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Studies on the reactive polysulfone–polyamide interface: interfacial thickness and adhesion

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Abstract

The reactive interface formed between an immiscible polymer pair, amorphous polyamide (aPA) and functionalized polysulfone (PSU), was studied by ellipsometry. Diblock copolymers were formed in situ by an interfacial reaction between the amine-terminated aPA and the end-functionalized PSU, whereas graft copolymers were formed between the amino-chain end groups of aPA and the PSU functionalized in the middle of the chains. It was found that the interfacial reaction significantly increased the interfacial thickness, even reaching the size larger than the coil size of the copolymers formed at the interface. The interface structure and the properties were affected by the position and type of functional groups incorporated to the PSU. The reactive interface resulting in the graft copolymers tended to be thicker than that forming the block copolymers. However, the thinner interface demonstrated a superior adhesion to the thicker interface. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polysulfone/amorphous polyamide; Reactive interface; Ellipsometry

1. Introduction

In order to improve a given polymer's properties it is common to add another type of polymer and form a blend or alloy. However, in many cases, the so-obtained polymer mixture is immiscible and has poor mechanical properties. Two reasons are given for this. First, because the interfacial adhesion between the matrix phase and the dispersed phase is poor, external forces easily cause crazing between the phases. Second, as different domain sizes are formed during the mixing of the immiscible phases, the internal structure of the blend is not homogeneous. This causes uneven stress concentration to be generated in the blends, when mechanically deformed.

Therefore, the addition of block or graft copolymers has been widely attempted in order to solve such problems in blends [1–3]. These copolymers can be located at the interface between the matrix phase and the dispersed domain phase and play the role of emulsifiers. Owing to the resulting reduced interfacial tension the dispersed domain sizes are found to be decreased and their size distribution is made more uniform. However, a problem with introducing a premade copolymer to the blend is that it is difficult for the copolymer to reach the interface so that in most cases an insufficient number of the copolymers are located at the interface to play the role of emulsifiers. Further, the copolymers can form micelles [4,5]. Thus, adding preformed copolymers is not always attractive from a commercial standpoint.

Recently, a procedure called “Reactive Processing” has been developed, in which reactive sites incorporating both blend components form covalent bonds between them, resulting in the in situ formation of the copolymer at the interface during mixing of the blend components [2,3,6,7]. In this process, the copolymer is exactly located at the interface after melt blending. Moreover, the synthesis of the copolymer emulsifier can be omitted. Although this method is industrially more appealing, the characteristics and properties of the interface are not fully understood yet.

The interfacial thickness, λ, is one of the most important characteristics of the polymer–polymer interface. Yukioka et al. had investigated the various kinds of interfaces by ellipsometry [8–11]. For example, they examined a reactive interface between poly(styrene-co-maleic anhydride)

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Table 1
Sample characterization

Sample	M_n[a]	M_w[a]	Weight fraction of reactive groups (wt.%)	Molarity of reactive groups (μmol/g)	Average number of reactive groups/chain	T_g (°C)[b]
nf-PSU	5300	21 700	0.0	0	0.0	180
PSU-g1.36MAH	9200	27 000	1.36	137	1.04	165
PSU-g0.92MAH	8000	21 300	0.92	93	0.75	165
PSU-g0.56MAH	6900	17 000	0.56	57	0.40	165
PSU-gCOOH	5300	24 000	0.38	84	0.45	160
PSU-ωPAH	5300	21 000	1.25	85	0.45	157
aPA	8400	32 800			1	97

[a] By GPC.
[b] By DSC.

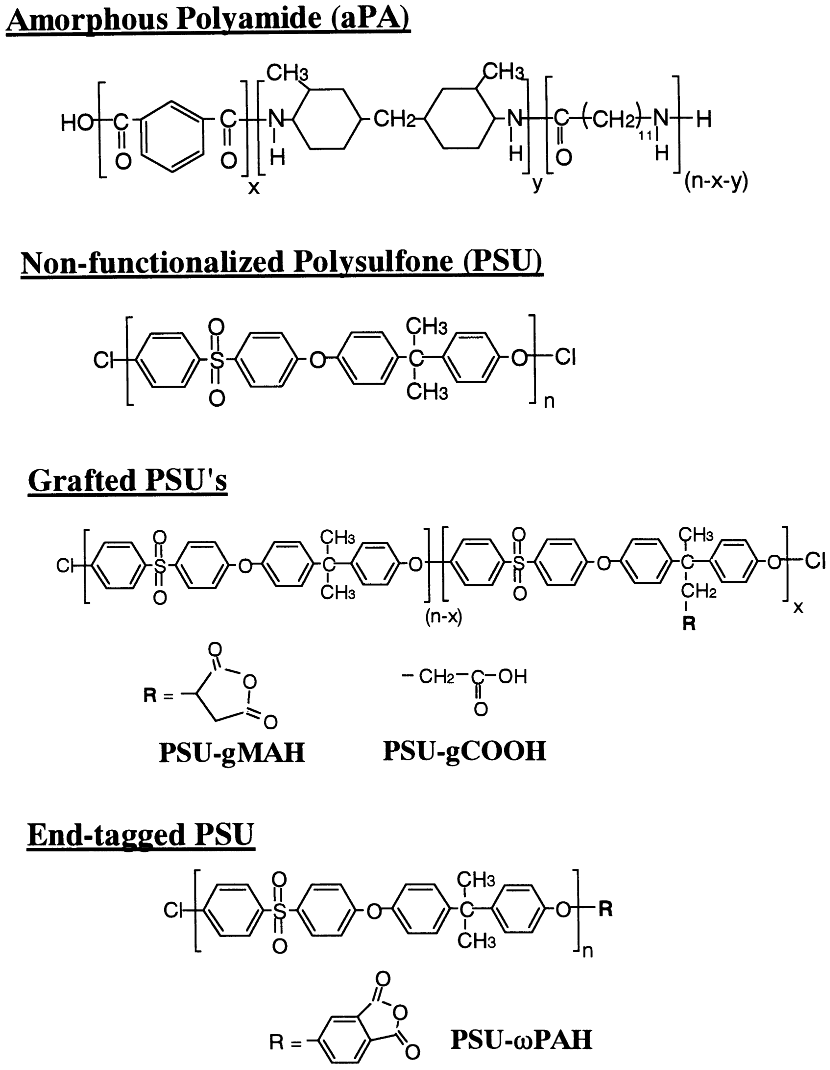


Fig. 1. Chemical structures of PSU and aPA samples.

(SMA) and amorphous polyamide (aPA) [11]. Maleic anhydride groups (MAH) distributed along the SMA backbone reacted with amine groups located at the end of nylon chains, and formed in situ copolymers at the interface. It was found that the attainable interfacial thickness was much larger than the calculated coil size of the copolymers, reaching the order of 50 nm. This implied that the chemical reaction at the interface induced deviation from an interface containing pre-made copolymers, which interfacial thickness was estimated to be in a range of a few nanometers.

The nature of interfacial adhesion is slowly becoming revealed both theoretically and experimentally by study of the fracture mechanism at the interface. Wool et al. proposed a theory based on the reptation model for the fracture mechanism at non-reactive interfaces [12,13]. As the polymer chains diffuse into the other polymer phase during annealing, they considered fracture toughness, G_c, as resulting from the energy necessary to pull the diffused chains out of the other polymer phase along a chain tube. Thus, the energy can be expressed as a function of the interfacial thickness, λ, where the polymer chains are interdiffused. For the immiscible amorphous A/B interface, G_c is proposed to vary with λ^2.

For the interface where pre-made block copolymers are present, two more factors are believed to contribute to the interfacial adhesion. One is the degree of polymerization, N, of the blocks and the other is the areal density of copolymer at the interface, Σ. Kramer et al. studied the role of the copolymer present at the polymer interface [14]. When they compared N with the average degree of polymerization between entanglements, N_e, they found that the mechanism of fracture at the interface changed depending on the relative lengths of N and N_e. It was also observed that the stress at the interface induced crazing as Σ was enhanced, in which G_c varied with Σ^2 in some cases [15].

The goal of this investigation is to study the characteristics and properties of the reactive interface of immiscible blends. The system chosen for study consists of polysulfone (PSU) and aPA as the blend components. Although PSU is a type of engineering plastic which has good mechanical properties and high heat resistance, this material is expensive and is difficult to process because of its high melt viscosity. The polyamide is cheaper and has excellent abrasion and chemical resistance as well as good mechanical properties. However, the PSU and aPA are strongly immiscible so that the obtained blends have inferior characteristics from those of the original polymers. Therefore, functional groups which could react with the amine groups located at the end of the aPA chains to form a reactive interface were introduced in the PSU chains. In the present study, the interfacial thickness of the reacted interface was investigated by time-resolved ellipsometry. Further, in order to examine the relationship between interfacial thickness and interfacial adhesion at the reactive interface, the fracture toughness was measured by an asymmetric double cantilever beam method (ADCB). The effects of functional groups incorporated in the PSU on the interface structure and properties are discussed in the present study.

2. Experimental

2.1. Materials (synthesis of polyarylethers)

The polymer specimens used in this study are listed in Table 1 with the characteristics of the individual sample and depicted in Fig. 1. PSU was functionalized with a low concentration of MAH, carboxylic acid (COOH), and phthalic anhydride (PAH) either at the middle of the chain (g) or at the chain end (ω). aPA containing one amino end group per chain was obtained from EMS Japan.

Three different types of functionalized PSUs were prepared by following synthetic procedures given in the literature [16–18]. As a control sample, PSU without functional group (nf-PSU) was also synthesized.

nf-PSU: 287.08 g (1 mol) dichlorodiphenylsulfone, 223.83 g bisphenol-A (0.9805 mol) and 140.97 g K_2CO_3 were dissolved in 1600 ml dry *N*-methyl-2-pyrrolidone (NMP, dried with CaH_2 and distilled). The mixture was heated at 190°C for 6 h in a nitrogen atmosphere. During this time, the azeotropic mixture of NMP and water was continuously removed. The solution was cooled down to room temperature, diluted with NMP (1600 ml) and then filtered. Next, the polymer was isolated by precipitation in water. The polymer was washed three times with hot water and dried at 130°C for 12 h. The elementary analysis indicated that 98% of one chain end was terminated by chlorine.

PSU-gMAH: 50 g of nf-PSU was dissolved in chlorobenzene and the resultant solution was heated to reflux. 11.3 g of MAH and 3.5 g dicumylperoxide were added over a period of 4 h. After refluxing for another hour, the solution was cooled down to room temperature and the polymer was isolated by precipitation in ethyl alcohol. The polymer was filtered and redissolved in NMP and again precipitated in a mixture of NMP/H_2O (1/4 by weight). After filtration the polymer was washed with hot water and dried. Finally, the product was dried at 130°C under vacuum for 12 h. The amount of anhydride groups was determined by potentiometric titration.

PSU-gCOOH: 28.71 g (0.1 mol) dichlorodiphenylsulfone, 20.08 g bisphenol-A (0.088 mol), 2.80 g diphenolic acid (DPA) (9.78 mmol) and 14.1 g K_2CO_3 (0.102 mol) were dissolved in 160 ml dry NMP. The mixture was heated at 190°C for 6 h in a nitrogen atmosphere. During this time, the azeotropic mixture of NMP and water was continuously removed. The solution was cooled to room temperature, diluted with NMP (160 ml), and then filtered. Next, an excess amount of acetic acid was added to the solution and after further stirring (30 min), the polymer was isolated by precipitation in water. The polymer was washed three times with hot water and dried at 130°C for 12 h. The amount of incorporated DPA units was estimated by

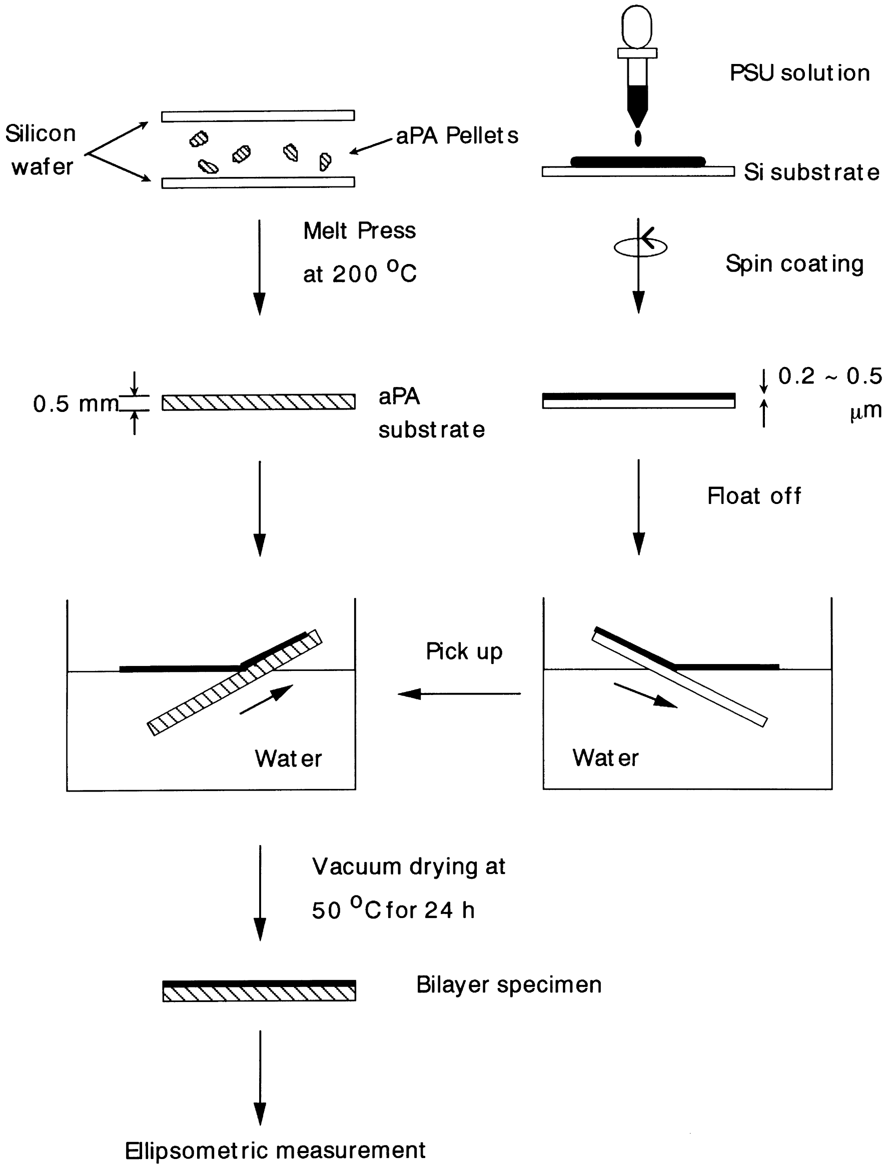


Fig. 2. Preparation of bilayer specimens.

^{1}H-NMR-spectroscopy (in 1/1 $CDCl_3/CF_3COOD$). The molar ratio of the DPA unit to the bisphenol-A unit was calculated from their signal intensities in the ^{1}H-NMR-spectra, in which the signal of the CH_2-groups of PDA was located at $\delta = 2.2$ ppm and 2.5 ppm and the signal of the CH_3-groups of bisphenol-A appeared at $\delta = 1.6$ ppm.

PSU-ωPAH: 287.08 g (1 mol) dichlorodiphenylsulfone, 228.28 g bisphenol-A (1 mol) and 140.97 g K_2CO_3 were dissolved in 1600 ml dry NMP. The mixture was heated at 190°C for 4 h in a nitrogen atmosphere. During this time, the azeotropic mixture of NMP and water was continuously removed. Then, 26.58 g (0.16 mol) of 4-fluorophthalic anhydride and 9.3 g (0.16 mol) KF were added and the solution was further stirred for 1 h. The solution was cooled down to room temperature, diluted with NMP (1600 ml) and then filtered. Next, the polymer was isolated by precipitation in water. The polymer was washed three times with hot water and dried at 150°C for 12 h. The amount of anhydride end-groups was determined by FT-IR.

2.2. Interfacial measurements

In order to measure the interfacial thickness using these PSU and aPA specimens, bilayer films were prepared by the method illustrated in Fig. 2. First, an aPA substrate with ca. 0.5 mm thickness was prepared by hot press melting the sample at 200°C between silicon wafers in order to obtain an optically flat surface. Meanwhile, a PSU film of 200–500 nm thickness was prepared by spin-coating from a 6 wt.% chlorobenzene solution onto a silicon wafer. Then, the thin PSU film was mounted on the aPA substrate by the floating-on-water and pick-up technique. Lastly, the bilayer

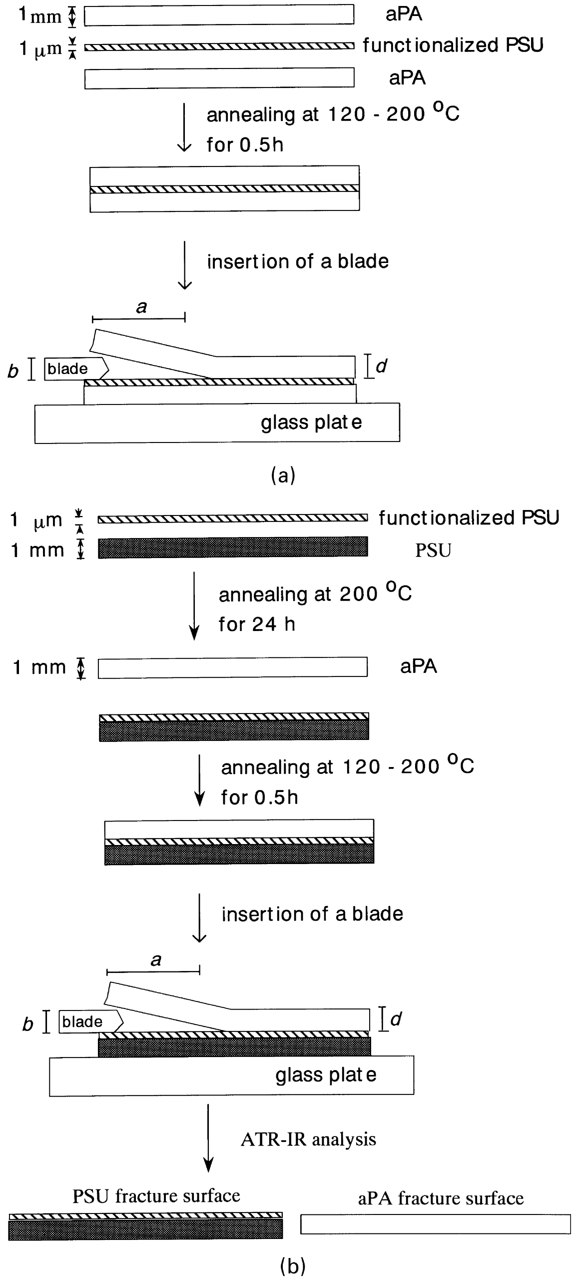


Fig. 3. Sample preparation for the ADCB method. (a) ordinary geometry, (b) modified geometry.

film was dried under vacuum at 50°C for 24 h. The bilayer films were heated at different temperatures under nitrogen atmosphere during the ellipsometric analysis.

Time-resolved ellipsometric analysis to determine the interfacial thickness of the bilayer samples was carried out using an automated ellipsometer (EL-8, Optec). The incident light of a He–Ne laser (632.8 nm) was applied to the specimen at an angle of incidence 70°. In order to use ellipsometry to determine the interfacial thickness between two polymers, it is necessary for the difference in refractive index between the phases to be larger than 0.02. The refractive index of nf-PSU (n_{PSU}) was estimated as 1.63 at room temperature and that of aPA (n_{aPA}) was 1.55 so that the present bilayer film fulfilled the requirement, $|n_{\mathrm{PSU}} - n_{\mathrm{aPA}}| > 0.02$. As optical homogeneity of the samples was also required for ellipsometry, special care was taken to minimize aPA crystallization as much as possible.

The bilayer film was placed in a hot chamber of the ellipsometer. During the measurement, nitrogen gas was purged into the chamber in order to remove the influence of water. The retardation, Δ, and reflection ratio, tan ψ, of reflected light were measured directly, from which both the interfacial thickness (λ) and the thickness of the upper layer, PSU, could be estimated using the pre-estimated values of n_{PSU} and n_{aPA} at the experimental temperature. The refractive index of the interphase was approximated to be uniform and equal to an average of the refractive index of each component polymer, $n = (n_{\mathrm{PSU}} + n_{\mathrm{aPA}})/2$. The details of the ellipsometric analysis and the computation were described in Refs. [8,9].

In addition, transmission electron microscopy (TEM) (JEOL, JEM-100CX) was used for the interface observation. The specimens were cryomicrotomed at −65°C by an ultramicrotome. The ultra-thin sections were then stained by vapor of ruthenium tetraoxide (RuO_4) for 10 min in order to enhance the contrast between two phases, in which the PSU phase was preferentially stained over the aPA phase.

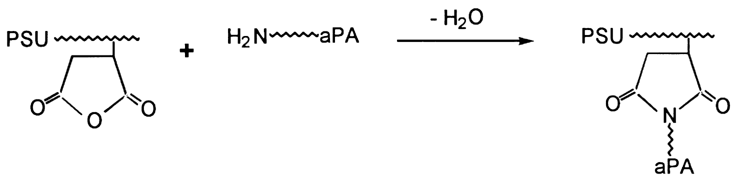
2.3. Measurement of adhesive energies

The ADCB method was performed in order to estimate the fracture toughness, G_c. Samples for ADCB having forms shown in Fig. 3(a) and (b) were prepared by the following method. First, aPA and non-functionalized PSU substrates were prepared on a hot press heated at 200°C and 240°C, respectively. Then, the substrates were cut out to have a dimension of 5.0 cm × 1.0 cm × 0.1 cm. Second, a thin functionalized PSU film of ca. 1 μm thick was prepared by spin-coating. For the sample shown in Fig. 3(b), the functionalized PSU film mounted onto the thick non-functionalized PSU plate was heated at 200°C for 24 h in advance. The specimen with three layers was then annealed at 120°C–200°C for 0.5 h.

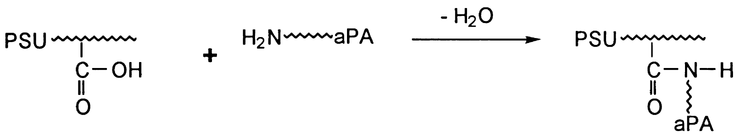
As a next step, the sample was placed on a glass plate and then a razor blade of thickness b was inserted at the interface between the functionalized PSU and aPA. Then, the blade was gradually pushed into the sandwich specimen along the interface until it reached 1 cm from the sample edge. Here, only the upper aPA layer was deformed by the insertion of the razor blade. After 24 h, a yielded crack length, a, between the edge of the blade and the crack tip was measured, and then the blade was pushed in again by 0.5 cm. This procedure was repeated three times and the obtained crack length was averaged.

The fracture toughness, G_c, was then calculated by the

(a) Graft copolymerization between PSU-gMAH and aPA



(b) Graft copolymerization between PSU-gCOOH and aPA



(c) Block Copolymerization between PSU-ωPAH and aPA

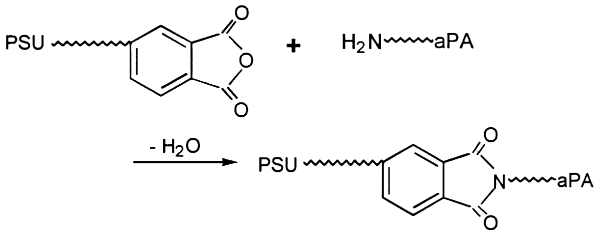


Fig. 4. Interface reaction between functionalized PSU and aPA. (a) Graft copolymerization between PSU-gMAH and Apa. (b) Graft copolymerization between PSU-gCOOH and aPA. (c) Block copolymerization between PSU-ωPAH and aPA.

following equation: [19],

$$G_c = \frac{3Ed^3b^2}{8a^4[1 + (0.64d/a)]^4},$$

where E was the Young's modulus of aPA (1.9 GPa), a was the crack length, and b and d were the thickness of the razor blade and the upper aPA layer, respectively.

The fracture surface was observed by an optical microscope (BH-2, Olympus). In order to examine the fracture surface, infrared spectroscopy in a total attenuated reflection mode (ATR-IR) was used (JEOL NR-1500 infrared spectrometer). A KRS-5 crystal plate with a refractive index of 2.4 was employed as an internal reflection element and the angle of the incident light was fixed to 45°.

3. Results and discussion

3.1. Interfacial thickness

3.1.1. nf-PSU/aPA

The interfacial thickness, λ, between aPA and nf-PSU was measured by ellipsometry. The measurement was carried out, while the specimen was heated for up to 0.5 h in the temperature range between 80°C and 200°C. However, the interfacial thickness stayed too thin to be measured by this technique, confirming the strong immiscibility between aPA and PSU.

The interfacial thickness of immiscible polymer pairs with infinite molecular weight was described by a thermodynamic expression, first proposed by Helfand and Tagami [20]. Recently, this model was modified by Broseta and coworkers for finite molecular weight [21]. The interfacial thickness, λ, of immiscible pairs was described by the following equation:

$$\lambda = \frac{2b}{\sqrt{6\chi_{AB}}}\left[1 + \frac{\ln 2}{\chi_{AB}}\left(\frac{1}{N_A} + \frac{1}{N_B}\right)\right],$$

where b is a Kuhn's segment length of 0.8 nm, χ_{AB} is a Flory–Huggins interaction parameter to show the degree of affinity or miscibility between A and B polymers and N_i is the number of segments per chain.

As the interfacial thickness of the PSU/aPA interface was less than the measurable limit of ellipsometry (ca. 2 nm), $\chi_{\text{PSU-aPA}}$ was estimated to be over 0.2 by using 2 nm for the λ value in the equation. The value of $\chi_{\text{PSU-aPA}}$ indicated strong immiscibility of the polymer pair. The equation suggests that the interfacial thickness will be enhanced by lowering the N_i value. It was then attempted to reduce the molecular weight of PSU from 5300 to 2350 in order to measure the interfacial thickness by ellipsometry. However, the thickness did not increase above the measurable limit of ellipsometry.

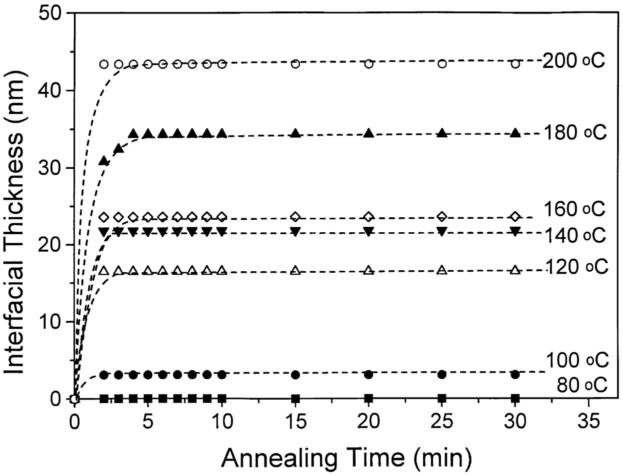


Fig. 5. Annealing time dependence of interfacial thickness, λ, in the PSU-g1.36MAH/aPA system at different temperatures.

3.1.2. PSU-gMAH/aPA

The interfacial reaction between the functionalized PSU and the amino end group of aPA produces in situ copolymers in different ways, as shown in Fig. 4. The MAH and COOH groups attached to the middle of the PSU chain produce graft copolymers, whereas the PAH group incorporated at the PSU chain end forms a block copolymer with aPA. The reaction between a primary amine at the end of aPA and a cyclic anhydride such as MAH or PAH forms a cyclic imide [6], whereas on the other hand, the reaction between a primary amine and COOH results in another amide linkage [22].

Fig. 5 shows the time dependence of the interfacial thickness of PSU-g1.36MAH/aPA at various reaction temperatures. Even though the interface between nf-PSU and aPA was too thin to be measured by ellipsometry, the reactive interface formed between PSU-gMAH and aPA became as thick as 45 nm at high temperatures. An increase in the interfacial thickness was not observed below 100°C. In this in situ graft copolymerization at the interface, the interfacial thickness became constant at 2 min of heating time at any reaction temperature. The same behavior was also observed in PSU-g0.92MAH/aPA and PSU-g0.56MAH/aPA systems.

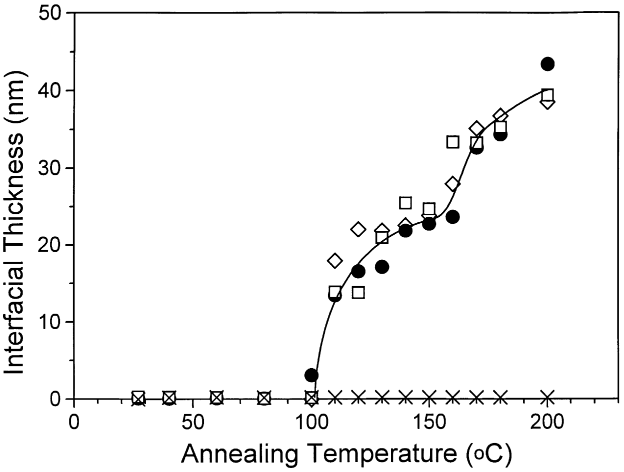


Fig. 6. Temperature dependence of the interfacial thickness in the PSU-gMAH/aPA system. (X) nf-PSU/aPA, (◇) PSU-g0.56MAH/aPA, (□) PSU-g0.96MAH/aPA, (●) PSU-g1.36MAH/aPA.

Fig. 6 was plotted from the final values of the interfacial thickness shown in Fig. 5, and indicates the effects of the reaction temperature and the concentration of the tagged MAH group on the interfacial thickness. The interfacial thickness increased drastically above the two glass transition temperatures (T_g); aPA's at 97°C and PSU's at 165°C. Here, the restriction of the chain mobility of both PSU and aPA under 97°C resulted in an unmeasurably thin interface. However, when one side of the polymer pairs, i.e. the aPA phase, started to possess mobility in the temperature range between the two T_g's, the interfacial thickness was significantly enhanced (e.g., to approximately 20 nm at 150°C). Finally, above the T_g of PSU at 165°C the interfacial thickness increased dramatically again as a result of having both phases in a rubbery state. Thus, it is essential for at least one of the phases to possess molecular mobility and preferably both in order for the functional groups to encounter efficiently to form covalent bonds between them, resulting in a thick interface. It was found in Fig. 6 that the interfacial thickness was almost independent of the MAH concentration incorporated into PSU studied here.

Next, in order to examine the amount of MAH group content needed in the system to produce a thick interface, samples with MAH content of 0.2 and 0.7 wt.% in PSU were prepared by diluting the neat PSU-g1.36MAH with the non-functionalized PSU. Fig. 7 demonstrates that an MAH content of 0.2 wt.% was sufficient in order to form a thick interface, although at the lower MAH concentrations the interfacial thickness was slightly decreased.

Next, the observed interfacial thickness of about 45 nm was compared with the calculated dimension of the coil size as follows. It was assumed that the coil size of the copolymer was not seriously changed by effects from the adjacent comonomer, such as steric hindrance or repulsive forces. Thus, the coil size of the copolymer formed at the interface could be roughly estimated from the following equation:

$$[\text{the coil size of the copolymer}] \approx 2\langle s^2\rangle^{1/2}_{\text{PSU}} + 2\,\langle s^2\rangle^{1/2}_{\text{aPA}},$$

where $\langle s^2\rangle^{1/2}$ is the root-mean-square radius of gyration of the component polymer. As the root-mean-square end-to-end distance, $\langle r^2\rangle^{1/2}_{\text{PSU}} = 7.53 \times 10^{-2}\,\text{M}^{1/2} = 12.4$ nm for PSU-g1.36MAH (estimated from the data for poly(sulfonyl-*p*-phenoxyphenylene)) [23], the $\langle s^2\rangle^{1/2}_{\text{PSU}}$ was roughly estimated to be 5.0 nm from the relationship, $\langle s^2\rangle = \langle r^2\rangle/6$. Similarly, $[\langle r^2\rangle_{\text{aPA}}]^{1/2} = 9.7 \times 10^{-2}\,\text{M}^{1/2} = 17.6$ nm (estimated from the data for nylon-12) [23], which resulted in $[\langle s^2\rangle_{\text{aPA}}]^{1/2}$ to be 7.2 nm. Then, the coil size of the copolymer calculated from the equation shown earlier is equal to 24.4 nm. In other words, the observed interfacial thickness

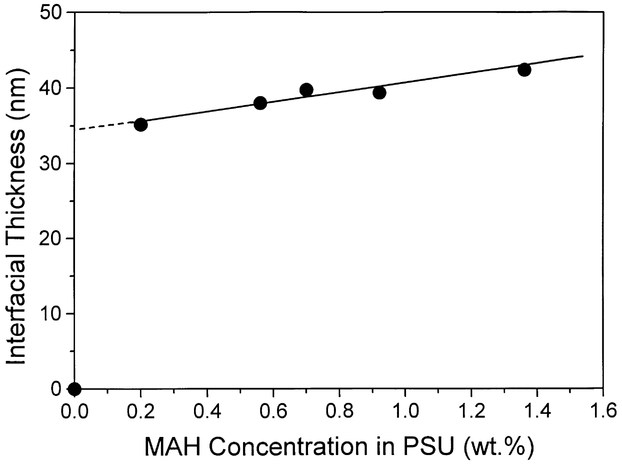


Fig. 7. Interfacial thickness as a function of the MAH concentration incorporated into PSU at 200°C.

of about 45 nm is almost twice as large as the coil size of the whole copolymer. This implies that the present reactive interface has a different structure from that of the interface in a ternary system composed of two blend component polymers and copolymers formed between them, in which the interfacial thickness is estimated to be in the range of a few nanometers according to the theory for polymer–polymer interfaces [11,24].

3.1.3. PSU-gCOOH/aPA and PSU-ωPAH/aPA

Fig. 8 shows a change in the interfacial thickness formed between aPA and PSU-ωPAH and between aPA and PSU-gCOOH, in which a PAH group was incorporated into the chain end of PSU and a COOH group was introduced in the middle of the PSU chain, respectively. During heating at a given temperature, the interface thickened in different ways. The PSU-gCOOH/aPA interface was formed as quickly as the PSU-gMAH/aPA interface, reaching a constant interfacial thickness in a few minutes of heating at 180°C. In contrast to the case of such an in situ graft copolymerization, it took a much longer time to form the PSU-ωPAH/aPA interface having the in situ block copolymerization. For example, at the same reaction temperature of 180°C, it took 10 min until the interfacial thickness became measurable by ellipsometry and 20 min until the interfacial thickness became constant. This final interfacial thickness of 20 nm at 180°C was slightly smaller than that of the PSU-gCOOH/aPA interface. For this system at 140°C, the increase of the interfacial thickness was observed at a later stage, ca. 20 min of heating time for the interfacial thickness to be measurable, and the final interfacial thickness stayed as small as 12 nm.

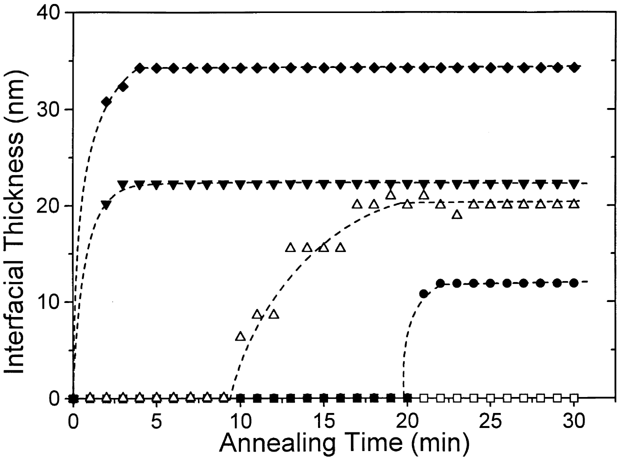


Fig. 8. Time dependence of interfacial thickness in differently functionalized PSU/aPA systems. (◆) PSU-g1.36MAH at 180°C, (▼) PSU-gCOOH at 180°C, (△), (●), (□), PSU-ωPAH at 180°C, 140°C, 80°C, respectively.

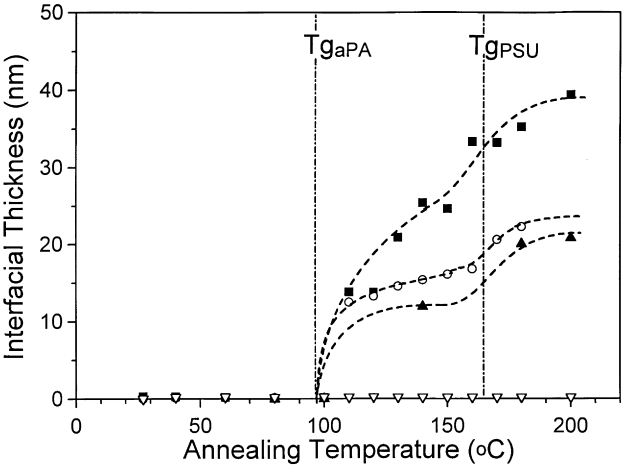


Fig. 9. Temperature dependence of interfacial thickness in differently functionalized PSU/aPA systems. (■)PSU-g0.92MAH, (○) PSU-gCOOH, (▲) PSU-ωPAH, (▽) nf-PSU. The concentration of the functional group was chosen at ca. 90 μmol/g.

The effects of the functional groups incorporated in the PSU on the interfacial thickness are summarized in Fig. 9. In order to eliminate the effects of the concentration of the functional group, a similar molarity was chosen at ca. 90 μmol/g. (The molecular weights of these PSU's are in a similar range.) A drastic increase in the interfacial thickness was observed at the two T_g's of the component polymers in any system; e.g. at 97°C (aPA) and 165°C (PSU), demonstrating the important contribution of the molecular dynamics to form the in situ copolymers at the interface. The interfacial thickness became larger above 100°C in the order of (PSU-gMAH) $>$ (PSU-gCOOH) $>$ (PSU-ωPAH). At 200°C, a temperature that was considerably higher than the T_g's of both component polymers, the interfacial thickness of PSU-gMAH/aPA was twice as large as that of PSU-ωPAH/aPA. It is worth noting here that the graft copolymerization at the reactive interface (PSU-gMAH, -gCOOH/aPA) tended to form a thicker interface compared to the block copolymerization (PSU-ωPAH/aPA).

3.1.4. Structure of the reactive interface

In the ellipsometric analysis, thickness of the upper PSU layer, d_2, and the interfacial region, d_3, during the annealing

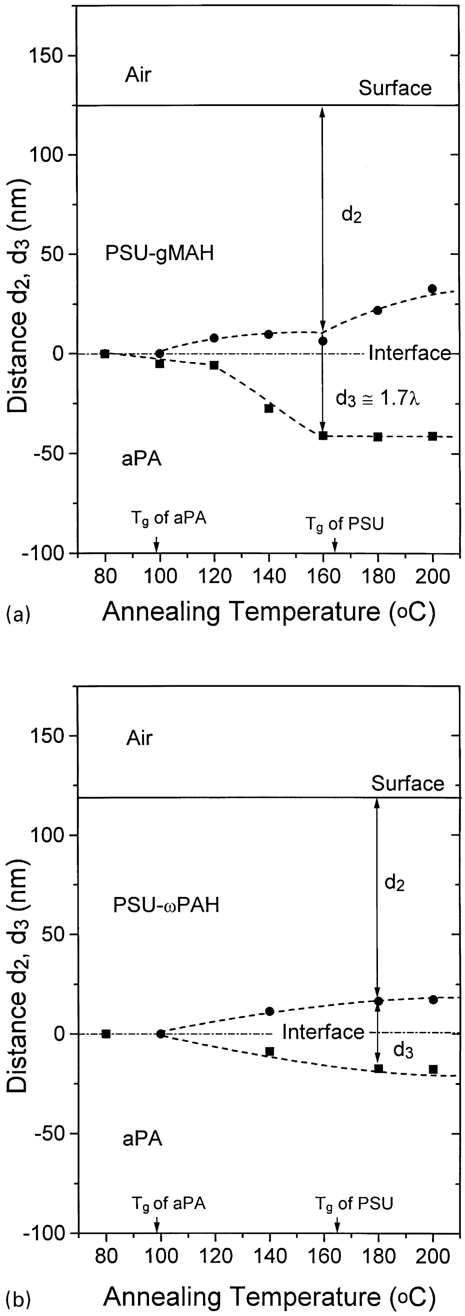


Fig. 10. Interface/interphase position in (a) the PSU-g1.36MAH/aPA system, and (b) the PSU-ωPAH/aPA system. The “0” in the vertical axis indicates the original interface position before annealing.

can be determined, in which d_3 has a relation, $d_3 = 1.7\lambda$. [25]. Fig. 10 indicates the locations of d_2 and d_3 from the surface at different reaction temperatures, in which the origin in the vertical axis was the position of the original interface before annealing.

In the case of the graft copolymerization between PSU-gMAH and aPA, the interface was formed more deeply into the aPA phase first than into the PSU phase. This tendency was significant in the temperature range between the two T_g’s, i.e. 97°C–165°C (Fig. 10(a)). In other words, such an asymmetric interface was formed, when the molecular dynamics of aPA were more dominant than those of PSU. A theoretical study on diffusion between a miscible polymer pair in melts also predicted a similar phenomenon [26]. Differences in molecular weight and molecular mobility between two phases would cause the asymmetry of the interface structure, in which the interface was preferentially developed toward the phase with the lower molecular weight and the higher mobility. However, above the T_g of PSU, i.e. 165°C, the interface was mainly thickened toward the PSU side, resulting in a symmetric interface at 200°C at the end.

On the contrary, in the block copolymerization between PSU-ωPAH and aPA, the interface was symmetrically thickened above the T_g of aPA (97°C), as shown in Fig. 10(b). The symmetry of the interface structure was not affected by the glass transition temperatures of the component polymers.

Although the interface structures of PSU-gMAH/aPA and PSU-ωPAH/aPA are not very clear, in order to interpret the fact that the interfacial thickness was much larger than the coil size of the copolymer produced at the interface, we can propose two plausible models: one is a micelle formation and the other is an undulation of the interface. In the former model, it can be considered that micelles composed of the resultant copolymers might be formed in the vicinity of the interface and the measurement of interfacial thickness by the ellipsometry includes the micelle region in addition to the actual interface region. The more the interfacial reaction progresses, the more the copolymers packed at the interface will seek a thermodynamically more stable state, in which the copolymers might escape from the interface and form micelles. In this case, it is necessary for the copolymer to possess not only the molecular dynamics but also an asymmetry in its architecture. For example, Leibler suggested that asymmetric chains ($f < 0.3$, where f is the volume fraction of the shorter block chain) tended to move to the bulk to form micelles, whereas more symmetric copolymer chains tended to locate at the interface [27]. Micelle formation was observed at other polymer–polymer interfaces. Nakayama et al. studied the reactive interface between COOH terminated polystyrene (PS) and epoxy terminated poly(methyl methacrylate) (PMMA), in which the diblock copolymer was formed in situ at the interface having an ester linkage between the blocks [4]. When they introduced 5% of pre-made block copolymer P(S-b-MMA), they observed micelle formation with 10 nm diameter by TEM. Washiyama also examined the cross-section of the interface between PS and poly(2-vinylpyrrolidone) (PVP) by TEM, introducing the pre-made diblock copolymer of styrene and 2-vinylpyrrolidone [28]. It was found that in the case of asymmetric diblock copolymers composed of a longer PS block and a shorter PVP block, the micelles were observed in the PS side.

However, the latter model of the undulated interface is considered to be formed as follows. The interfacial tension

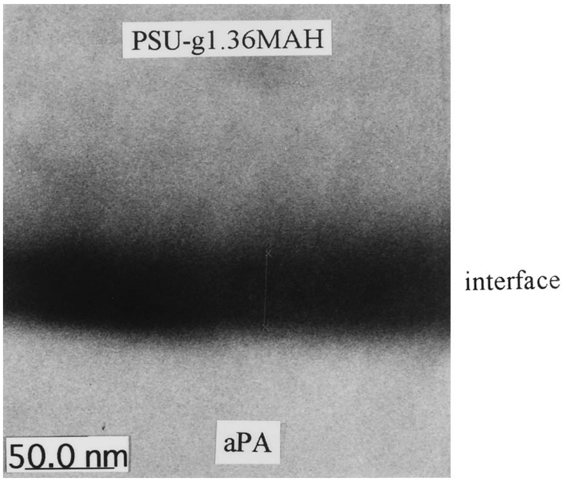


Fig. 11. TEM photograph of bilayer specimen composed of PSU-g1.36MAH and aPA annealed at 200°C for 0.5 h.

decreases dramatically with the progress of interfacial reaction, which thermodynamically destabilizes the interface. This state can cause an increase of the interfacial area, i.e. undulation of the interface, as a result of thermodynamically stabilizing the system. For example, Kramer studied the reactive interface between hydrogenated PS mixed with amine-terminated deuterated PS and SMA, in which the graft copolymer was formed at the interface [29]. In this system, it is reported that the undulation of the interface was observed.

In order to investigate the structure of interface in this work, the interface between PSU-g1.36MAH and aPA annealed at 200°C for 0.5 h was examined by TEM, as shown in Fig. 11. The TEM photograph shows that the interface area was stained predominantly. The thickness of the darkened interface was in good agreement with the interfacial thickness measured by ellipsometry, 42 nm. However, both micelle formation and undulation of interface could not be confirmed clearly from the TEM picture even at higher magnifications because of lack of contrast. The microtomed TEM specimen might be too thick to observe the undulation.

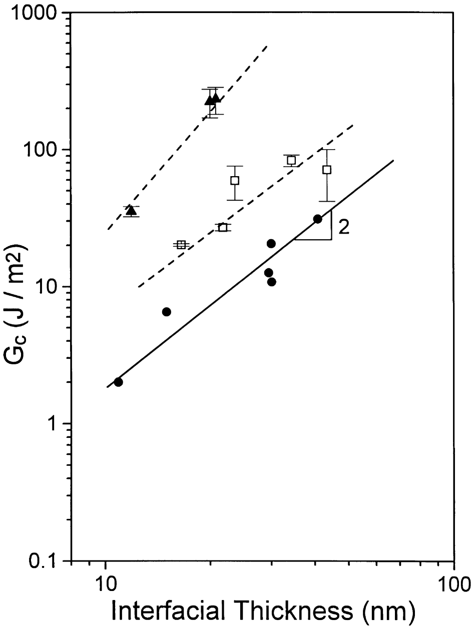


Fig. 12. Fracture toughness, G_c, as a function of interfacial thickness in different systems. (●) PC/SAN with 25 wt.% AN content (non-reactive), (□) PSU-g1.36MAH/aPA, (▲) PSU-ωPAH/aPA.

3.2. Interfacial adhesion

In the present study, the interfacial adhesion was evaluated by the ADCB method. In this method, it was assumed that all the elastic energy was dissipated in a very small region ahead of the crack tip, in which released elastic energy came only from the bending of the beam. The validity of ADCB test has been demonstrated in measuring PS and PMMA [30].

The fracture toughness, G_c, obtained from ADCB is useful to estimate interfacial adhesion and was compared to λ in non-reactive interfaces. However, for reactive interfaces, G_c has to be related to the amount of copolymer formed at the interface because the reinforcement mechanism is believed to be because of a “stitching” effect by the copolymers located at the interface. Boucher et al. found that at the reactive interface between functionalized polypropylene (PP) and polyamide-6 (PA6), a substantial reinforcement of the interface was observed with the relationship $G_c \sim \sum^2$, similar to that at the non-reactive interface with pre-made block copolymers [31].

In order to estimate the $\sum$ value by X-ray photoelectron spectroscopy (XPS) following Boucher’s paper [31], one of the phases has to be removed in order to expose the interface. However, in the present study there is a problem that the copolymers located at the interface might be lost during the process of removing one phase because the interfacial thickness was much thicker than the coil size of the copolymer. Further, after the removal of one phase, they employed XPS to determine the amount of copolymers exposed at the surface. However, the analytical depth of XPS, i.e. a few nanometers, is not appropriate to measure the amount of the copolymers in our case. Thus, Boucher’s method can be applied only to the very thin interface, in which it is essential to determine the interfacial thickness in advance.

Then, in the present study the results of the fracture toughness, G_c, are related to λ, instead of the areal density of the copolymer at the interface, Σ, as shown in Fig. 12. The results on a non-reactive and immiscible interface composed of polycarbonate (PC) ($M_n = 26\,600$, $M_w = 37\,500$) and poly(styrene-co-acrylonitrile) (SAN) ($M_n = 61\,000$, $M_w = 128\,000$) with acrylonitrile content (AN) of 25 wt.% are also cited in the figure, which showed a comparable fracture toughness [32]. The results for the non-reactive system indicated that the fracture toughness

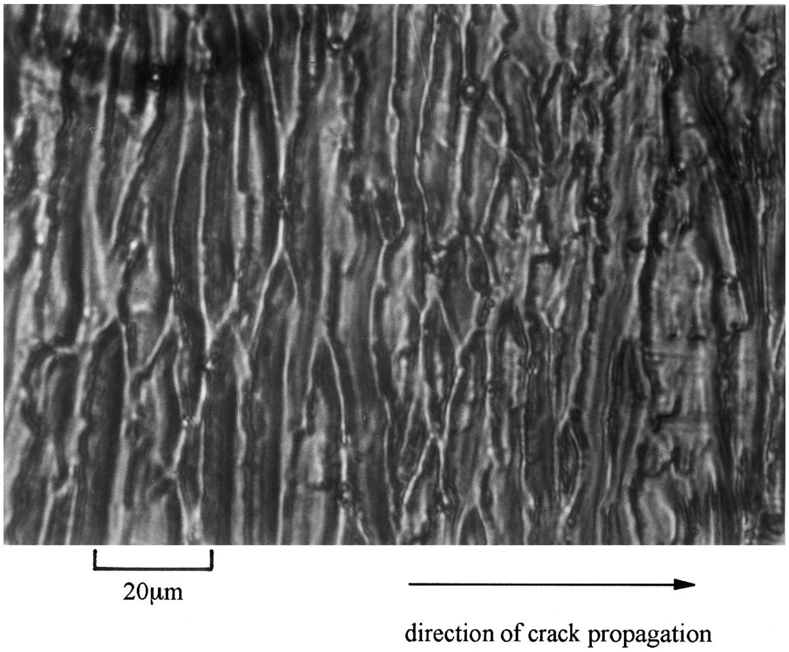


Fig. 13. Optical micrograph of the PSU fracture surface in PSU-ωPAH/aPA annealed at 200°C.

increased as the increase in the interfacial thickness following the relationship, $G_c \sim \lambda^2$.

In contrast, both reacted interfaces of aPA with PSU-gMAH and PSU-ωPAH showed much higher fracture toughness than the non-reactive PC/SAN interface, although the interfacial thickness was of the same magnitude. Especially, the G_c values in the PSU-ωPAH/aPA system was one order of magnitude higher than those in the non-reactive system. What is more interesting is that the G_c values of the PSU-ωPAH/aPA system resulting in the block copolymer at the interface were significantly higher than those of the PSU-gMAH/aPA system forming the graft copolymer. It should be noted that if there are micelles in the systems, the copolymers participating in the micelle formation might not contribute to the interfacial adhesion efficiently compared to those staying at the interface because they form no junctions between PSU and aPA. Therefore, if there are micelles in the system, the PSU-gMAH/aPA system with the higher interfacial thickness than PSU-ωPAH/aPA system might possess more micelles compared to the PSU-ωPAH/aPA system, resulting in a smaller amount of the stitching copolymers left at the interface. However, the block copolymers in the PSU-ωPAH/aPA system seems to stay more stably at the interface, reinforcing the interface more efficiently.

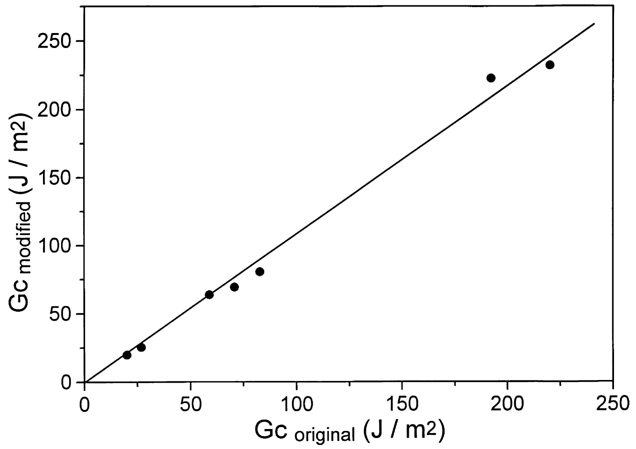


Fig. 14. Similarity in fracture toughness, G_c, of the specimens with different geometries shown in Fig. 3(a) and (b).

Further, the fracture surface was roughly observed by an optical microscope. In the PSU-gMAH/aPA system prepared at both 140°C and 200°C, any morphology was not observed and the fracture surface was smooth and flat in the optical microscope level, indicating that adhesive (interfacial) failure most likely occurred. Although the same tendency was observed in the PSU-ωPAH/aPA system prepared at 140°C, the fracture surface annealed at 200°C became very rough even in the optical microscope level. Fig. 13 shows the optical micrograph of the fracture surface of the PSU side in the PSU-ωPAH/aPA system prepared at 200°C. It demonstrated that the locus of the failure was not located at the interface. Many stripes were observed running perpendicular to the direction of the blade insertion. As the fracture toughness of this PSU-ωPAH/aPA system prepared at 200°C was very high in the present study, such a strongly reinforced interface seemed to cause cohesive failure at one of the phases.

In order to identify the locus of failure, XPS was first attempted using standard Al radiation. However, the characteristic elements, nitrogen in aPA and sulfur in PSU, were not stable during the measurements so that infrared spectroscopy in an ATR-IR was chosen as an alternative method.

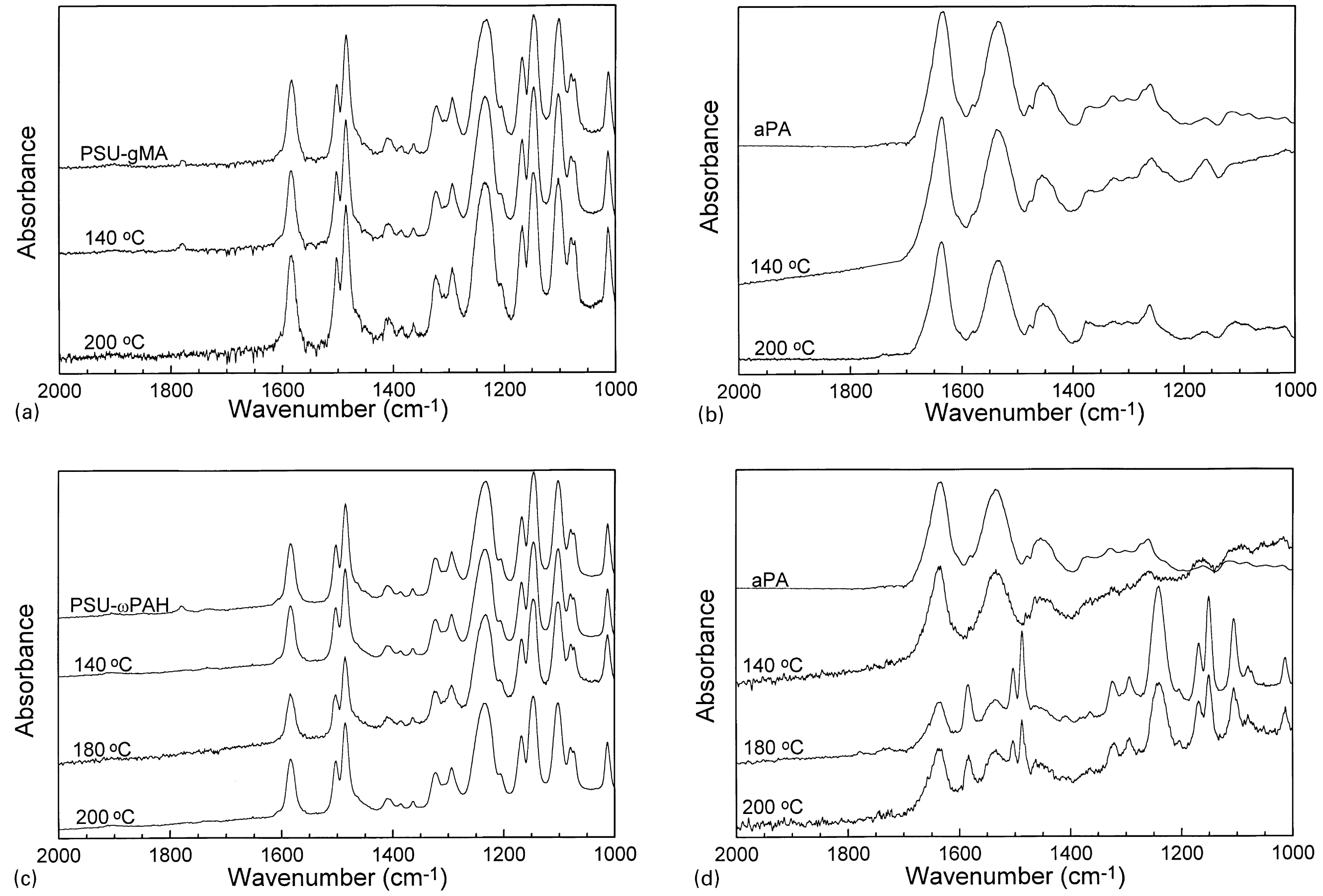


Fig. 15. ATR-IR spectra of the fracture surfaces in specimens annealed at different temperatures. (a) The PSU side in the PSU-gMAH/aPA system. (b) The aPA side in the PSU-gMAH/aPA system. (c) The PSU side in the PSU-*ω*PAH/aPA system. (d) The aPA side in the PSU-*ω*PAH/aPA system.

Under the present experimental conditions (KRS-5 internal reflection element, 45° of the incident light), the IR beam has a penetration depth around 1 μm from the sample surface in contact with the crystal at 2000 cm^{-1} in the mid-IR range [33] so that in order to determine the locus of failure this method is inferior to XPS with an analytical depth of a few nanometers. As such a deep penetration depth will confuse the interpretation of the data if the sample has the geometry shown in Fig. 3(a), the arrangement shown in Fig. 3(b) was employed to analyze the fracture surface. Although the geometry was modified, it was confirmed that there was no difference in fracture toughness, as shown in Fig. 14.

Fig. 15(a)–(d) show the results obtained from the ATR-IR measurements. Fig. 15(a)–(b) are the IR spectra of the PSU fracture surfaces and the aPA fracture surfaces in the PSU-gMAH/aPA system, respectively. As an absorption peak of reactive group in PSU-gMAH, an only small peak because of the C=O stretching of cyclic anhydride was observed near 1775 cm^{-1} in Fig. 15(a). However, the same peak was no longer observed, when the bilayer film was annealed at 200°C. Here, a quantitative analysis of the interfacial reaction using the IR data was not attempted because the intensity of the cyclic anhydride peak was too low. Other peaks of PSU-gMAH were completely same as those of nf-PSU. The reaction could be also traced from a change in the absorption peak of the amino end group of aPA. However, a peak near 1650 cm^{-1} of aPA in Fig. 15(b) included both contributions from the amido group and the amino end group of aPA, which were unseparable in the spectrum. This peak scarcely changed with the reaction so that one could not use it for a quantitative analysis of interfacial reaction either.

In the PSU-gMAH/aPA system, the fracture surfaces of both sides indicated the same IR spectrum as that of each component polymer. In other words, the failure occurred probably at the interface because there was no material observed from the other phase. If the failure was strictly interfacial, chain scission or pulling-out of the connecting copolymers should occur.

On the contrary, in the PSU-*ω*PAH/aPA system, the fracture surface of the PSU side (Fig. 15(c)) showed the same spectrum as that of PSU itself except for a small peak near 1775 cm^{-1} because of the C=O stretching of cyclic anhydride in reactive group of PSU-*ω*PAH, however, the fracture surface of the aPA side annealed above 180°C (Fig. 15(d)) showed the absorption peaks from PSU in addition to those from aPA. Although the failure of the PSU-*ω*PAH/

aPA system annealed at 140°C occurred at the interface, the failure of the same material but annealed at higher temperatures occurred at the PSU bulk as a result of the strong interface formed by the block copolymers, as also observed by a photograph shown in Fig. 13.

From the ATR-IR measurements, it is risky to precisely define the locus of failure because of the deep penetration depth of this technique, however, it is obvious that the PSU-ωPAH/aPA interface reinforced by the block copolymers was even tougher than the PSU bulk as observed as the craze in the PSU bulk.

4. Conclusion remarks

The reactive interface formed between aPA and functionalized PSU with MAH, COOH and PAH either at the middle of the chain (g) or at the chain end (ω) was studied by ellipsometry. The interfacial thickness, λ, of the reactive system was much thicker than that of the nf-PSU/aPA system.

λ (reactive) $\gg$ λ (non-reactive)

Further, the reactive interface was even thicker than the coil size of the copolymer formed in situ at the interface and the value estimated for the equilibrium interface in a ternary system composed of the immiscible polymer pairs, A, B, and its copolymer A–B based on the theory for the polymer–polymer interface. This might imply the presence of micelles resulted from the copolymers or the undulation of interface. However, it was not possible to confirm both micelle formation and undulation of interface by TEM observation. The interfacial thickness, λ, was also affected by the position and type of functional groups incorporated to the PSU, as

λ (PSU-gMAH) $>$ λ (PSU-gCOOH) $>$ λ (PSU-ωPAH).

The ADCB method demonstrated that the reactive processing drastically reinforced the interfacial adhesion between PSU and aPA. The fracture toughness, G_c, was significantly improved and tended to increase with increase in the interfacial thickness in the same reactive system. However, despite the fact that the PSU-ωPAH/aPA system had a thinner interface than the PSU-gMAH/aPA system, the PSU-ωPAH/aPA system showed higher fracture toughness than the PSU-gMAH/aPA system.

In future work, the interface structure will be pursued more thoroughly. Although the estimation of the areal density of the copolymers formed at the interface, Σ, might be difficult in thick interfaces, it is important to clarify the reactivity at the interface in order to elucidate the structure and the properties of the reactive interface.

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