Ellipsometric analysis on the *in situ* reactive compatibilization of immiscible polymer blends

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Time-resolved ellipsometric analysis was carried out to investigate the change in interfacial thickness between amorphous nylon and styrenic polymers during annealing at high temperatures (170–210°C). The styrenic polymers were neat poly(styrene-*co*-maleic anhydride) (SMA) and single-phase mixtures of SMA with poly(styrene-*co*-acrylonitrile) (SAN). Here SMA is known to be reactive with the chain end of nylon, forming a graft copolymer at the interface between the phases. The interfacial thickness increased with annealing time and then attained a constant value, depending on temperature and net concentration of reactive sites (maleic anhydride units) in the styrenic phase. The interface established at late stages was tremendously thick, ranging from 10 to 50 nm. The thickest interface is several times the coil size of the component polymer. This may suggest drawing of the whole graft copolymer chain into the interface to establish a smooth concentration gradient at the interface. Formation of such a thick interface seems to be characteristic of a reactive system in which chemical reaction induces deviation from an equilibrium interface in a ternary system consisting of polymer A, polymer B and A–B graft or block copolymer. Thus the study provided a preliminary understanding of the *in situ* reactive compatibilization of polymer blends in terms of the interfacial problem.

(Keywords: immiscible blends; ellipsometry; reactive processing)

INTRODUCTION

Much attention has been paid to the reactive processing of immiscible polymer blends. This approach is effective to control morphology and to design high-performance polymer blends. Reactive processing involves *in situ* reaction of functionalized components to form a block or graft copolymer at the interface between the phases[1–9]. The copolymer is believed to play the role of an emulsifier, which provides a fine morphology and increases the adhesive strength between the two phases. However, so far there have been limited studies on the interface of compatibilized blends.

In our previous articles, we established the experimental technique for ellipsometric analysis on the interfacial thickness between two bulk layers of dissimilar polymers[10] and applied it to the kinetics of interdiffusion of miscible polymers[11] and to the equilibrium interfacial thickness of immiscible ones[12]. In this paper, we extend the analysis to the interface in reactive blends. We carry out ellipsometric analysis on the time variation of interfacial thickness during reaction. The polymer/polymer combinations employed are amorphous nylon (polyamide)/poly(styrene-*co*-maleic anhydride) (aPA/SMA) and amorphous nylon/poly(styrene-*co*-acrylonitrile) (aPA/SAN) containing a small amount of SMA. The amino end-group of aPA is expected to react with the maleic anhydride (MA) unit of SMA[6,7]. The polymer/polymer systems offer a nice opportunity for experimentation: first, the difference in refractive index between aPA (1) and the styrenic polymer (2) phases is large enough for ellipsometric measurement at the reaction temperature ($n_1 - n_2 > 0.02$); secondly, by changing the MA content in SMA and the loading of SMA on SAN, one can set up a series of polymer/polymer combinations with different concentrations of reactive groups in the styrenic phase.

EXPERIMENTAL

The polymer specimens used in this study and their characteristics are shown in *Table 1*. SAN-25 (acrylonitrile content = 25 wt%) and SMA-23 (MA content = 23 wt%) were kindly prepared and supplied by Mitsubishi-Kasei Polytech Co. Ltd. SMA-8, SMA-14 and aPA were commercial polymers.

We prepared a bilayer specimen composed of a thin (ca. 600–700 nm) SMA film and a thick (ca. 0.5 mm) aPA 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 of 6 wt% solution in chlorobenzene onto a silicon wafer, and the thickness was measured by the stylus method. The latter was mounted on the former by the floating-on-water and pick-up technique[10,11]. The bilayer specimen thus prepared was dried under vacuum

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Table 1 Characteristics of polymer specimens

Code	$M_w \times 10^{-4\,a}$	$M_w/M_n{}^a$	T_g^b (°C)
SMA-8[c]	22.3	2.2	112
SMA-14[c]	17.1	2.2	123
SMA-23[c]	11.9	2.1	142
SAN-25[d]	15.6	2.0	105
aPA[e]	1.5–2.0[f]	–	97

[a] From g.p.c.

[b] From d.s.c.

[c] Poly(styrene-*co*-maleic anhydride)

[d] Poly(styrene-*co*-acrylonitrile)

[e] Amorphous nylon (Grilamide TR55LX, EMS Japan Co.); prepared by polycondensation of isophthalic acid, 4,4′-diamino-3,3′-dimethyl-dicyclohexylmethane and laurolactam

[f] Viscosity-average molecular weight

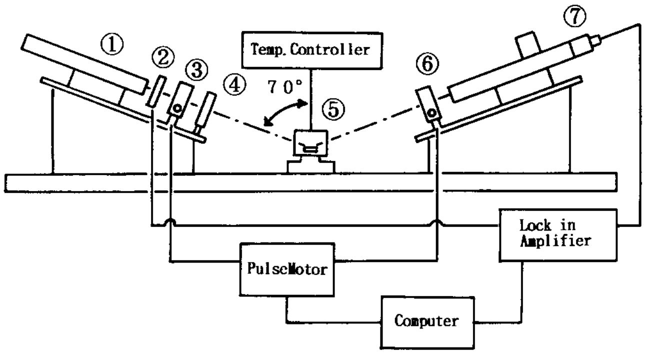


Figure 1 The automated ellipsometer: (1) He–Ne laser, (2) chopper, (3) polarizer, (4) compensator, (5) hot chamber, (6) analyser and (7) photodiode

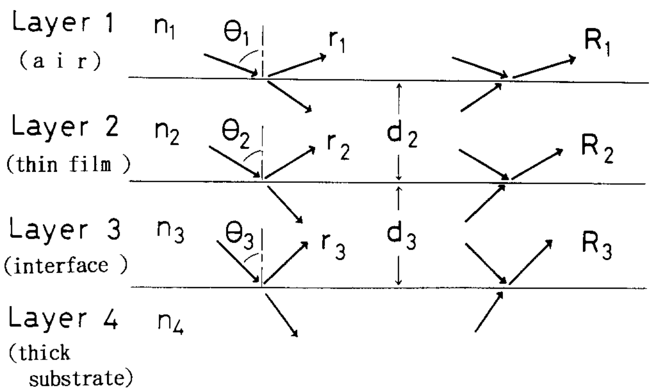


Figure 2 Four-layer model for ellipsometric analysis

(10^{-2} Pa) at 60°C for 24 h. We also prepared a bilayer specimen of thin film of SMA-23/SAN-25 blend mounted on the thick aPA.

Ellipsometric measurement was carried out by an automated ellipsometer (EL-8, Optec Co. Ltd). Incident light from a He–Ne laser (632.8 nm) was applied to the bilayer specimen at an incident angle of 70° as shown in *Figure 1*. 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*[13]. Before analysis of interfacial thickness, we also measured the temperature dependence of refractive indices of neat polymer films spin-coated on the silicon wafer and the results were used for the data analysis. Then, since the values of refractive indices n_1, n_2 and n_4 and 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:

$$\rho = \frac{R_m^{\mathrm{p}}}{R_m^{\mathrm{s}}} = \frac{|R_m^{\mathrm{p}}|\exp(\mathrm{i}\Delta_{\mathrm{p}})}{|R_m^{\mathrm{s}}|\exp(\mathrm{i}\Delta_{\mathrm{s}})} = \frac{|R_m^{\mathrm{p}}|}{|R_m^{\mathrm{s}}|}\exp[\mathrm{i}(\Delta_{\mathrm{p}}-\Delta_{\mathrm{s}})] = \tan\psi\exp(\mathrm{i}\Delta) \qquad (1)$$

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

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

where ρ is the relative amplitude of parallel (R_m^{p}) to 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:

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

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

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

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

RESULTS AND DISCUSSION

Figure 3 shows the temperature dependence of the refractive indices of the component polymers. One can see that there is enough difference in refractive index between aPA and styrenic polymers at the reaction temperatures (170–210°C).

In *Figure 4* are shown the time variations of interfacial thickness λ in aPA/SMA-23 system at various reaction temperatures. At low temperatures (170, 190°C), the observed λ increases with time and then levels off at ca. 10 min. At higher temperature (210°C), the reaction seems to be so fast that one could not detect the time variation of λ at the early stage. In *Figure 5*, similar time variations are shown for a-PA/SMA systems with different MA contents.

The results in *Figures 4* and *5* imply that the reaction between aPA and SMA has taken place to generate graft copolymer and the interface is thickened. However, the interface attained at late stages is tremendously thick. It is much thicker than that conceivable for aPA–SMA graft copolymer (see *Figure 6*). That is, as typically demonstrated in the caption of *Figure 6*, when A–B block (or graft) copolymer is located at the interface betwee immiscible polymers A and B (*Figure 6c*), the interface will be thickened to ca. $2\lambda_0$, λ_0 being the interfacial thickness between non-reactive polymers A and B (*Figure 6a*), and the interfacial thickness in neat

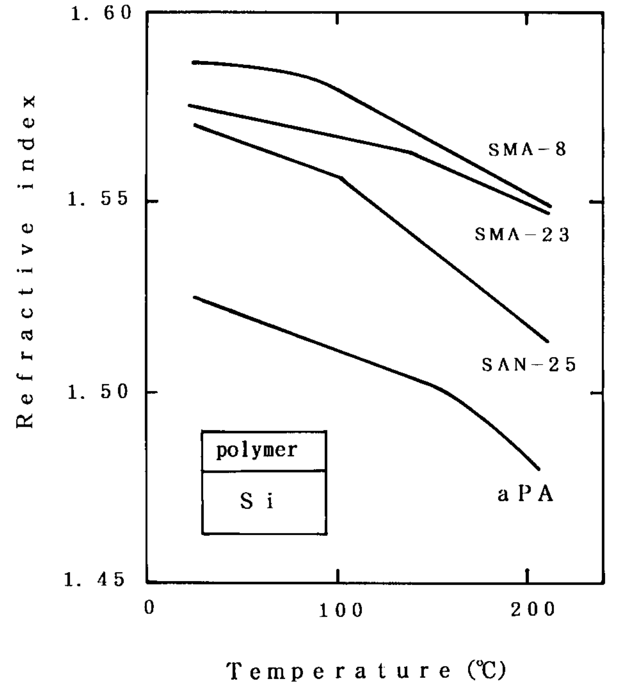


Figure 3 Temperature dependence of refractive index

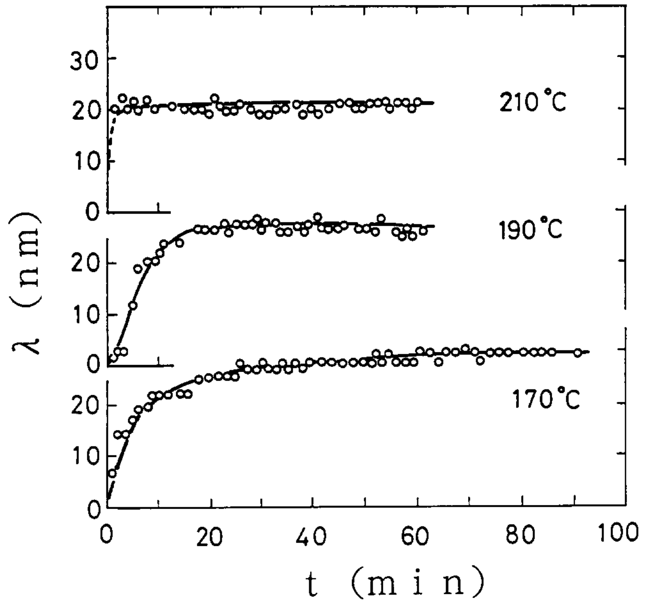


Figure 4 Time variation of interfacial thickness in aPA/SMA-23 system at various annealing temperatures

A–B block copolymer (*Figure 6b*) is ca. $5\lambda_0$; but these values are still smaller than the coil size of the component polymers[14]. Note that the attainable thickness in aPA/SMA, $\lambda = 20$–30 nm, is much larger than the root-mean-square radius of gyration $\langle S^2\rangle_0^{1/2}$ of polystyrene (representative of SMA), estimated[15] to be 14 nm by $\langle S^2\rangle_0^{1/2} = 2.97\times10^{-2} M_w^{1/2}$, and root-mean-square end-to-end distance[15] $\langle R^2\rangle_0^{1/2} = 9.7\times10^{-2} M_w^{1/2} =$ 14 nm for nylon-12 (representative of aPA). It suggests that the whole copolymer chains are drawn into the interface to generate a very smooth concentration gradient (*Figure 6d*). The formation of such a very thick interface is expected to be characteristic of a reactive system in which the chemical reaction induces a deviation from the equilibrium state in the ternary system of A/B/A–B (*Figure 6c*).

Furthermore if one plots the attainable thickness at late stages as a function of MA content at various reaction temperatures as in *Figure 7*, one can hardly see any systematic change: i.e. at low temperature (170°C) the thicker interface is established when more reactive sites are available, while at 190°C an optimum MA content exists to attain the thickened interface, and at higher temperature (210°C) the interface is thinner than those at lower temperatures when the MA content is high. The results may imply that, when the MA content is too high

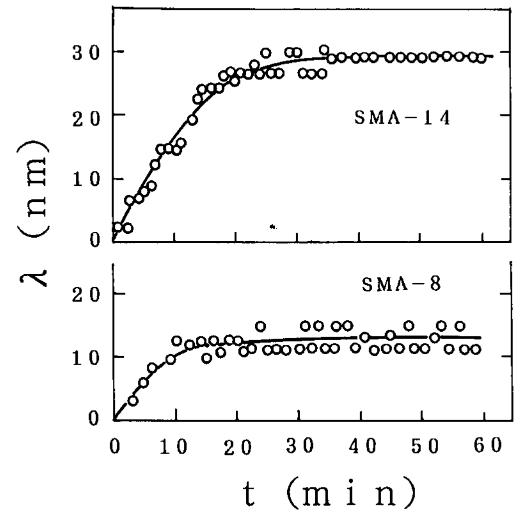
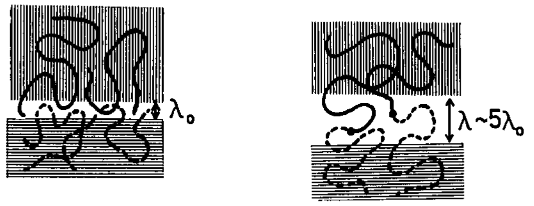
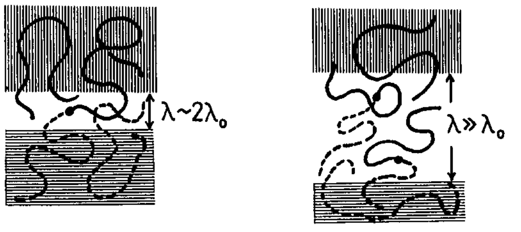


Figure 5 Time variation of interfacial thickness in aPA/SMA with different MA contents at 190°C



(a) A/B (non-reactive)

(b) A-B



(c) A/B/A-B

(d) reactive A/B

Figure 6 Schematic illustrations of polymer–polymer interfaces: (a) between polymers A and B (non-reactive); (b) between microdomains of neat A–B block copolymer; (c) consisting of polymer A, polymer B and A–B block copolymer; and (d) generated by reaction between polymers A and B. Note that the interface is the white space between the shaded regions, which exclude dissimilar chains. According to the theory of polymer–polymer interfaces[14], typical values of equilibrium thickness for interfaces of (a), (b) and (c) are 1.4, 6.9 and 2.3 nm, respectively; assuming $M_A = M_B = 10^5$, the root-mean-square end-to-end distance $= 7.5\times10^{-2} M^{1/2}$ (nm), $(\delta_A - \delta_B)^2 = 0.5$ cal mol^{-1} and $T = 300$ K, where M and δ are the molecular weight of the polymer and the solubility paremeter, respectively

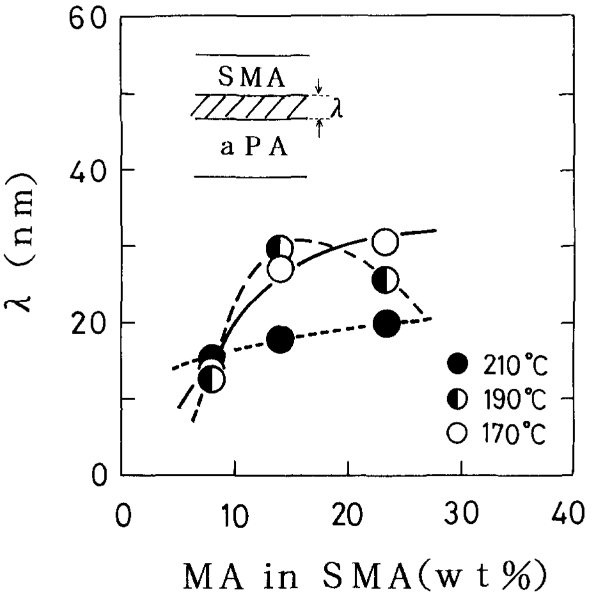


Figure 7 Interfacial thickness attainable in aPA/SMA systems at various temperatures as a function of MA content of SMA

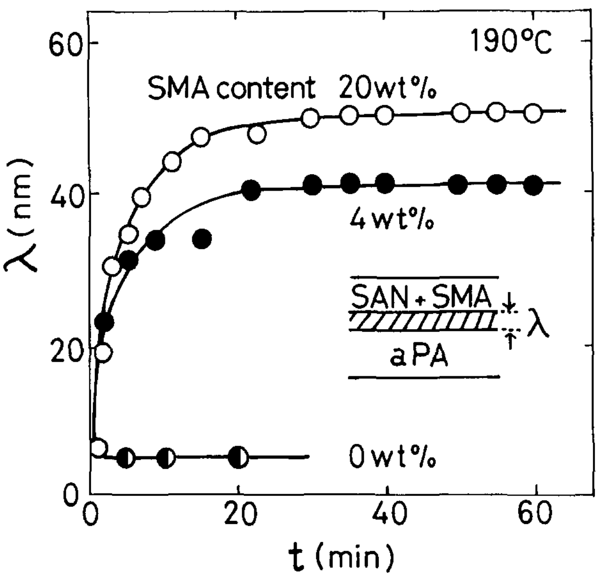


Figure 8 Time variation of interfacial thickness in aPA/(SMA+SAN) systems

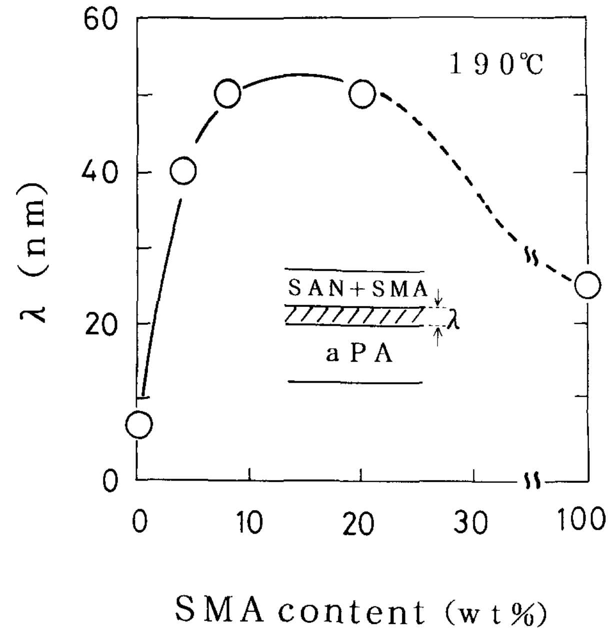


Figure 9 Interfacial thickness attainable in aPA/(SMA+SAN) systems at 190°C as a function of SMA content

and/or reaction temperature is too high, the graft reaction occurs so frequently that gelation takes place at the interface* and the gelled layer would prevent further interdiffusion of dissimilar polymers, resulting in a thin interface.

In *Figure 8* are shown similar results for the interface between aPA and the blend of SAN-25 and SMA-23. Here SMA and SAN with similar styrene contents are known to be miscible[16,17] and the reactive polymer SMA is diluted with a non-reactive polymer SAN. When the reactive polymer is present, the interfacial thickness increases with time and then levels off. The attainable thickness is smaller when SMA content is less. In contrast, in the non-reactive system of aPA and neat SAN the thickness remains constant. In *Figure 9* the attainable thickness is plotted as a function of SMA content. Increasing the SMA content, the thickness increases, attains a maximum and then decreases.

The maximum thickness of 50 nm is much larger than those of in aPA/SMA systems in *Figure 5*. It may be achieved by an appropriate reaction rate, which promotes the drawing of many SMA chains into the interface by the gel point. The increase of interfacial thickness with SMA content in the low SMA content regime clearly illustrates the so-called 'compatibilizing effect' of SMA for nylon/SAN and nylon/ABS (acrylonitrile–butadiene–styrene) blends. The decrease of thickness in the high SMA content regime may suggest again that the excess reactive sites do not always contribute to the thickened interface, as discussed above.

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* Gelation would occur by the crosslinking of SMA by aPA having two amino end-groups, which could be provided by interchange reactions at high temperatures, such as aminolysis and amidolysis

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