The interfacial tension reduction resembles that obtained when block copolymers are added to immiscible polymer blends. That is, interfacial tension decreases sharply with a small amount of interfacial agents and then reaches a plateau above the critical concentration of the interfacial agents. Cho *et al.* also reported the effect of end-sulfonated polystyrene (e-SPS) on the reduction of interfacial tension between PA6 and PS by the interfacial reaction between PA6 and e-SPS.[28] They reported that the degree of reduction is up to 80%. An analogous situation is therefore expected at the interface between PA6 and SEBS-gMA and between PA6 and PS-gMA. Through the interfacial reaction between PA6 and the maleinated polymers, the *in situ* graft copolymer of PA6-SEBS or PA6-PS forms directly at the interface, leading to the reduction of the interfacial tension.

It is known that the formation of two dispersed phases in nonreactive ternary immiscible blends can be predicted by eq 1, which has been obtained by rewriting

$$\lambda_{12} = \gamma_{23} - \gamma_{13} - \gamma_{21} \qquad (1)$$

the Harkin's equation by Hobbs *et al.*,[4] where γ_{23}, γ_{13}, and γ_{21} are the interfacial tensions between polymers **1**, **2**, and **3** indicated in Figure 1 and λ_{12} is defined as the spreading coefficient for polymer **1** on polymer **2**. The spreading coefficient indicates the ability of one polymer to spread on the another polymer in a ternary immiscible blend. When λ_{12} and λ_{21} are both negative, the dispersed phases will remain isolated or stuck together as indicated in parts b and c of Figure 1. If λ_{12} is positive, polymer **1** will spread on polymer **2** extensively to encapsulate polymer **2** completely. Applying this equation to the two blend systems composed by PA6, PC, and SEBS or PS (i.e.; PA6 is polymer 3, PC is 2 and SEBS or PS is 1), the first and third terms of the interfacial tensions, (γ_{23} = PC on PA6 and γ_{21} = PC on SEBS or PS), in eq 1 are assumed to be constant when SEBS-gMA is incorporated at variety ratios, while the second term (the interfacial tension between PA6 and SEBS or PS) is expected to be reduced through interfacial reaction. As a result, the spreading coefficient of SEBS or PS on PC, λ_{12}, increases as the interfacial reactivity increases. This means that the ability of SEBS and PS to spread on the PC domains increases as the interfacial reactivity increases. Regarding the phase formations of PA6/PC/un-SEBS and PA6/PC/un-PS, the spreading coefficient of SEBS or PS on PC in these blends is expected to be negative. The increase of the spreading coefficient will lead to the conversion of the spreading coefficient from negative to positive, which means a change from the "stack formation" to the "capsule formation". Taking into account the difference of the morphology development between PA6/PC/SEBS system and PA6/PC/PS system when the unmodified and its maleinated polymers are incorporated together as shown in Figure 10, it is speculated that the degree of the reduction of interfacial tension

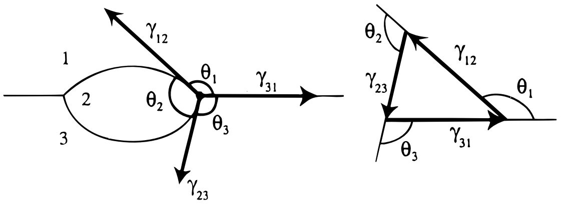

Figure 11. Schematic illustration of interfacial tension balance at interfaces of three liquids and the Neumann triangle.

through the interfacial reaction is different between those two blend systems. This may arise from the difference of the site of reaction between SEBS-gMA and PS-gMA. In the reaction between PA6 and SEBS-gMA, the PEB block is the reaction site; hence, PEB blocks partially come into contact with the PA6 phase through the interfacial reaction. A tendency for a reduction of the interfacial tension is therefore assumed to be the difference between PA6/SEBS-gMA and PA6/PS-gMA. According to the literature reporting the interfacial tensions in a melt state between polymers, the interfacial tensions between PA6 and polyethylene, which resembles the interface between PA6 and PEB, are reported as 12.5−13.2 dyn/cm at 290 °C.[29] On the other hand, the interfacial tension between PA6 and PS is reported as 7.3 dyn/cm at 240 °C.[28] These results indicate that the interfacial tension between PA6 and PS is lower than that between PA6 and PEB. This is consistent with the fact that the PS block of SEBS rather than the PEB block prefers to lie at the interface between the SEBS phase and the PA6 phase. It is known that in a block copolymer contacting an immiscible homopolymer, the block having the lower interfacial tension between the block and the homopolymer prefers to be in contact with the homopolymer.[30] At the interface between PA6 and SEBS-gMA, the PEB block has to come into contact with the PA6 phase after the interfacial reaction, which may cause the interfacial tension to increase. Thus, the degree of the reduction of the interfacial tension as a function of the interfacial reactivity is much higher in the case of the PA6/PS-gMA interface than in the PA6/SEBS-gMA interface. This is assumed to be the reason for the difference of the morphology development through an interfacial reaction between the PA6/PC/SEBS and PA6/PC/PS blend systems. In the PA6/PC/PS blend system, the lower interfacial reactivity is enough to obtain the reduction of γ_{13} in eq 1 to convert the spreading coefficient, λ_{12}, from negative to positive, while in the PA6/PC/SEBS system, the higher interfacial reactivity is required to convert the spreading coefficient from negative to positive.

The Concept of Neumann's Triangle. As mentioned in the above discussion, the morphology development induced by the interfacial reaction can be well explained in terms of the change of interfacial tension balance in the three components. The spreading coefficient obtained by eq 1, however, gives negative values both for the "stack formation" and for the "isolated formation", and hence, it cannot clearly distinguish between the two formations. Inoue *et al.* applied the concept of Neumann's triangle to three polymer melts for the prediction of the phase formation of ternary immiscible blends.[31] Figure 11 illustrates the small liquid lens floating in between the two liquids, and a triangle can be constructed with the contact angles at the edge of the small lens and with the lines having magnitudes equal to those of the corresponding interfacial tensions. This is called Neumann's triangle.[21] Applying this concept to the ternary immiscible polymer blends where polymer **3** forms a matrix and polymers **1** and **2** are dispersed phases, the possible shapes and locations of a floating polymer drop laminated by the other two polymers are assumed to be as illustrated in Figure 12. The case of Figure 12a where the polymer drop is thin and spreads widely between the two polymers indicates the disappearance of the interface between polymer **1** and **3** in the ternary blend. In this case the "capsule formation" of polymer **2** on polymer **1** will be achieved. If the polymer drop exists in polymer **1** as in Figure 12b, this means that there is no interface between **2** and **3** and thus the "capsule formation" of **1** on **2** will be achieved. If the polymer drop exists in polymer **3** as shown in Figure 12c, no interface between **1** and **2** will be achieved in the blends and thus the two polymers are separately dispersed in the polymer **3** matrix. In the case of Figure 12d, the polymer drop is floating between the two polymers and takes a lens shape. This means that there can be three kinds of interfaces of the pairs of the respective three polymers and thus indicates that the polymer **1** and **2** are stuck together in the polymer **3** matrix (Figure 1b). Inoue *et al.* carried out this "droplet-sandwich experiment" for poly(styrene-*co*-acrylonitrile) (SAN)/PC/poly(butylene-terephthalate) (PBT) ternary system, varying the styrene/acrylonitrile ratio in SAN.[31] The prediction of phase formation by this method is in good agreement with the morphologies obtained by melt blending. This method gives the same prediction as that from the equation by Hobbs[4] and, moreover, can successfully distinguish the "stack formation" from the "isolated formation".[31]

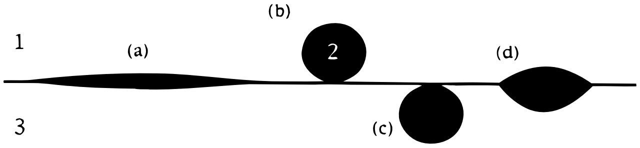

Figure 12. Possible locations and shapes of a floating polymer drop between two polymers appearing in a "droplet-sandwich experiment".

We applied this concept to the PA6/PC/SEBS blend system to discuss the morphology development induced by the interfacial reaction. "Droplet-sandwich experiments" were carried out with the laminates where small pieces of SEBS were sandwiched by PA6 and PC (PC/SEBS/PA6) and where small pieces of PC were sandwiched by the other two polymers (SEBS/PC/PA6). The annealing temperature and time are held at same conditions for the blending procedure, and the cross sections of the laminates were observed under a microscope. Figure 13 shows the cross sections of droplets of (a) PC/un-SEBS/PA6, (b) PC/SEBS-gMA/PA6, (c) un-SEBS/PC/PA6, and (d) SEBS-gMA/PC/PA6 laminates. In the laminates in which un-SEBS is incorporated (Figure 13a,c), the droplets show the lens shape floating between the two polymers (Figure 13a,c). In the laminates with SEBS-gMA, on the other hand, the SEBS-gMA droplet widely spreads between the two polymers (Figure 13b) while the PC droplet is involved in the SEBS-gMA layer (Figure 13d). The laminates of PC/PS/PA6 also show a similar tendency, as shown in Figure 14, which means the un-PS droplet takes a lens shape between PA6 and PC, while PS-gMA spreads widely on the interface between PA6 and PC. These results well agree with the phase formations obtained in the two blend systems. This insists that the driving force of the morphology development from the "stack formation" to the "capsule formation" through the interfacial reaction is the change of the balance of interfacial tensions.

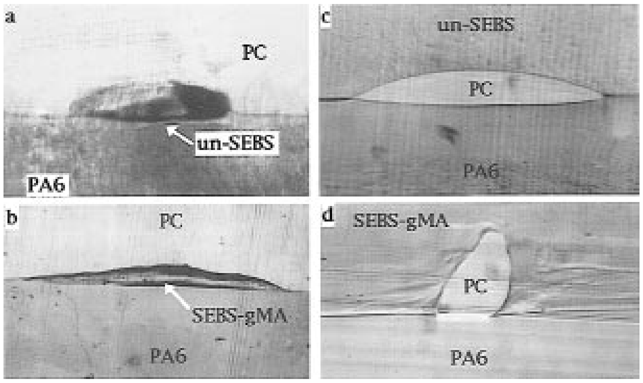

Figure 13. Cross-sectional views of the laminated films composed of PA6, PC and SEBS after annealing at 260 °C and for 10 min: (a) PC/un-SEBS/PA6; (b) PC/SEBS-gMA/PA6; (c) un-SEBS/PC/PA6; (d) SEBS-gMA/PC/PA6 laminates.

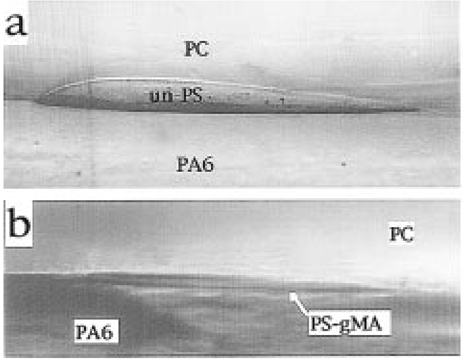

Figure 14. Cross-sectional views of the laminated films composed of PA6, PC, and PS after annealing at 260 °C and for 10 min: (a) PC/un-PS/PA6; (b) PC/PS-gMA/PA6laminates.

Conclusion

This paper described the morphology development of immiscible ternary blends through an interfacial reaction between the matrix and one dispersed phase. In the blends of PA6 and PC where PA6 is the continuous matrix, the added maleinated polymers (SEBS-gMA and PS-gMA) react with the amine end groups of PA6, and this interfacial reaction induces the change of the formation of the two dispersed phases from the "stack formation" to the "capsule formation". TEM observations for the interfacial situation of SEBS in the blends of PA6 and PC suggest that the change of the phase formation is caused by the change of the interfacial situation between SEBS and PA6 through the interfacial reaction. Through the discussion in terms of the equation proposed by Hobbs *et al.* and the experiments using Neumann's concept, the driving force of this morphology development is assumed to be the reduction of the interfacial tension by the interfacial reaction between PA6 and the maleinated polymers. Incorporation of both the maleinated polymers and their unmodified polymers can control the degree of interfacial reactivity which then affects the final morphology. The tendency of morphology development is different between PA6/PC/SEBS and PA6/PC/PS blend systems when both the unmodified and the maleinated polymers are incorporated at various ratios into the blends of PA6/PC. This may come from the difference of degree of the reduction of interfacial tensions as a function of the interfacial reactivity that can be changed by varying the ratio of the maleinated polymer to its unmodified polymer. Direct measurements of interfacial tensions between the polymers at the processing temperature and of the reduction of the interfacial tensions by the interfacial reaction would support this explanation. Unfortunately, there are only limited studies regarding the measurements of interfacial tensions of polymer pairs. Although some theories provide interfacial tensions,[32-34] they involve some assumptions and thus do not necessary give accurate interfacial tensions.[28] The collection of precise interfacial tension data for various polymer pairs would help us to find the other ternary blend systems exhibiting the similar morphological development and could provide a new approach to design compatibilizers.

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