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Linear Viscoelasticity and the Measurement of Interfacial Tension in a Partially Miscible Polymer Mixture

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ABSTRACT: A hybrid rheological approach utilizing thermal analysis, microscopy, and oscillatory viscoelastic measurements is presented here for estimating the interfacial tension, γ_{12}, of a partially miscible polymer mixture. The mixed composition of each of the bulk phases affects its complex modulus and T_g, along with γ_{12} and the blend morphology, as a whole. The inverted form of an appropriate rheological model connecting all the above properties is used to evaluate the interfacial tension. It is demonstrated that partial miscibility also affects the interfacial tension predictions obtained by the harmonic method.

I. Introduction

Interfacial tension of an immiscible polymer mixture comes from the excess free energy.[1] This is the result of the existence of interfacial region where the component molecules are mixed. The interfacial tension of immiscible polymer mixture was considered by Helfand and Tagami[2−4] within the framework of the mean-field approximation. When the component polymers are infinitely long chains, the interfacial tension can be written as[2−4]

$$\gamma_{12}^{\infty} = k_B T \frac{b}{v}\left(\frac{\chi_{12}}{6}\right)^{1/2} \tag{1}$$

where T is the temperature, b is the statistical segment, v is the specific monomer volume, k_B is the Boltzmann constant, and χ_{12} is the Flory−Huggins polymer−polymer interaction parameter. This model works well for immiscible symmetric polymers in the case of $\chi_{12}N \gg 1$, where N is essentially the degree of polymerization. Ermoshkin and Semenov[5] have derived the interfacial tension as eq 2 where the effect of $\chi_{12}N_i$ has been taken into account. Here N_i is essentially the degree of polymerization of polymer i.

$$\gamma_{12} = \gamma_{12}^{\infty}\left(1 - K\left(\frac{1}{\chi_{12}N_1} + \frac{1}{\chi_{12}N_2}\right)\right) \tag{2}$$

where $K = 2 \ln 2$. Similar formula have also been obtained with $K = \ln 2$ by Helfand and co-workers,[6] with $K = \pi^2/12$ by Broseta and co-workers[7] and with $K = 3[1 - (1/6)^{1/3}]$ by Tang and Freed.[8]

In the interfacial region of a polymer A and B mixture, free energy differs from the sum of free energy of bulk polymer A and B. The difference is the surface excess energy

$$F^E = F - F_A^0 - F_B^0 \tag{3}$$

where F, F_A^0, and F_B^0 are free energy of interfacial region, bulk polymer A phase, and bulk polymer B phase, respectively. For a partially miscible polymer mixture, a certain part of polymer B is diffused into bulk polymer A phase, and vice versa.[9−11] For this case, the volume fraction of polymer A in bulk polymer A phase and in bulk polymer B phase is not very close to 1 and 0, respectively. Here, we can say the interfacial tension in a partially miscible polymer A and B mixture is the tension in the interfacial region between polymer A-rich phase and polymer B-rich phase. Ermoshkin and Semenov's numerical calculations[8] show that the interfacial tension decreases about 10% by considering this partial miscibility when $\chi_{12}N$ is around 5.

Partially miscible polymer mixtures include bisphenol A polycarbonate (PC)−poly(methyl methacrylate) (PMMA),[9,10] polystyrene (PS)−PMMA,[11] PC−liquid crystalline polymer (LCP),[12] PC−poly(acrylonitrile−butadiene−styrene),[13] and others.[14]

Conventional methods[15] on measuring the interfacial tension of immiscible polymer mixture include pendant drop,[16] Neumann triangle,[17] breaking thread,[18] imbedded fiber retraction,[19,20] and rheological methods.[21−24] Most of these analyses consider the interfacial tension in the region between polymer A and B phases where the partial miscibility has not been taken into consideration.

In our present study, a method is presented to measure the interfacial tension of polymer A-rich phase and polymer B-rich phase from the linear viscoelasticity behavior, employing the hybrid approach[25] where double-reptation model[26−28] defines the complex modulus of the continuous phase and dispersion phase for input into the emulsion model.[29,30]

II. Theory

Linear Viscoelasticity of Bulk Phases. The bulk phases in a partially miscible polymer mixture is not in a pure state as discussed in the previous section. The double-reptation model of Tsenoglou[26,27] and des Cloizeaux[28] is often used to represent dynamic viscoelastic data of miscible linear polymer melts.[31] The double-reptation mixing rule is also available to define the complex modulus of bulk phases in a partially miscible polymer

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mixture.[25] The starting point is a mixing rule for the relaxation modulus

$$G(t) = [\sum_i \phi_i G_i^{1/2}(t)]^2 \tag{4}$$

where ϕ_i is the volume fraction of component i. The storage and loss moduli of the component 1-rich bulk phase are then given in terms of the pure-component properties, as follows:[25,27]

$$G'_{1-\mathrm{rich}}(\omega) \cong \sum_{i=1}^{2}\sum_{j=1}^{2}(G_{Ni}^0)^{1/2}(G_{Nj}^0)^{1/2}\phi_i'\phi_j'\left[1 + \frac{1}{4}\left(\left(\frac{G_{Ni}^0}{G_i'(\omega)} - 1\right)^{1/2} + \left(\frac{G_{Nj}^0}{G_j'(\omega)} - 1\right)^{1/2}\right)^2\right]^{-1} \tag{5}$$

$$G''_{1-\mathrm{rich}}(\omega) \cong \sum_{i=1}^{2}\sum_{j=1}^{2}(G_{Ni}^0)^{1/2}(G_{Nj}^0)^{1/2}\phi_i'\phi_j'(G_{ij} + 1/G_{ij})^{-1} \tag{6}$$

where

$$G_{ij} = \frac{G_{Ni}^0 - G_i'(\omega)}{2G_i''(\omega)} + \frac{G_{Nj}^0 - G_j'(\omega)}{2G_j''(\omega)} \tag{7}$$

G_N^0 denote the plateau modulus. The zero shear viscosity is obtained from the limit of G''/ω as ω goes to zero and is given by

$$\eta_{1-\mathrm{rich}}^0 = \eta_1^0\phi_1'^{\,2} + \frac{4\sqrt{G_{N1}^0}\sqrt{G_{N2}^0}\phi_1'\phi_2'}{G_{N1}^0/\eta_1^0 + G_{N2}^0/\eta_2^0} + \eta_2^0\phi_2'^{\,2} \tag{8}$$

where ϕ_i' and ϕ_j' are volume fractions of component i and j in component 1-rich phase, respectively. ϕ_i' and ϕ_j' can be measured experimentally.[10] For the case where the plateau modulus is the same for both members of the binary pair and $G_N^0 \gg G'$ and G'', eqs 5 and 6 reduced approximately to the following equations, which are independent of the plateau modulus:

$$G'_{1-\mathrm{rich}}(\omega) = \phi_1'^{\,2}G_1'(\omega) + \frac{8G_1'(\omega)G_2'(\omega)\phi_1'\phi_2'}{G_1'(\omega) + 2\sqrt{G_1'(\omega)}\sqrt{G_2'(\omega)} + G_2'(\omega)} + \phi_2'^{\,2}G_2'(\omega) \tag{9}$$

$$G''_{1-\mathrm{rich}}(\omega) = \phi_1'^{\,2}G_1''(\omega) + \frac{4G_1'(\omega)G_2'(\omega)\phi_1'\phi_2'}{G_1'(\omega) + G_2'(\omega)} + \phi_2'^{\,2}G_2''(\omega) \tag{10}$$

With a similar procedure, the dynamic modulus of component 2-rich phase can be evaluated.

The double-reptation model has a definite limit for bidisperse systems but works satisfactorily for polydisperse systems with broad molecular weight distribution (including the PC and PMMA systems examined in this study). Following the ideas of Milner[32] and Tuminello,[33] Lee and Denn[25] have shown that the double-reptation combining rule works well for highly polydisperse components, though the double-reptation combining rule assumes that the two components are monodisperse. The double-reptation combining rule also assumes that the two components have similar glass transition temperature (T_{g}). When the T_{g}s of two components are dramatically different, the monomeric frictions of the components in mixed state may be different from those in the pure state at the identical temperature.[34−36] This difference comes from the change of effective glass transition temperature of components by mixing. This difference may be compensated by using the dynamic moduli of each component measured at the same temperature from the effective glass transition temperature in eqs 5 and 6. For example, the dynamic moduli of PC in the pure state were measured at $T_{\mathrm{g}1} + \Delta T$ for input into eqs 5 and 6, where $T_{\mathrm{g}1}$ is the T_{g} of PC in the pure state, $\Delta T = T - T_{\mathrm{g}1}'$, and $T_{\mathrm{g}1}'$ is the T_{g} of PC in the PC-rich phase.

Interfacial Tension from the Emulsion Model. The interfacial tension contributes to the storage modulus when the relaxation time due to interfacial tension is longer than the measuring time (reciprocal frequency) in the oscillatory shear measurement. The Palierne emulsion model is available to estimate the interfacial tension from the dynamic measurement.[21−24,37] In this model, the only fitting parameter is Laplace pressure, γ_{12}/R_v, where R_v is the volume average radius of dispersion droplets. When the droplet polydispersity is less than 2.3, the volume average radius can be used as in eq 12 in place of the size distribution.[38] When we know the complex modulus of matrix phase and dispersion phase, the complex modulus of the mixture are obtained by the emulsion model as follows:[29,30]

$$G^* = G_{\mathrm{M}}^* \frac{1 + 3\phi^{\mathrm{D}}H^*}{1 - 2\phi^{\mathrm{D}}H^*} \tag{11}$$

where

$$H^* = \frac{4(\gamma_{12}/R_v)[2G_{\mathrm{M}}^* + 5G_{\mathrm{D}}^*] + [G_D^* - G_{\mathrm{M}}^*][16G_{\mathrm{M}}^* + 19G_{\mathrm{D}}^*]}{40(\gamma_{12}/R_v)[G_{\mathrm{M}}^* + G_{\mathrm{D}}^*] + [2G_{\mathrm{D}}^* + 3G_{\mathrm{M}}^*][16G_{\mathrm{M}}^* + 19G_{\mathrm{D}}^*]} \tag{12}$$

where G_{M}^* and G_{D}^* are complex moduli of matrix and dispersion phases, which are calculated by eqs 5 and 6. The relaxation time due to the Laplace pressure is

$$\tau_{\mathrm{D}} = \frac{R_v\eta_{\mathrm{M}}}{4\gamma_{12}}\frac{(19K + 16)(2K + 3 - 2\phi^{\mathrm{D}}(K - 1))}{10(K + 1) - 2\phi^{\mathrm{D}}(5K + 2)} \tag{13}$$

where ϕ^{D} is bulk volume fraction of dispersion phase which is different from the bulk composition before mixing. ϕ^{D} can be measured by experimentally.[9] K is the zero shear viscosity ratio of the dispersion and matrix. When the experimental data are enough in the terminal region, the relaxation time can be directly determined from the relaxation time spectrum.[39]

III. Experimental Section

Polymers. The PC and PMMA used in this study were LG-DOW 201-15 and LG IH830, respectively (Table 1). The molecular weight and the glass transition temperatures were measured using the procedure reported elsewhere.[10,11] Mixtures of PC/PMMA in weight fractions of 1.0, 0.8, 0.6, 0.4, 0.2, and 0.0 are prepared by a corotating twin-screw extruder at 523 K.

Rheology. Oscillatory shear measurements were carried out on a Rheometrics mechanical spectrometer RMS 800 under a nitrogen atmosphere at 523 K for all mixtures. The dynamic moduli of pure PC were measured at $T_{\mathrm{g}1} + (523 - T_{\mathrm{g}}{'}_1)$ and

Table 1. Characteristics of Polymer Samples Used in PC−PMMA Mixtures

sample	$\bar{M}_w$ [a]	$\bar{M}_n$ [a]	T_g, K[b]	ΔC_p, J g^{-1} K^{-1} [b]
PC[c]	58 069	21 681	423.6	0.21
PMMA[d]	80 778	43 623	380.3	0.2

[a] Measured in our laboratory by GPC (tetrahydrofuran 25 °C). [b] Measured in our laboratory by DSC. [c] LG-DOW 201-15. [d] LG Chem. IH830.

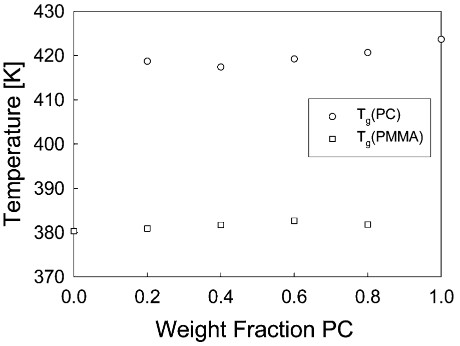

Figure 1. Effect of mixture composition on the T_g(PC) and T_g(PMMA) for PC−PMMA mixtures.

$T_{g1} + (523 - T_{g1}'')$ for input into the double-reptation combining rule, and the dynamic moduli of pure PMMA were measured at $T_{g2} + (523 - T_{g2}')$ and $T_{g2} + (523 - T_{g2}'')$. The disk samples were prepared by a compression molding at 523 K. Oscillatory shear measurements were made at 5% strain, which was within the linear range for all samples. 200 and 2000 g transducers were used in the low- and high-frequency ranges, respectively.

Scanning Electron Microscopy. The molded samples were annealed for 15 min in the oven at 523 K to obtain an equilibrium morphology of dispersions. The morphology of the cross section of the molded samples prepared by cryogenic fracturing was examined by JEOL scanning electron microscopy (SEM) after gold sputter coating. The volume-average radius of droplets (R_v) was determined from several micrographs.

IV. Results and Discussion

Thermal Properties and Phase Compositions. PC−PMMA are known to be partially miscible,[10] and two glass transitions are observed in Figure 1. The glass transition temperatures of PC in the PC−PMMA mixtures are shown to decrease with an increase in the PMMA weight fraction, and the glass transition temperatures of PMMA in PC−PMMA mixtures are shown to increase with an increase in the PC weight fraction. This is a definitive evidence of the partial miscibility of the PC and PMMA. Fox equation is available to obtain the apparent weight fraction of PC-rich phase and PMMA-rich phase as in eqs 14 and 15.[10]

$$w_2' = \frac{T_{g2}(T_{g1} - T_g')}{T_g'(T_{g1} - T_{g2})} \tag{14}$$

$$w_1'' = \frac{T_{g1}(T_{g2} - T_g'')}{T_g''(T_{g2} - T_{g1})} \tag{15}$$

where w_2' is the apparent weight fraction of polymer 2 in the polymer 1-rich phase. T_{gi}' is the observed T_g of polymer i (= 1 and 2 for PC and PMMA), and T_{gi} is the T_g of the unmixed polymer i. Furthermore, the bulk compositions after mixing are expressed as eqs 16 and 17.[9]

Table 2. Apparent Weight Fraction (w) of PC and PMMA Components in the PC-Rich Phase and the PMMA-Rich Phase and Bulk Weight Fraction (W) of PC-Rich Phase and PMMA-Rich Phase

	PC/PMMA (80/20)[a]	PC/PMMA (60/40)[a]	PC/PMMA (40/60)[a]	PC/PMMA (20/80)[a]
w_2' [b]	0.07	0.11	0.15	0.12
w_1'' [b]	0.05	0.08	0.04	0.02
W' [b]	0.85	0.64	0.44	0.21

[a] Mixture composition given as overall weight fraction. [b] Single prime and double prime denote PC-rich phase and PMMA-rich phase, respectively, and subscripts 1 and 2 denote PC and PMMA components.

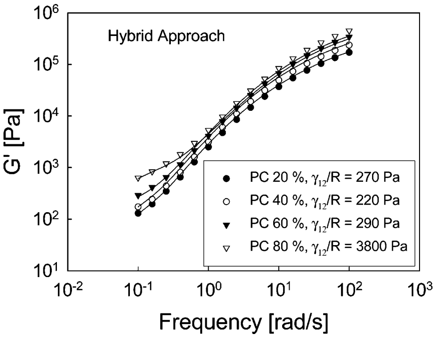

Figure 2. Storage modulus of the PC−PMMA mixtures at 523 K compared with the curves computed from the hybrid approach using eqs 5, 6, and 11.

$$W' = \frac{W_2 - w_2''}{w_2' - w_2''} \tag{16}$$

$$W = \frac{W_2 - w_2'}{w_2'' - w_2'} \tag{17}$$

where w' is the apparent weight fraction of polymer 1-rich phase and W_2 is the weight fraction of polymer 2 in the mixture. The apparent weight fractions of PC and PMMA in the PC-rich phase and the PMMA-rich phase are shown in Table 2. Also, the bulk weight fraction of PC-rich phase (W') and PMMA-rich phase (W'') are shown in Table 2. Here the volume fraction of dispersion phase in eq 11 can be evaluated. We can use the weight fractions in Table 2 as the volume fractions because the melt density of PC is almost same as that of PMMA at 523 K.[10]

Linear Viscoelasticity and Interfacial Tension. The storage modulus of the PC−PMMA mixtures at 523 K is shown in Figure 2, together with the curves computed from the hybrid approach using eqs 5, 6, and 11. The plateau moduli of PC and PMMA at 523 K were determined for these calculations and found to be 2.31 × 10^5 Pa for the PC and 4.34 × 10^5 Pa for the PMMA. The agreement is very good with the indicated Laplace pressure (γ_{12}/R_v) as a fitting parameter. Here, it is worth noting that the PC/PMMA (60/40) and (40/60) mixtures show cocontinuous morphology even after long time annealing.[9] So the emulsion model may be not valid for these compositions. The PC/PMMA (80/20) mixture also shows cocontinuous morphology in the injection-molded specimen as shown in Figure 3a but shows droplet morphology after 15 min annealing at 523 K in Figure 3b. For the PC 80% mixture, the Laplace pressure is 3800 Pa by the hybrid approach. When the partial

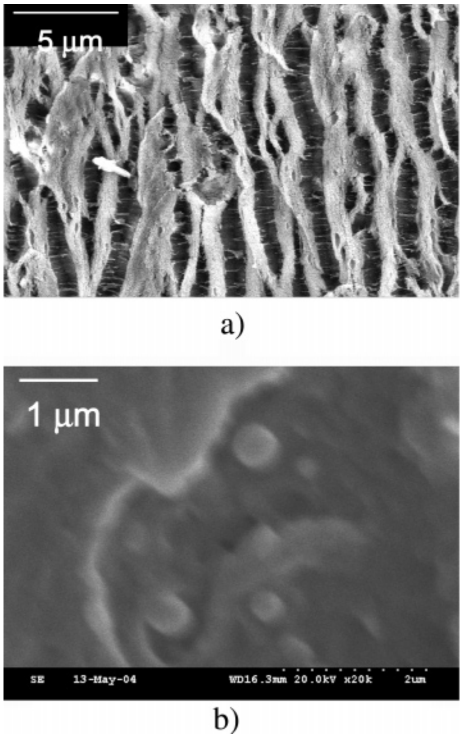

Figure 3. Scanning electron micrograph obtained from cryogenically fractured cross-sectional surfaces of injection-molded specimen of PC/PMMA (80/20) mixture. (a) Injection-molded specimen; PC is etched by 30% NaOH solution. (b) 15 min annealing at 523 K.

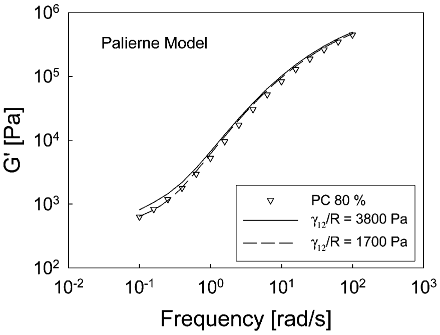

Figure 4. Storage modulus of PC/PMMA (80/20) mixture compared with the curves computed from the Palierne model, neglecting the partial miscibility.

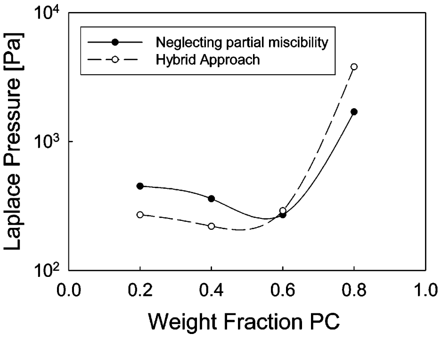

Figure 5. Laplace pressure of PC−PMMA mixtures for all compositions.

miscibility is not taken into account, the Laplace pressure is 1700 Pa in Figure 4. The Laplace pressures for all compositions are plotted in Figure 5. We can see the Palierne model overestimate the Laplace pressure in the PMMA-rich mixtures and underestimate the Laplace pressure in the PC-rich mixtures when we neglect the changes of complex modulus in each bulk phase. The volume average droplet radius (R_v) is 600 nm for the PC 80% mixture (Figure 3b). For this case, the interfacial tension from the hybrid approach is 2.28 mN/m. Neglecting the partial miscibility, the interfacial tension determined by the Palierne model is 1.02 mN/m. PMMA is also partially miscible with polystyrene (PS).[11] The relaxation time of PS droplets in the PMMA matrix at 463 K is measured as 6.5 s by Rieman and co-workers.[21] The interfacial tension can be calculated by eq 13 and found to be 2.2 mN/m. If we apply the hybrid approach to this system, the interfacial tension is recalculated as 1.8 mN/m. Here, we can see that the effect of considering the partial miscibility is significant in the measurement of interfacial tension, and the partial miscibility should be taken into account in any experimental methods to measure the interfacial tension.

Flory−Huggins Polymer−Polymer Interaction Parameter (χ_{12}). In this section, we are to compare the interfacial tension determined by the hybrid approach with the calculated interfacial tension by using eq 2. In calculation, the lattice site volume can be determined in an arbitrary way.[8] But the calculation results are significantly changed by the statistical segment (b) and the χ_{12} value. For a PS−PMMA mixture, the interfacial thickness is measured by Kressler and co-workers as 50 ± 30 Å.[40] If we use the interfacial thickness of 50 Å, the χ_{12} is determined to be 0.024 with the interfacial tension of 1.8 mN/m by using eq 2. This value is comparable to the composition-dependent χ_{12} values determined by Kim and Burns,[11] which is 0.02−0.024. For a PC−PMMA mixture, we do not have the interfacial thickness value. So we are to evaluate the interfacial thickness with the interfacial tension of 2.28 mN/m and the χ_{12} of 0.04.[10] The interfacial thickness is calculated to be 95 Å, which seems reasonable value compared to the similar system.[6,40] It is worth nothing that the interfacial tensions determined by the hybrid rheological approach are almost consistent with the conventional thermodynamic models represented as eq 2, though these thermodynamic models assume that bulk phases compositions are close to the pure state.

Harmonic Method. The harmonic method is often used for the measurement of the interfacial tension between two polymers.[41] The harmonic mean equation is

$$\gamma_{12} = \gamma_1 + \gamma_2 + \frac{4\gamma_1^{\mathrm{d}}\,\gamma_2^{\mathrm{d}}}{\gamma_1^{\mathrm{d}} + \gamma_2^{\mathrm{d}}} + \frac{4\gamma_1^{\mathrm{p}}\,\gamma_2^{\mathrm{p}}}{\gamma_1^{\mathrm{p}} + \gamma_2^{\mathrm{p}}} \qquad (18)$$

where γ_1 and γ_2 are surface tension of components 1 and 2. Superscript d and p denote dispersive and polar component of the surface tension, respectively. The surface tension of injection-molded specimens of PC and PMMA were measured by using the contact angle measuring system G2 (KRUSS GmbH, Germany) following the procedure as reported elsewhere.[41−43] In the PC/PMMA (80/20) mixture, the PC-rich phase contains 7% of PMMA and the PMMA-rich phase contains 5% of PC in Table 2. The PC/PMMA (93/7) and PC/PMMA (5/95) mixtures were prepared by the melt extrusion. We measured the surface tension of injection-molded specimens of the PC/PMMA (93/7) mixture and the PC/PMMA (5/95) mixture. The surface tensions are reported in Table 3. The interfacial tension between PC and PMMA is calculated to be 3.19 mN/m at 523 K by using eq 18, while the interfacial tension between the PC-rich

Table 3. Surface Tension of PC−PMMA Mixtures and Components by Contact Angle Measurements

material	γ	γ^{d}	γ^{p}	$-(\mathrm{d}\gamma/\mathrm{d}T)$
PMMA	38.25	26.39	11.85	0.07
PC	45.35	38.10	7.25	0.06
PC/PMMA (93/7)	41.98	35.26	6.72	0.06
PC/PMMA (5/95)	38.43	26.90	11.53	0.07

mixture and the PMMA-rich mixture is calculated to be 2.01 mN/m at 523 K by using eq 18, which is close to the interfacial tension from the hybrid rheological approach.

V. Conclusions

In this paper, we present an indirect method for estimating the interfacial tension of a partially miscible polymer mixture; it utilizes thermal, viscoelastic, and microscopy measurements. For a PC−PMMA mixture where the complex modulus of each of the bulk phases is changed after mixing, the interfacial tension is determined to be 2.28 mN/m at 523 K. If changes of complex modulus are neglected, the interfacial tension is 1.02 mN/m. For a PS−PMMA mixture, the interfacial tension is recalculated using the hybrid approach and found to be 1.8 mN/m, in accord with data from the literature.[21] The interfacial tension of PC−PMMA and PS−PMMA mixtures evaluated via the hybrid approach are almost consistent with the thermodynamic calculations using eq 2. This work, therefore, stresses the importance of realistically assuming that each of the separate phases is actually a miscible blend rather than approximating it as a pure ingredient and of accounting for changes of the complex modulus of each of the bulk phases of mixed composition. It also demonstrates that partial miscibility strongly affects the interfacial tension predictions obtained by the harmonic method.

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