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Interfacial Tension Measurement of a Reactive Polymer Blend by the Neumann Triangle Method

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The interfacial tension (γ) of a polymer blend plays a crucial role in determining the morphology because it governs the dispersed phase size. Various experimental methods[1−5] have been employed to measure γ between two immiscible polymer pairs. Among many methods, the breaking thread (BT)[2,3] and imbedded fiber retraction (IFR)[4] methods have been widely employed to determine γ of high molecular weight polymer pairs. However, as described elsewhere,[6] because plots of the amplitude of a thread instability (or the shape functions) versus time in BT (or IFR) for reactive polymer blends do not give straight lines, γ could not be measured in principle using these two methods. Some research groups[7,8] have speculated that γ would decrease with increasing the amount of in-situ compatibilizer in a reactive polymer blend, because the dispersed domain size decreases. But others[9,10] argued that the decreased domain size of the dispersed phase is mainly due to the decrease in the coalescence even though the decrease in γ is not completely excluded. The calculation of γ of a reactive polymer blend from the change in dispersed domain size[7,8] or from an emulsion model[11] would not be warranted since an external shearing (or elongational) force should be added. Thus, the direct measurement of γ of a reactive polymer system without applying any external force is needed. Previously, we[12] employed the Neumann triangle method (NT) to measure γ between poly(butylene terephthalate) (PBT) and polystyrene (PS) with 1 wt % of poly(styrene-*co*-glycidyl methacrylate) (PS-GMA). Nakamura and Inoue[13] applied the NT for the first time to a ternary immiscible polymer blend and explained the multiphase morphology developed by melt processing. Zhang et al.[14] also used the NT to measure γ between polyamide 6 and maleic anhydride-grafted polypropylene. However, the effect of the amount of in-situ compatibilizer on γ of a reactive blend has not been studied in detail, especially for larger amounts of in-situ compatibilizer. In this communication, we applied the NT to measure γ of a reactive polymer blend and showed that when the amount of in-situ compatibilizer exceeds a critical value, γ becomes negative. We correlated this negative γ to the interfacial roughening.

NT is based on the fact that at equilibrium any point on the interface that three phases meet together balances the interfacial tension in Figure 1.[15]

$$\gamma_{12} \cos \theta_{12} + \gamma_{23} \cos \theta_{23} + T = \gamma_{13} \cos \theta_{13} \qquad (1)$$

where θ_{ij} is the contact angle between two phases of i and j and T is the line tension existing along the line on which all three phases meet. To obtain γ_{12}, two values of γ_{23} and γ_{13} should be determined a priori by other methods such as BT or IFR, even if all θ_{ij}'s are measured. Although the sign and magnitude of T are still in argument,[15] we neglect T for our reactive polymer blend. This is because for a blend without in-situ compatibilizer, the calculated γ_{12} from γ_{23}, γ_{13}, and three θ_{ij}'s with the assumption of $T = 0$ was within experimental error compared with γ_{12} obtained from BT or IFR.[6,12] Furthermore, the size effect of the middle phase does not change three θ_{ij}'s, as will be described later.

The exact determination of three θ_{ij}'s becomes most important when one of these angles approaches 90°. The most desirable experimental condition is that the specimen should be cut (or polished) along the thickness

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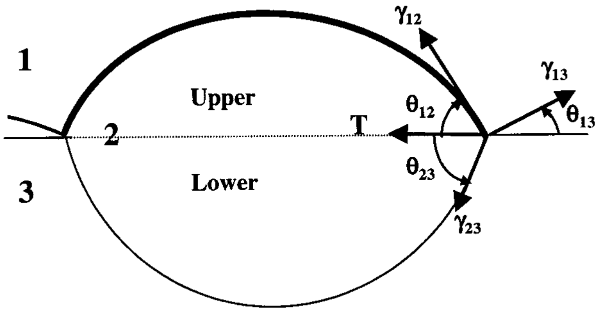

Figure 1. Neumann triangle vector balance at one periphery.

direction through the exact half of the middle phase.[16] Also, the top view of the middle phase should be a circle; otherwise, the three angles observed by a microscope do not represent the direction of interfacial tension at the equilibrium.[16] In the NT method, there are two interfaces for the middle phase, namely, 1−2 interface and 2−3 interface in Figure 1. In this study, component 2 (PBT) reacts with component 1 (PS-GMA in PS phase); thus, in-situ graft (or block) copolymers are formed in the interface, while component 2 does not react with component 3 (PMMA). With increasing amount of PS-GMA in phase 1, the interface between (PS + PS-GMA) and PBT became immobilized because of large amounts of in-situ formed graft copolymers near the interface,[17−20] which is a phenomenon similar to BT and IFR cases. But, the interface between PBT and PMMA could still be mobile. Thus, this interface adjusted itself to make the condition that the summation of three interfacial tension vectors at the periphery is zero.

All neat polymer materials used in this study are introduced in ref 12. Various compositions of PS and PS-GMA were solution-blended in toluene followed by precipitation with methanol. The PS/PS-GMA blend and PMMA were compression molded at 160 °C to 1.2 mm thickness plates by using a ferro-type metal plate with a very smooth surface. A small piece of PBT in a spherical shape with the diameter of ~80 μm was prepared by breaking up PBT thread in PS matrix and removing PS matrix by using cyclohexane. Then, the PBT sphere was sandwiched between two plates of PS/PS-GMA blend and PMMA and completely embedded by annealing at 130 °C for 24 h under vacuum. The sandwiched specimen was annealed in the heating block at 240 °C for 30 min under a nitrogen atmosphere, followed by quenching in cold water. Finally, the specimen was polished with extreme care so that the cutting conditions mentioned above were satisfied. At least five specimens at one condition were examined. The three contact angles were determined from the OM with 1000× magnification. The interface roughness between (PS + PS-GMA) and PBT phase was observed by an atomic force microscope (AFM; Autoprobe CP. Park Scientific Instruments) and a field-emission scanning electron microscope (FE-SEM; Hitachi S-4200). The specimen for AFM was prepared by etching out (PS + PS-GMA) with cyclohexane at 40 °C for 48 h. The image of AFM was obtained at the top part of the PBT phase in the specimen.

We investigated the effects of size and shape of the middle phase as well as the density difference between the two matrices on contact angle change. Using PBT sphere with a diameter of ~300 μm, we obtained almost the same results as those of 80 μm, which indicates the negligible size effect. The use of the PBT sphere was very essential for large amounts (say more than 5 wt %) of PS-GMA. Because any initial shape (say rectangular or cylindrical shape) of PBT tended to transform into a spherical shape, the reducing interfacial area misleads one to overestimate the areal density (Σ) of graft copolymers in the interface, thus a larger decrease in γ than it really has.[6] That is the reason why we used PBT with spherical shape. The PMMA plate was placed at the lower position throughout the experiment. The reverse position of the PMMA plate (namely, the PMMA plate was placed at the upper position) did not affect the contact angles, which implies that the gravity effect due to the density difference between PMMA and PS was considered not to affect γ of our system.

Figure 2a−d gives the perpendicular section (namely side view) of the samples with various amounts of PS-GMA annealed at 240 °C for 30 min. The same side views were obtained even though each specimen was annealed up to 2 h at 240 °C.[21] This implies that the shapes for all cases shown in Figure 2 are in their steady states. It is seen in Figure 2 that, with increasing amount of PS-GMA, the interface delineating the upper part from the lower part of PBT phase lowered down. This is because without PS-GMA $\gamma_{\mathrm{PS/PBT}}$ at 240 °C is 4.51 mN/m, which is larger than $\gamma_{\mathrm{PBT/PMMA}}$(2.53 mN/m) measured by the BT method.[6] Thus, most of the PBT phase is located in the PMMA phase to reduce the interfacial energy. But, with increasing PS-GMA, the in-situ formed PS-*g*-PBT copolymers reduced the interfacial tension between PBT and PS; thus, the PBT phase moved toward the PS phase.

The change in three contact angles with the amount of PS-GMA is given in Figure 3. The values of $\theta_{\mathrm{PMMA/PS}}$ for all the specimens were found to be zero. With increasing amount of PS-GMA, $\theta_{\mathrm{PMMA/PBT}}$ continuously decreased, while $\theta_{\mathrm{PS/PBT}}$ increased up to 5.0 wt % and leveled off. A continuous change in $\theta_{\mathrm{PMMA/PBT}}$ even at large amounts of PS-GMA is attributed to the mobile nature of the interface between PBT and PMMA phases. This behavior is due to the requirement of the interfacial tension balance. With $\theta_{\mathrm{PS/PMMA}}$ and $\theta_{\mathrm{PMMA/PBT}}$ as well as the predetermined $\gamma_{\mathrm{PBT/PMMA}}$ and $\gamma_{\mathrm{PS/PMMA}}$, $\gamma_{\mathrm{(PS+PS-GMA)/PBT}}$ was calculated and given in Figure 3.[22] With increasing PS-GMA content, $\gamma_{\mathrm{(PS+PS-GMA)/PBT}}$ decreased very rapidly at small amounts of PS-GMA, and then it decreased gradually. Even for a blend with 0.5 wt % of PS-GMA, γ was reduced more than half of that of a blend without PS-GMA. Finally, $\gamma_{\mathrm{(PS+PS-GMA)/PBT}}$ became negative at larger amounts of PS-GMA. It was, however, impossible to obtain a well-defined spherical shape of PBT for blends with PS-GMA having larger than ~20 wt %; thus, we could not calculate γ for these blends.

Recently, by using forward recoil spectrometry, Jiao et al.[23] studied the interface between two reactive layers consisting of poly(styrene-*ran*-maleic anhydride) and PS phase with various initial concentrations of benzylamine end-functionalized deuterated PS (dPS−NH$_2$). They found that the interface starts to roughen at a critical initial concentration ($\varphi_{0,c}$) of PS−NH$_2$ corresponding to $\gamma \sim 0$. Even pinch-offs were observed when the initial concentration of PS−NH$_2$ is much larger than $\varphi_{0,c}$. In this situation, a negative γ was predicted by a self-consistent mean-field theory.[24] Since a negative γ was calculated as shown in Figure 3, we examined the interface between (PS + PS-GMA) and PBT phases by

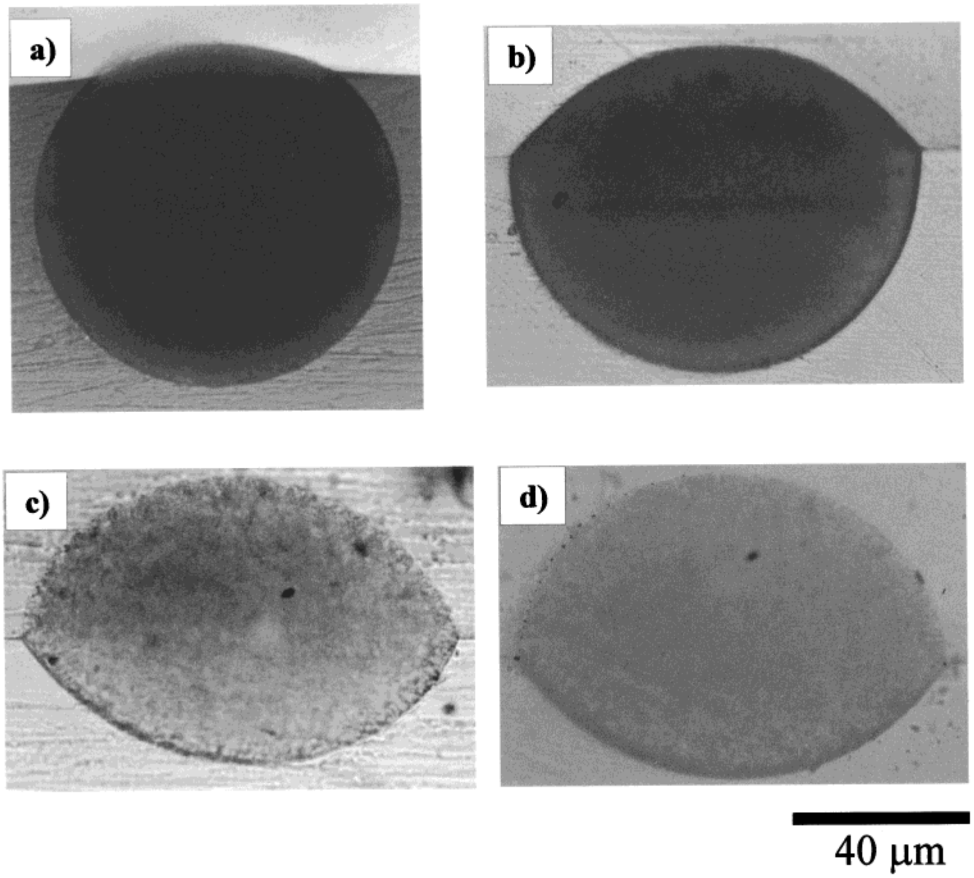

Figure 2. Cross-sectional view of the PBT middle phase annealed at 240 °C for 30 min for various amounts of PS-GMA. PBT phase (middle) is sandwiched between (PS + PS-GMA) (top) and PMMA (bottom). The weight percents of PS-GMA in total PS phase: (a) 0, (b) 4, (c) 10, and (d) 16.7.

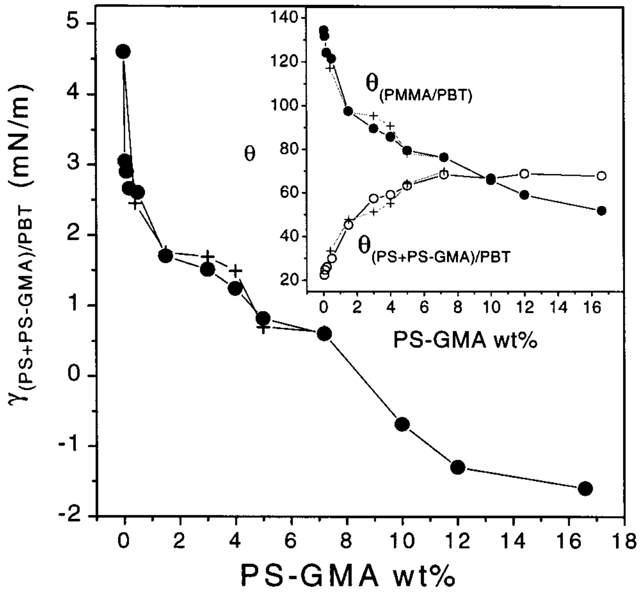

Figure 3. Change of the interfacial tension and the contact angles with amount of PS-GMA in total PS phase for two different PBT sphere sizes: (●) 80 μm; (+) 300 μm.

AFM, and the results are given in Figure 4.

For a specimen without PS-GMA, the interface was very smooth with a root-mean-square (rms) roughness of ~1.8 nm. It is almost impossible to obtain a rms roughness of less than 1.0 nm because of the soft material of the interface. Even if the amount of PS-GMA in PS phase is 4.0 wt %, the roughness of the interface of PBT and PS was slightly increased to 2.5 nm. However, for another specimen with 10 wt % of PS-GMA, the roughness of the interface was considerably increased with a rms roughness of ~10 nm, which is close to the radius of gyration ($R_g \sim 9$ nm) of PS-*g*-PBT copolymer. The height of the bumps was 30−40 nm, and the corrugation wavelength was 200−300 nm. It is noted that after etching the top phase (PS + unreacted PS-GMA) we found via FT-IR that PBT did not exist in the etched solution. This indicated that almost all of the in-situ formed copolymers existed at the interface; thus, PBT surface covered with PS-*g*-PBT was observed in AFM images. For a specimen with 100 wt % of PS-GMA the interface roughened very much, and the altitude of the roughness was increased to 300 nm (Figure 4d). Also, some parts of the roughened interface seemed to be taken off during the etching, which was clearly observed by SEM image.[6] Similar behavior to results given in Figure 4d was reported for the blend consisting of aliphatic amine-terminated PS and anhydride-terminated PMMA.[25]

Now, we consider the physical meaning of a negative γ calculated in this study. From the definition of γ, $\gamma = \mathrm{d}E/\mathrm{d}A$, in which d$E$ and dA are the changes in interfacial energy and interfacial area, respectively, γ should become zero (or negative) for an interface with a considerable roughening in the absence of an external force. This is because an area generation due to the interfacial roughening would increase enormously the

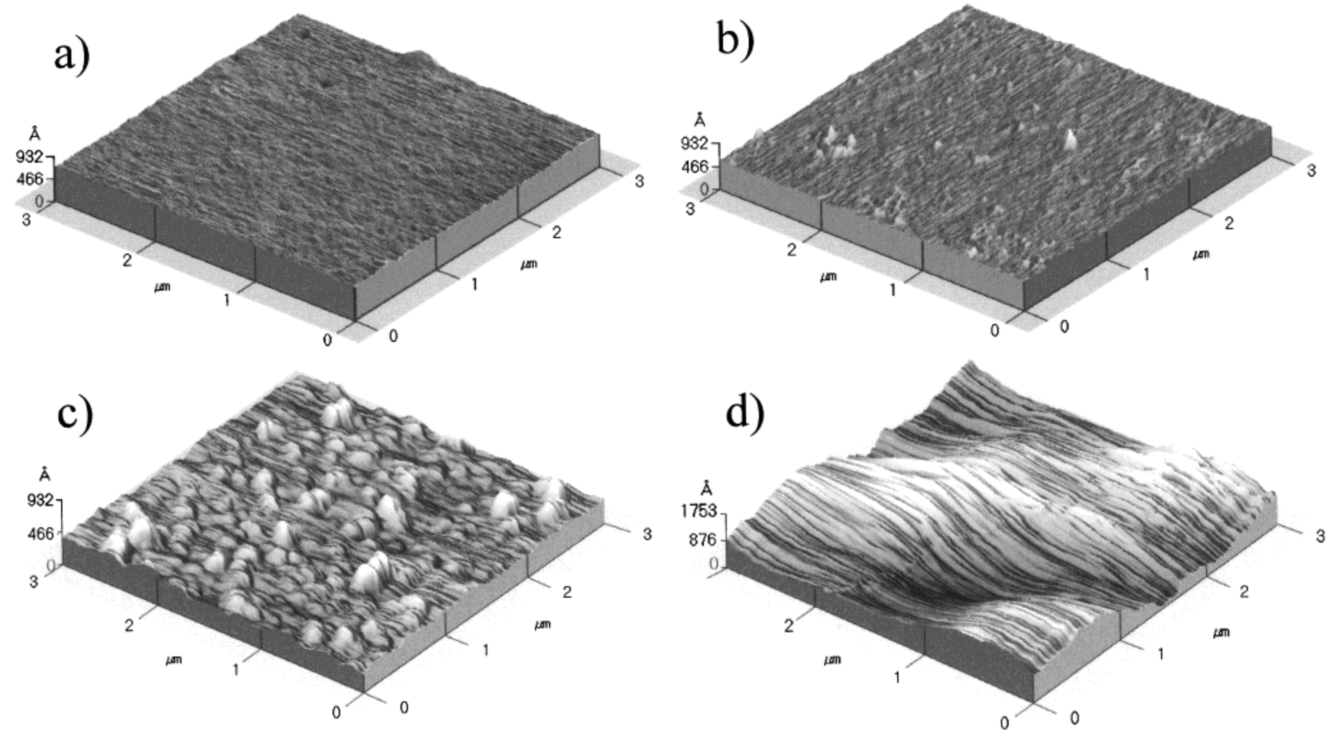

Figure 4. AFM images of the interface between (PS + PS-GMA) and PBT. Since only the phase consisting of PS and unreacted PS-GMA, but not PS-*g*-PBT, was etched out by cyclohexane, the images represent the PBT surface covered with PS-*g*-PBT. The weight percents of PS-GMA in total PS phase: (a) 0, (b) 4, (c) 10, and (d) 100.

interfacial energy for the case of $\gamma > 0$. It is noted that during the mixing the energy can be generated for a system with $\gamma < 0$, whereas there is no energy change for the case of $\gamma = 0$. Since an interface between two homopolymers with zero or negative γ energetically prefers to a mixed state, the interface disappears eventually.

For a reactive blend employed in this study, γ decreased with increasing the concentration of the copolymer at the interface. This is because of reduction in the unfavorable contacts of PBT and PS chains. When a specimen showed a small but positive γ, the interface does not need to roughen, as shown in Figure 4b. With the interface being completely covered with single layer of graft copolymers, the areal density of graft copolymer (Σ) has its critical value (Σ_{crit}) where $\gamma = 0$. In this situation, PBT segments in the bulk phase and those in copolymer layer cannot be separated, and the same for the PS segments. More reaction at Σ_{crit} gives the areal density larger than Σ_{crit}, which results in an interface roughening; thus, a negative γ is obtained. When the reaction does not further proceed due to low concentration of remaining PS-GMA chains near the interface, increased interfacial area resulting from the roughening can accommodate a larger amount of copolymers; thus, Σ approaches the Σ_{crit}. The interface, however, will remain to be roughened due to its reduced mobility of graft copolymers and large energy barrier for it to diffuse into bulk phases. This implies that a corrugated interface does not transform into a flat interface at zero (even negative) γ in a reactive blend, which corresponds to a specimen with 10 wt % of PS-GMA (Figure 4c). Jiao et al.[23] observed similar corrugated interface to Figure 4c for a system with a small negative γ. Because the interface roughness as shown in Figure 4c remains even at a longer annealing (2 h) at 240 °C, only PS-GMA chains near the interface participated in the reaction, and the interface reached a steady state, resulting in a mild interface roughening. Finally, as the reaction continues to occur, which might correspond to a blend with 100 wt % PS-GMA (Figure 4d), the interface roughens severely and might proceed toward a complete mixing after experiencing repeated pinch-offs of tiny PBT clusters covered with graft copolymers. In this situation, the system remains to have a negative γ.

Now, we estimate the Σ_{crit} (or $(z^*/R_g)_{\mathrm{crit}}$ in which z^* is the interfacial excess):

$$\Sigma_{\mathrm{crit}} = \frac{(z^*/R_g)_{\mathrm{crit}} b N_{\mathrm{av}}}{\sqrt{6N} V_{0,\mathrm{ref}}} \tag{2}$$

where b is the Kuhn length (1 nm),[18] N_{av} is the Avogadro number, N is the number segment of PS-*g*-PBT copolymer, and $V_{0,\mathrm{ref}}$ is the reference monomer volume taken as 142 cm^3/mol calculated from $(v_{\mathrm{sp,PS-GMA}}[\mathrm{M}]_{0,\mathrm{PS-GMA}} v_{\mathrm{sp,PBT}}[\mathrm{M}]_{0,\mathrm{PBT}})^{0.5}$. N is defined by $M_{\mathrm{copolymer}}$ divided by $[\mathrm{M}]_0$ taken as 151. Also, $(z^*/R_g)_{\mathrm{crit}}$ was evaluated by using a self-consistent mean-field theory:[24]

$$-\frac{\gamma - \gamma_0}{\gamma_0} = \frac{1}{\sqrt{\chi N}} f(z^*/R_g) \tag{3}$$

$$f(z/R_g) = 1.38(z/R_g) - 0.51(z/R_g)^2 + 0.45(z/R_g)^3 \tag{4}$$

Using the χ of 0.16 at 240 °C,[18] $\chi N = 75$ and $R_g = 9$ nm when $M_{\mathrm{copolymer}}$ is taken as the sum of M_n of PS-GMA and M_n of PBT.[18,20] Using eqs 2−4 with $\gamma = 0$, Σ_{crit} is calculated to be 0.21 chain/nm^2.

To obtain experimentally Σ for a reactive blend, the amount of PS-*g*-PBT copolymers formed at the interface should be measured.[18] However, due to a very small amount of copolymer, Σ was instead calculated in this study as follows:

$$\Sigma = \delta\rho_{\text{copolymer}}N_{\text{av}}/M_{\text{copolymer}} \qquad (5)$$

where the interface thickness (δ) was assumed as 2 times rms roughness of interface measured by AFM, and $\rho_{\text{copolymer}}$ is the density (g/cm^3). From the results in Figure 4, Σ for a blend with 10 wt % is calculated to be 0.17 chains/nm^2, which is close to the predicted Σ_{crit} (0.21). This led us to conclude that (i) the zero γ given in Figure 3 roughly corresponds to the interfacial roughness of an order of R_g and (ii) negative γ determined by NT might be reasonable as long as the experimental criteria of NT described above are satisfied.

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(21) It is, however, noted that during short annealing times the side views kept changing. For instance, the side view (or contact angles) for a specimen with 16.7 wt % of PS-GMA annealed for 3 and 5 min was very similar to that for specimens with 1.5 and 4 wt % of PS-GMA annealed for 30 min or longer, respectively. But, at annealing times longer than 7 min, the side view of the above blend did not change with time. In this study, the maximum amount of PS-GMA in the total PS phase was ~16.7 wt %. This is because the interface between PBT and PS phase for a blend with PS-GMA more than ~20 wt % became too quickly immobilized; thus, the top view of the middle PBT phase could not become a circular shape.
(22) $\gamma_{\text{(PS+PS-GMA)/PMMA}}$ at 240 °C measured by BT decreased from 1.09 to 0.67 mN/m with increasing the amount of PS-GMA in total PS phase from 0 to 16.7 wt %.[6] The values of $\gamma_{\text{(PS+PS-GMA)/PBT}}$ given in Figure 3 were obtained after this change was considered.
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