Ellipsometric studies on immiscible polymer–polymer interfaces

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Ellipsometry was employed to estimate the thickness of the interface λ between two bulk layers of dissimilar polymers. The polymer/polymer combinations investigated were poly(methyl methacrylate) (PMMA)/poly(styrene-*co*-acrylonitrile) (SAN) (AN content <10 and >33 wt%), PMMA/poly(methyl methacrylate-*co*-styrene) (MS) and polystyrene/MS. They provide a series of immiscible combinations with various values of the Flory interaction parameter χ ranging from 1.72×10^{-3} to 8.71×10^{-2}. The bilayer specimen prepared by the spin-coating technique was annealed at 130°C ($>T_g$) and the time variation of λ was observed during annealing. The observed λ attained a constant value after annealing for $\sim$1 h and then remained constant. The constant value was assumed to be the equilibrium thickness. The thickness ranged from $\sim$5 to 40 nm, depending on the magnitude of χ. The thin interface ($< \sim 10$ nm) was nicely explained by the recent theory by Broseta *et al.*, which deals with the effect of molecular weight on λ within the strong segregation limit.

(Keywords: ellipsometric studies; immiscible; polymer–polymer interface)

INTRODUCTION

In our previous papers, we established the experimental technique for the ellipsometric analysis of the interfacial thickness between two bulk layers of dissimilar polymers[1] and applied it to the kinetics of interdiffusion of miscible polymers[2]. In this paper, we extend the analysis to the interface between immiscible polymers.

There are many theoretical[3–8] and experimental studies[9–13] on the interface between immiscible polymers. Among them, the most interesting is the recent theory by Broseta *et al.*[8]. It is a modified version of the Helfand–Tagami theory[5] and deals with the effect of molecular weights and polydispersity of the component polymers on the interfacial thickness and interfacial tension. The theory stimulated experimental studies on the polymer interface to reveal the relationship between the interfacial properties and the molecular and thermodynamic parameters of the component polymers.

In this paper, we measure the interfacial thickness between immiscible polymers by ellipsometry and discuss the results in the light of the recent theory by Broseta *et al.* The immiscible polymer/polymer combination employed was poly(methyl methacrylate) (PMMA)/poly(styrene-*co*-acrylonitrile) (SAN). The PMMA/SAN system offers a unique opportunity for experimentation. First, the difference in the refractive index between PMMA(1) and SAN(2) is large enough for ellipsometry ($n_1 - n_2 > 0.02$). Second, by changing the acrylonitrile (AN) content of SAN, one can set up a series of immiscible combinations with various degrees of immiscibility (or various magnitudes of the Flory interaction parameter χ), as demonstrated by the miscibility window in *Figure 1*[2]. The asterisks in *Figure 1* represent the experimental points in this study. Also employed were the PMMA/poly(methyl methacrylate-*co*-styrene) (MS) and polystyrene (PS)/MS systems. In these systems, the value of χ can also be changed by changing the copolymer composition and the effect of χ on the interfacial thickness can be investigated.

EXPERIMENTAL

The polymer specimens used in this study and their characteristics are shown in *Tables 1* and *2*. SAN and PMMA were prepared and supplied by Mitsubishi-Kasei Polytech. Co., Ltd and Sumitomo Chemical Co., Ltd, respectively. PS and MS were commercial polymers.

We prepared a bilayer specimen composed of a thin

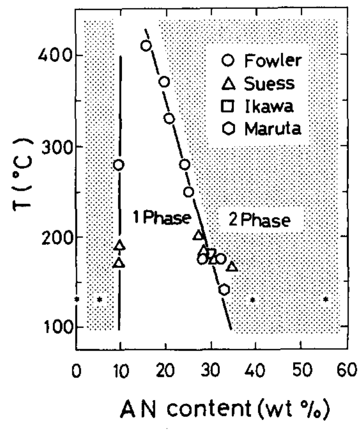

Figure 1 Miscibility window of the PMMA/SAN system (from ref. 2). Asterisks show the experimental points in this study

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Table 1 Characteristics of the polymer specimens

Code	AN content[a] (wt%)	$M_w(\times 10^{-4})$[b]	M_w/M_n[b]	n[c]
SAN-55	55.0	2.1	1.8	1.555
SAN-40	38.7	7.4	2.2	1.564
SAN-5	5.7	25.9	2.2	1.583
SAN-0(=PS)	0	18.0	2.0	1.590
PMMA	–	15.1	2.1	1.488

[a] From elemental analysis
[b] From g.p.c.
[c] Refractive index by ellipsometry ($\lambda' = 546.1$ nm)

Table 2 Characteristics of the polymer specimens

Code	MMA content[a] (mol%)	$M_w(\times 10^{-4})$[b]	M_w/M_n[b]	n[c]
MS-20	24.0	19.9	2.2	1.561
MS-30	32.8	18.3	2.1	1.555
MS-60	58.9	12.5	2.0	1.525

[a] From n.m.r.
[b,c] See *Table 1*

(~600–700 nm) SAN film and a thick (~0.5 mm) PMMA substrate. The substrate was prepared by melt-pressing between two silicon wafers to create an optically flat surface. The thin film was prepared by spin-coating onto a silicon wafer. The latter was mounted on the former by the floating-on-water and pick-up technique[2]. The bilayer specimen thus prepared was dried under vacuum (10^{-2} Pa) at 60°C for 24 h. We also prepared bilayer specimens of different combinations; thin MS film on PMMA and thin MS film on PS.

The bilayer specimen was inserted into a hot chamber kept at 130°C and annealed under a nitrogen atmosphere. Then, after appropriate intervals, it was quenched at ambient temperature and used for ellipsometry. The ellipsometric measurement was carried out using a Simadzu ellipsometer (model EP-10, Simadzu Manufacturing Co., Ltd). Incident light of $\lambda' = 546.1$ nm was applied to the bilayer specimen at an incident angle of 70°. The retardation Δ and reflection ratio $\tan\psi$ of reflected light were determined from ellipsometric readings. For data analysis, we used the four-layer model as shown in *Figure 2*[7]. Since the values of the refractive indices n_1, n_2 and n_4 and the thickness d_2 are known, one can estimate n_3 and d_3 by selecting the best set of these values to fit the observed values of Δ and $\tan\psi$ for the four-layer model:

$$\rho = \frac{R_m^p}{R_m^s} = \frac{|R_m^p|\exp(i\Delta_p)}{|R_m^s|\exp(i\Delta_s)} = \frac{|R_m^p|}{|R_m^s|}\exp\{i(\Delta_p - \Delta_s)\} = \tan\psi\exp(i\Delta) \qquad (1)$$

$$R_m^v = \frac{r_m^v + R_{m+1}^v\exp(-iD_{m+1})}{1 + r_m^v R_{m+1}^v\exp(-iD_{m+1})} \qquad (v = \mathrm{p,s}) \qquad (2)$$

$$D_m = 4\pi n_m d_m \cos\theta_m/\lambda' \qquad (3)$$

where ρ is the relative amplitude of the parallel (R_m^p) to the perpendicular (R_m^s) reflection coefficient in the incident plane, n_m and d_m represent the refractive index and thickness of the mth layer, respectively, and r_m is the Fresnel reflection coefficient at the boundary between the mth and $(m+1)$th layers:

$$r_m^p = \frac{n_{m+1}\cos\theta_m - n_m\cos\theta_{m+1}}{n_{m+1}\cos\theta_m + n_m\cos\theta_{m+1}}$$
$$r_m^s = \frac{n_m\cos\theta_m - n_{m+1}\cos\theta_{m+1}}{n_m\cos\theta_m + n_{m+1}\cos\theta_{m+1}} \qquad (4)$$

$$n_1\sin\theta_1 = n_2\sin\theta_2 = n_3\sin\theta_3 = n_4\sin\theta_4 \qquad (5)$$

Numerical calculation for the best fit was carried out by a Hitachi computer (Hitac M-660K). The four-layer model in *Figure 2a* implies that the refractive index at the interface is approximated to being uniform and equal to $n_3 = (n_1 + n_2)/2$ (*Figure 2b*). Taking account of the composition profile at the interface[5,7,8], the interfacial thickness λ was determined as $\lambda = d_3/1.7$ (*Figure 2b*).

RESULTS AND DISCUSSION

Figure 3 shows the interfacial thickness λ of SAN/PMMA systems as a function of annealing time at 130°C. Here the SAN specimens have various AN contents. Note that all the SAN specimens are located outside the single-phase regime in *Figure 1*. The observed λ attains a constant value within ~1 h and then remains constant. The constant value in the later stages is assumed to be the equilibrium thickness. The values of the equilibrium thickness thus estimated are in the order of nanometres to tens of nanometres depending on the AN content. According to the recent neutron critical reflection analysis by Fernandez *et al.*[13], the λ value of the PS/deuterated PMMA system is estimated to be ~2 nm. This is close to our result in *Figure 3* (see the SAN-0

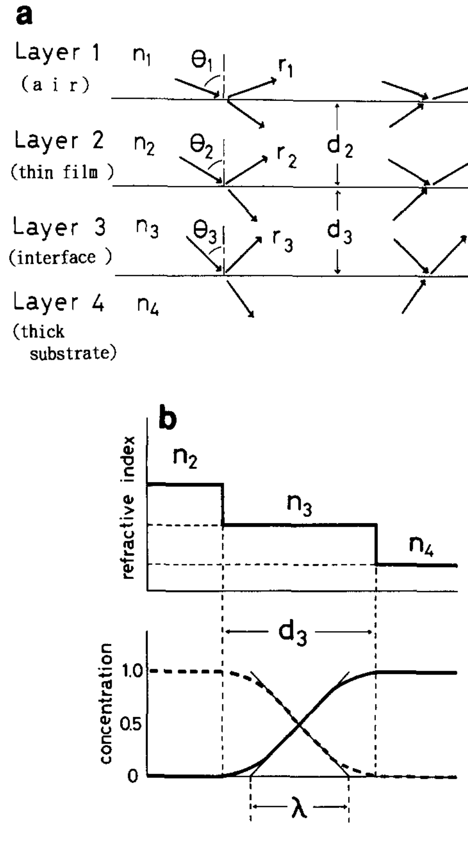

Figure 2 (a) Four-layer model for ellipsometric analysis. (b) Concentration profile at the polymer–polymer interface and a stepwise approximation of the refractive index profile for ellipsometry

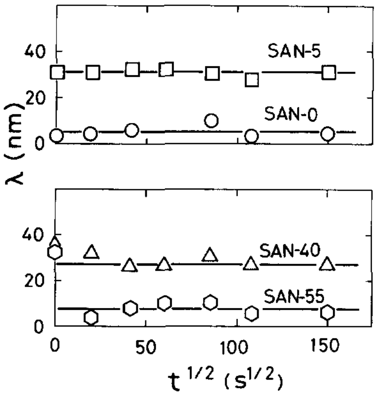

Figure 3 Time variation of the interfacial thickness of PMMA/SAN systems during annealing at 130°C

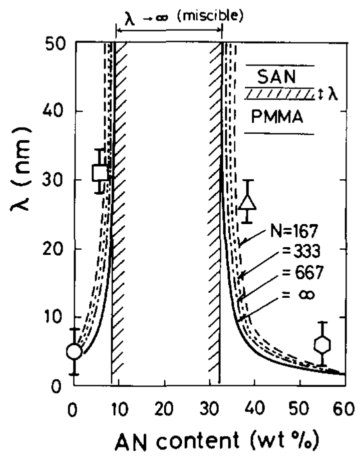

Figure 4 Interfacial thickness *versus* AN content of SAN. Symbols are the same as in *Figure 2*. The four curves are calculated using equation (9) assuming $N_A=N_B=N$: $N=167$ (broken), $N=333$ (dotted), $N=667$ (chain) and $N=\infty$ (solid). This demonstrates that equation (9) is applicable only for the thin interface

system). If one plots λ *versus* AN content, one finds that the larger the deviation from the single-phase region, the thinner is λ, as shown in *Figure 4*. It is interesting to compare the results with theory.

From Helfand and Tagami[5], the interfacial thickness between dissimilar polymers having infinite molecular weights is given by:

$$\lambda_\infty=2b/(6\chi)^{1/2} \qquad (6)$$

where b is the Kuhn segment length. The χ values of the SAN/PMMA system may be adequately estimated by the binary interaction model[14]:

$$\chi=BV_r/RT \qquad (7)$$

$$B=B_{13}\phi_1+B_{23}\phi_2-B_{12}\phi_1\phi_2 \qquad (8)$$

where B_{ij} is the interaction parameter between components i and j (1 = styrene, 2 = AN and 3 = MMA; $B_{13}=0.181$, $B_{23}=4.11$ and $B_{12}=6.74\,\mathrm{cal\,ml^{-1}}$), V_r is a reference volume (molar volume of the segment, assumed to be $80\,\mathrm{ml\,mol^{-1}}$), R is the gas constant, T is the absolute temperature and ϕ_i is the copolymer composition of SAN. Then, assuming $b=0.8$ nm, one can calculate λ as a function of AN content. The results are shown by the solid line in *Figure 4*. The solid line interprets the trend mentioned above, i.e. the higher χ, the thinner λ. However, nice agreement between the theoretical and observed values is seen only for PMMA/PS(= SAN-0) and there exists a definite deviation for other combinations.

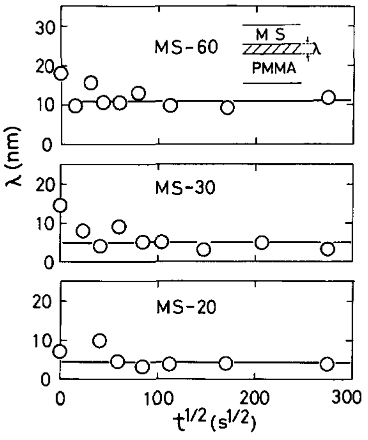

Figure 5 Time variation of the interfacial thickness of the PMMA/MS system

Recently, the Helfand–Tagami theory was modified by Broseta *et al.*[8] to involve the molecular weight dependence of λ:

$$\lambda=\frac{2b}{(6\chi)^{1/2}}\left[1+\frac{\ln 2}{\chi}\left(\frac{1}{N_A}+\frac{1}{N_B}\right)\right] \qquad (9)$$

where N_i is the degree of polymerization in polymer i (the number of Kuhn segments per chain). On the basis of equation (9), we carried out case studies assuming $N_A=N_B=N$ and employing three values of N (= 167, 333 and 667; the N values correspond to $M_n=5\times10^4$, 10×10^4 and 20×10^4, respectively)*. The results are shown by broken, dotted and chain lines. This situation was made better by taking into account the molecular weight dependence, but there still existed a deviation between the observed and the calculated values for the thick interface. This is not surprising, because the theory is for the strong segregation regime, i.e. the theory is valid for an interface thinner than the coil size of the component polymers. The deviation could be partly caused by the composition distribution in SAN, e.g. for the PMMA/SAN-40 system, a fraction with less AN content preferentially locates near the interface† and may render a thicker interface than expected from the overall AN content of 40.

Figure 5 shows the time variation of the interfacial thickness in MS/PMMA systems during annealing at 130°C. The λ values in the late stages, which are assumed to be the equilibrium ones, are plotted as a function of MMA content in *Figure 6*. As expected, λ increases with increasing MMA content, i.e. with decreasing χ. The data are located between the two lines calculated by equations (6) and (9). The agreement between the measured and the calculated λ is much better than in the SAN/PMMA systems in *Figure 4*. This is to be expected, because all the λ values in *Figure 5* are small and within the strong segregation limit for which equations (6) and (9) are valid.

Figure 7 shows the time variation of the interfacial

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* The N or M_n values cover the range of those of the polymer specimens in this paper

† The composition in SAN-40 is far from the azeotrope in copolymerization. Copolymer chains with less AN content have smaller χ with PMMA (see *Figure 1*)

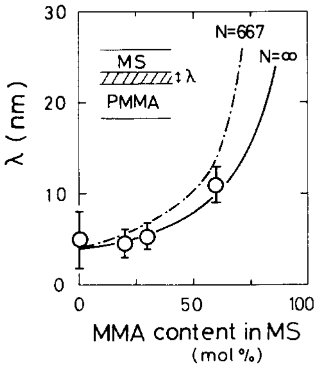

Figure 6 Interfacial thickness *versus* MMA content in MS. Chain and solid lines indicate λ calculated using equation (9), assuming $N(=N_A=N_B)$ is 667 and ∞, respectively

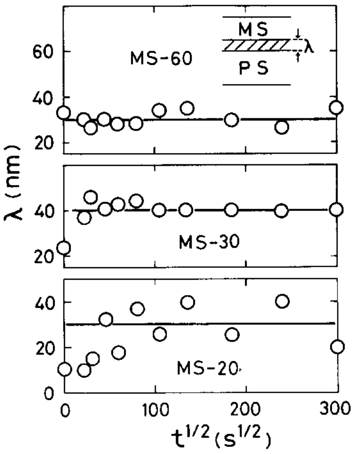

Figure 7 Time variation of the interfacial thickness of the PS/MS system

thickness in MS/PS systems during annealing. In the systems with small χ (see *Table 3*), the interface is shown to be very thick. Although the observed values of λ are out of the strong segregation limit, we calculated the λ values by equation (9) using the molecular weights of each component polymer and compared these with the observed values in *Table 3*. Serious differences are seen in *Table 3*. This suggests a limit to the applicability of equation (9) to thick interfaces.

Table 3 Interfacial thicknesses of the MS/PS systems

Combination	$\lambda_{obs.}$ (nm)[a]	$\lambda_{calc.}$ (nm)[b]	$\chi(\times 10^2)$[c]
MS-60/PS	30±5	10	1.012
MS-30/PS	40±3	28	0.323
MS-20/PS	30±10	56	0.172

[a] From *Figure 7*

[b] From equation (9)

[c] From equations (7) and (8), where B is simplified to $B_{12}\phi_2^2$

CONCLUSIONS

The interfacial thickness λ in a series of dissimilar polymer/polymer combinations with different χ was measured by ellipsometry. The observed values of λ ranged from 5 to 40 nm, depending on the degree of immiscibility χN. The thin interface ($< \sim 10$ nm) was nicely interpreted by a recent theory by Broseta *et al.*, which was presented for the polymer–polymer interface within the strong segregation limit.

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