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# Studies on interfacial reaction kinetics and properties at a reactive compatibilization interface

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**Abstract**

Rheometry, ellipsometry and atomic force microscopy (AFM) have been used to monitor the reaction at a poly(styrene/maleic anhydride) (SMA)/polyamide 6 (PA6) interface at 200 °C for various period of time. The interfacial reaction can be divided into three distinct stages by the results of complex viscosity ($\eta^*$). In the initial stage, $\eta^*$ increases with time and there is a second-order reaction to a first-order reaction transition. In the second stage, a reaction depletion layer forms and $\eta^*$ does not change with the reaction time. In the late stage, $\eta^*$ increases slowly again. The interfacial thickness increases with time in the early stage then keeps constant by building up the undulated interface. Moreover, there is an asymmetry interface which deeply develops into SMA layer as proved by ellipsometer.

*Keywords:* Interfacial reaction; Complex viscosity; Interfacial thickness

## 1. Introduction

Polymer blending provides an efficient way to produce materials with desirable properties. However, the blend polymers are usually immiscible and have poor mechanical properties due to the inferior interfacial adhesion between the matrix phase and the dispersed phase, which can be enhanced by adding graft and block copolymers as compatilizers into the blends. However, the copolymers easily form micelles and not enough copolymers are located at the interface to play the role of emulsifiers [1,2].

To solve this problem, reactive compatibilization between the functional groups on the two different immiscible polymers is developed, due to the in situ formation of the copolymer is just located at the interface of the polymer phases, which can prevent the coalescence of the minority phase droplets and enhance the mechanical properties of the blending polymers [3,4].

In spite of the practical applications of the interfacial reactions, studies of the interfacial reaction kinetics and properties are still lacking [5–16]. For several reasons, first, it can be difficult to gain the amount or rate of the copolymer formed in such experiments because a few functional groups are involved in the interfacial reaction. Second, highly functionalized polymers can form densely cross-linked structures at the interface. Moreover, the complex flow in the mixers and extruders can bring a lot of difficulties in studying the interfacial reaction kinetics.

In order to exclude the complex effect of the blending flow, O'Shaughnessy [17–19] and Fredrickson [20,21] established a planar interface in which they summarized the theoretical results on the interfacial reaction kinetics. Computer simulations are also carried out on the interfacial kinetics and properties [22,23].

There have been some experimental studies of the interfacial reaction kinetics and properties by the planar model. Macosko et al. [10,11] have studied the reaction kinetics by forward recoil spectrometry (FRES) and size exclusion chromatography (SEC) with a fluorescence detector, to monitor the reaction model of the end-functional polymers at a PS/PMMA interface. The results indicate the in situ copolymer formation is limited by the reaction rate, rather than the diffusion of reactive chains through the bulk. They and Jiao et al. [12,13] also observed the interfacial

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morphology can be changed during the interfacial reaction by AFM and TEM. Interfacial reaction induced roughing in polymer blends, due to the decreased of the interfacial tension. Kim et al. [24,25] also reported the interfacial tension became negative for a rough interface. Oyama et al. [15] proposed the pseudo-first-order kinetics for a system of PA6/PSU-MAH by X-ray photoelectron spectroscopy (XPS). Inoue and co-workers [14,26] established the experimental technique for ellipsometric analysis on the interfacial thickness of the in situ reactive compatibilization of the immiscible polymer blends. The results indicated the interfacial thickness increased with annealing time and then attained a constant value.

Recently, Kim et al. [27] introduced a rheological methods to study the interfacial reaction kinetics for PS-mCOOH/PMMA-GMA, and proposed three distinct stages for the change of $\eta^*$ with time. They also investigated the change of the interfacial morphology by AFM and TEM, and found that microemulsions were formed in a bulk phase.

In this paper, we will first present the experimental results on the interfacial reaction by rheological technique combination with ellipsometry and AFM. The aims at investigating the changes in viscosity properties ($\eta^*$) and interfacial thickness with reaction time to gain some general laws of the interfacial reaction, including building a reaction depletion layer, diffusion of PA chains controlling the coupling reaction, and the formation of the undulation interface.

## 2. Experimental section

### 2.1. Materials

The characteristics of the polymers used in this study are listed in Table 1. Poly(styrene/maleic anhydride) (SMA) was purchased from Sigma Chemical Company. Polystyrene (PS) and polyamide 6 (PA6) are commercial grade.

### 2.2. Rheological measurements

The samples for the rheological testing were prepared by compression molding, 170 °C for SMA and 240 °C for PA6. The samples were then annealed at 80 °C under vacuum for 5 days to allow relaxation of chains at the surface because of compression. Under a nitrogen environment, the two round samples (the high viscous PA6 was put at the bottom, while the low viscous SMA was mounted on the top of PA6 to avoid the flow of the low viscous polymer out) were placed into a rheometer at 200 °C. The complex viscosity ($\eta^*$) was monitored with reaction time. The strain amplitude ($\gamma_0$) and the angular frequency ($\omega$) were 0.005 and 0.5 rad/s, respectively, which lie in the linear viscoelastic regime.

### 2.3. Interfacial thickness measurement

At first, a PA6 substrate with 0.5 mm thickness was prepared by compression molding at 240 °C between the glass plates in order to obtain an flat surface. Meanwhile, a SMA film of about 300 nm thick was prepared by spin-coating from a 6 wt% toluene solution onto the PA6 substrate. The bilayer specimen thus prepared was dried under vacuum at 50 °C for 24 h, then measured in a hot chamber of the ellipsometer. The thickness of the interface and the upper layer SAM could be obtained by four model stimulation. The refractive index, $n_{\mathrm{SMA}}=1.53$, $n_{\mathrm{PA6}}=1.60$, $|n_{\mathrm{SMA}}-n_{\mathrm{PA6}}|\geq 0.02$, refractive index of the interface was assumed to be uniform, $n_{\mathrm{interface}}=(n_{\mathrm{SMA}}+n_{\mathrm{PA6}})/2$. The details of the ellipsometric analysis and the computation were as described in Ref. [26].

### 2.4. Interfacial morphology

PA6 was dissolved in HCOOH (6 wt%) and spun at 2000 rpm onto the silicon wafers ($2\times 2$ cm$^2$). After drying, a layer of 6 wt% SMA from toluene was spun directly onto the PA6. The toluene did not dissolve or significantly swell the PA6 film. Then the sample was divided into four parts after drying, which were annealed under vacuum for 0, 0.5, 1.5, 2.5 h at 200 °C, respectively. The SMA layer was removed by selective solvent toluene at room temperature for 24 h. Then, the interfacial morphology was obtained by an atomic force microscope (AFM) (SPA300HV/SPI3800N) from Seiko instruments industry, Co. Ltd.

## 3. Results and discussion

### 3.1. Rheological properties

For a reactive blend, graft (or block) copolymers in situ formed at the interface are able to result in the changes of the complex viscosity ($\eta^*$). Rheological methods can be used to monitor the interfacial reaction. Fig. 1 shows the

Table 1
Molecular characteristics of the polymers used in this study

| Polymer | $M_n$ ($\times 10^{-3}$) | Functionality | $T_g$ (°C) | $T_m$ (°C) | $\eta\times$(Pa s) at $\omega=0.5$ rad/s |
|---|---|---|---|---|---|
| SMA | 1.9 | 0.25 | 120 | – | $1.8\times 10^2$ (at 200 °C) |
| PS | 72 | 0 | 132 | – | $6.8\times 10^3$ (at 200 °C) |
| PA6 | 24 | – | – | 220 | $9.8\times 10^2$ (at 230 °C) |

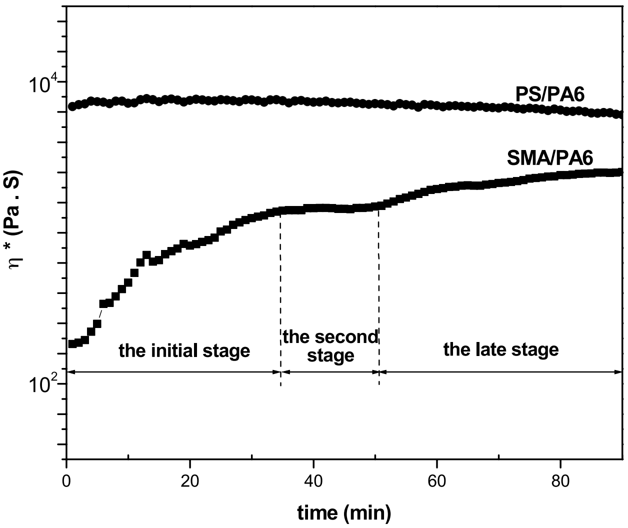


Fig. 1. Plots of $\eta^*$ vs. time for SMA/PA6 (■) and PS/PA6 (●) blends at 200 °C, respectively.

change of the complex viscosity ($\eta^*$) for SMA/PA6 and PS/PA6 with time at 200 °C. There is an obvious distinction between the two blends systems. The $\eta^*$ for PS/PA6 blend almost does not change with time. These results are expected, since no reaction in the interface of PS and PA6. For SMA/PA6 blend, the interfacial reaction as predicted by theory can be divided into three distinct stages by the results of complex viscosity ($\eta^*$). In the initial stage (before 30 min), $\eta^*$ increases with time since the equal opportunities for the two reactants lead to a second-order reaction, which is controlled by the reaction rate. After a short time, the reaction is likely to become a first-order because of the slow diffusion rate of $NH_2$ groups. When the in situ formed copolymers are sufficient to inhibit the interfacial reaction, a reaction depletion layer forms, during which $\eta^*$ does not change with the reaction time (during 30–50 min). In the late stage (after 50 min), the two reactants again meet in the interface and the copolymers still can be formed, which make $\eta^*$ increase slowly again.

The $\eta^*$ increase is an evidence of the copolymer formation from the reaction of SMA with PA6. In the early stage, the slope of $\eta^*$ vs. time is significant, which shows the rapid interfacial reaction. At the beginning of the reaction, the couple reactive ends are compact so that the reaction opportunities for PA6's chains and SMA's chains should be equal. Therefore, the interfacial reaction should be second-order for the two reactive groups. Fredrickson [20] and O'shaughnessy's studies [18] predicted at the initial reaction stage the number of the copolymer chains per area, Σ, increasing with time was given by

$$\frac{d\Sigma}{dt} = k(t) n_A n_B \tag{1}$$

where $k(t)$ was the rate constant and $n_A$ and $n_B$ were the number density of the reactive chains, respectively.

In the SMA/PA6 system, because a SMA chain has ∼5 MAH functional groups and a PA6 chain has one $NH_2$ group, excessive amount of MAH functional groups leads to a short second-order reaction and the copolymer formation is limited by the reaction rate rather than the diffusion of the reactive chains through the bulk according to the experimental results of Ref. [11]. The following reaction should be controlled by the diffusion rate of more dilute PA6's $NH_2$ end groups. There are several reasons sustain the assumption. (1) A SMA chain contains more reactive groups than a PA6 chain. (2) The reaction temperature, 200 °C is over the glass temperature of SMA and PA6, and under the melt temperature of PA6, then SMA chains have relatively high mobility rate. (3) A low molecular weight SMA chain easily adopts a low-entropy stretched configuration and enters into a dense copolymer brush in the interface. When they are some changes in the density of the reactive groups in the interfacial region and $NH_2$ groups of PA6 have less reaction opportunities than MAH groups of SMA, consequently, the next reaction should become first-order. Then there is a conversion from second-order to first-order of the interfacial reaction kinetics. Similar to the study of Kim et al. [27], the conversion $[X(t)]$ of the in situ formed copolymers can be obtained by the change of $\eta^*$ as follow.

$$[X(t)] = \frac{[\eta^*(t) - \eta_0^*(t)]}{[\eta_{\mathrm{sat}}^* - \eta_{\mathrm{no,sat}}^*]} \tag{2}$$

where $\eta^*$, $\eta^*_{\mathrm{sat}}$ is the complex viscosity of SMA/PA6 and the plateau value after 30 min, the subscribe 'no' in $\eta^*$ represents the system of PS/PA6 without SMA, and which are the initial complex viscosity of SMA/PA6 from Fig. 1.

Then the reaction rate equations for the second-order reaction kinetics (Eq. (3)) and the first-order reaction kinetics (Eq. (4)) are as follows.

$$\frac{\ln[(M - X_A)/M(1 - X_A)]}{[C_{B0}(M - 1)]} = k_2 t \tag{3}$$

$$-\ln(1 - X_A) = k_1 t \tag{4}$$

where $k_1$ and $k_2$ are the reaction constants, $M = C_{B0}/C_{A0}$, $C_{A0}$ and $C_{B0}$ are the initial concentrations of the reactive groups MAH and $NH_2$, respectively. Fig. 2 shows the plots of the conversion vs. reaction time by Eqs. (3) and (4), respectively. On the basis of the above results, there is a conversion from second-order reaction kinetics to first-order reaction kinetics.

After 30 min, the in situ formed copolymers attain an extent width at the interface and the more dilute PA6 end groups near the interface have completely reacted. The interfacial reaction was terminated and no copolymers formed results in the $\eta^*$ does not change with the reaction time. The interfacial reaction can only occur when PA6 chains penetrate through the no $NH_2$ end groups layer and the copolymer layer to meet the SMA chains in the copolymer interface. Obviously, the diffusion rate of PA6 through the bulk layer is different from the one through the

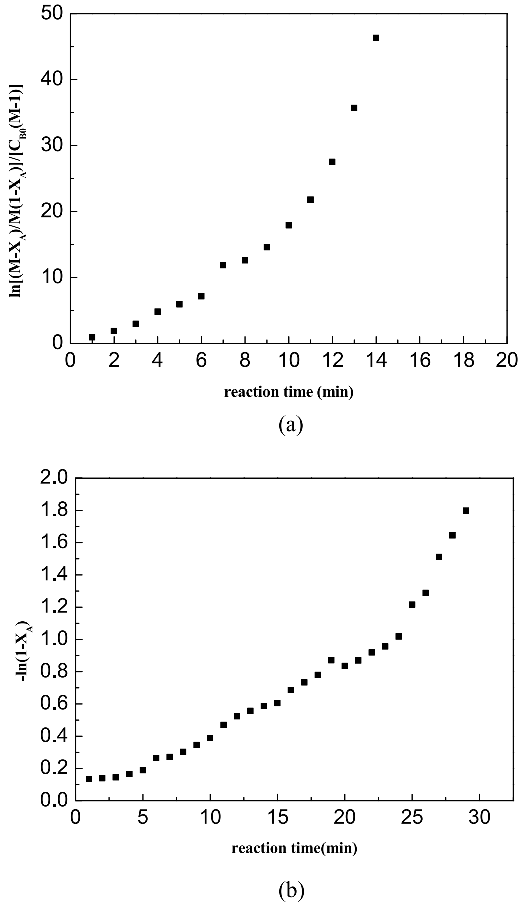
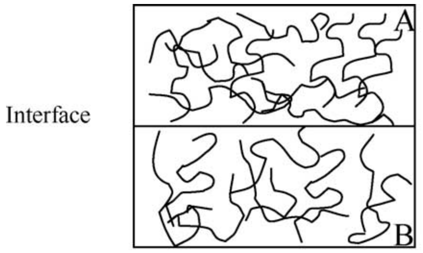


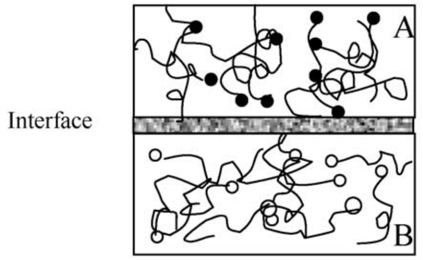
Fig. 2. Plots of conversion vs. reaction time for SMA/PA6 by Eqs. (3) and (4), respectively.

copolymer layer. The former belongs to the self-diffusion in PA6 phase, the later is the penetration rate through the copolymer layer, which should be much slower than the self-diffusion due to the densely copolymer barrier. Then the time from 30 to 50 min is exactly the time of the penetration of PA6 chains, during which there is no interfacial reaction between SMA and PA6 which leads to no change in complex viscosity $\eta^*$. Theory studies predicted a depletion layer builds up on a time scale $\propto \rho_0^{-2}$, where $\rho_0$ is the densities of the reactive groups. There is still no experimental results can prove the above quantity relation. However, for a reactive compatibilization system, building depletion layer depends on the end groups' reactivity. In the case of the weakly reactive pairs (Fig. 3(b)), there is no depletion layer. Only strong reactivity can lead to build up a reaction depletion layer (Fig. 3(c)).

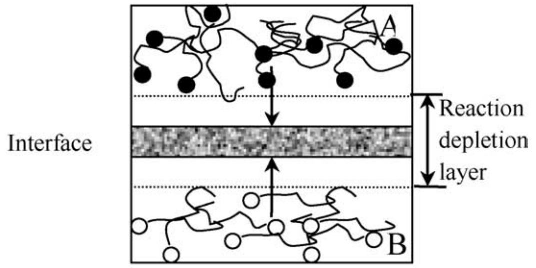
After 50 min, $\eta^*$ increases again, which indicates that PA6 chains can meet with SMA chains at the interface and there are increasing copolymers by the interfacial reaction between $NH_2$ groups and MAH groups. However, the slope of $\eta^*$ vs. time is much less than that at the early stage. The results show a dramatically slow reaction rate compared with the early stage. The reaction during the late stage is a complex process. The dense copolymer layer at the interface



(a) A/B (non-reactive)



(b) Weakly reactive A/B



(c) Strongly reactive A/B

Fig. 3. Schematic illustrations of the depletion layer formation. (a) Non-reactive A/B; (b) weakly reactive A/B without a reactive depletion layer; (c) strongly reactive A/B with a reactive depletion layer.

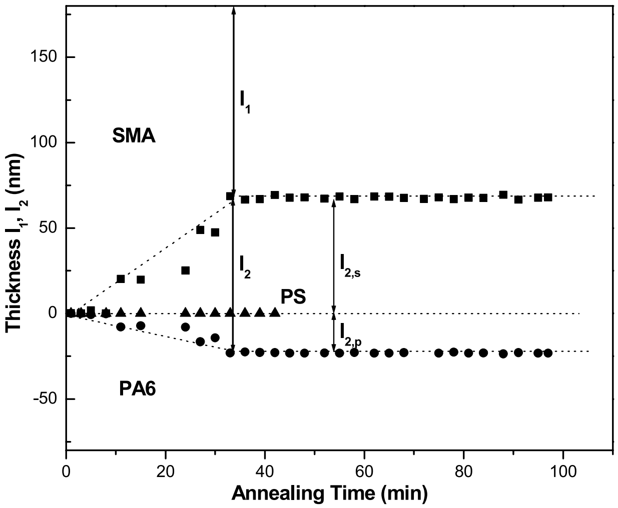


Fig. 4. The interfacial region, $l_2$, of SMA/PA6 with reaction time at 200 °C. $l_1$ is the distance from the top surface to interface, which equals to the thickness of the upper SMA layer, $l_{2,s}$ and $l_{2,p}$ are the contributions from SMA layer and PA6 layer to the interfacial region, $l_2 = l_{2,s} + l_{2,p}$.

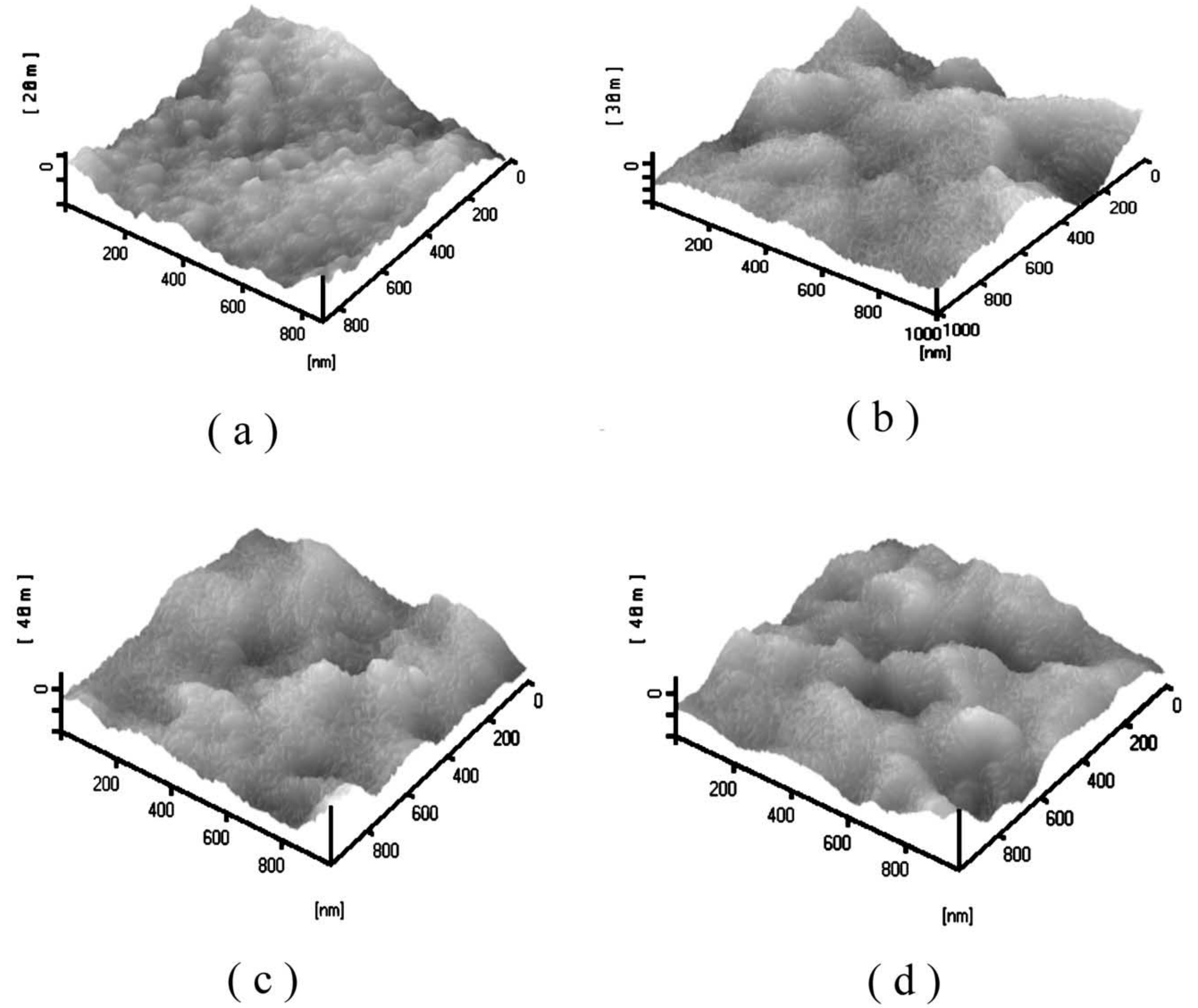


Fig. 5. AFM images ($1\times1$ μm$^2$) of the interfacial morphology development of SMA/PA6 with reaction time at 200 °C after SMA is selectively removed by toluene. (a) 0 h; (b) 0.5 h; (c) 1.5 h; (d) 2.5 h. The values of rms roughness at reaction times (a)–(d) are 4, 10, 13, and 17 nm, respectively.

inhibits the further reaction. Meanwhile, the diffusion of PA6 chains through the bulk also can affect the interfacial reaction. Therefore, the reaction rate should be controlled by the already formed copolymers barrier at the interface and the diffusion of PA6 chains. For SMA/PA6 system, relatively low PA6 chains density with slower diffusion rate would make PA6 take a long time to reach the interface to participate in the reaction. Therefore, PA6 chains diffusion is likely to control the interface reaction.

### *3.2. Interfacial thickness*

The miscibility between the two polymers can be evaluated through the interfacial thickness. When the two polymer films are put together and heated above their glass transition temperature, a broad interface will develop with time in miscible systems, whereas the formation of a thin interface is characteristics of the immiscible systems. The interfacial thickness between SMA and PA6 was measured by ellipsometer in our studies. Fig. 4 shows the typical time variation of the interfacial thickness at 200 °C. The interfacial thickness of PS/PA6 stays very thin and less than the measurable limit of ellipsometer, indicating the strong immiscibility between PS and PA6. However, the interfacial reaction between SMA and PA6 produces the in situ copolymers in different ways. The interfacial region, $l_2$ increases with reaction time and then reaches constant as thick as 67 nm at 30 min, taking account of the composition profile at the interface layer, the interfacial thickness $h$ was determined as $h=l_2/1.7$ [26], nearly 40 nm, which was large enough to exceed the coil size of the copolymer produced at the interface [14]. Because the molecular weight of PA6 is much higher than SMA, the differences in molecular weight and molecular mobility lead to an asymmetry interface as shown in Fig. 4 by ellipsometric analysis, where $l_1$ is the distance from surface to interface, which equals to the thickness of the upper SMA layer. From the change of $l_1$, $l_2$ with reaction time at 200 °C, there is an asymmetry interface which more deeply develop into SMA phase than into PA6 phase ($l_{2,s} > l_{2,p}$). In order to interpret the fact of the thick interface of the reactive compatibilization, Koriyama et al. [14] proposed two plausible models: one is an undulated interface and the other is a micelle formation. In the former model, some experiments already proved there is an undulated interface after the interfacial reaction [12,13]. In our experiment, the interfacial thickness keeps constant after 30 min. The undulated interface model exactly interprets our results. The constant interfacial thickness does not mean a saturated interfacial area and $\eta^*$ can still increase.

### 3.3. Interfacial morphology

Interfacial morphology of the system of SMA/PA6 was studied by scanning force microscopy (AFM). In this case, SMA is selectively removed by toluene. As shown in Fig. 5, the roughness with reaction time increases from 4 to 17 nm, which indicates the interfacial reaction can lead the interfacial roughness to increase. A reasonable explanation for the undulated model is that the copolymer formation has reduced the SMA/PA6 interfacial tension, even to zero, and the thermal fluctuations during the interfacial reaction may lead to the undulated interface, which can be covered by more copolymers than flat interface [13]. The roughness increase is due to the more interfacial reactions. In early stage (before 30 min), the roughness increases 6 nm. However, 2 h later, the roughness increases 7 nm, which shows the rapid reaction in the early stage. On the other hand, during 0.5–1.5 h, the roughness increases only 3 nm. The small increasing in roughness further proves that there is reaction depletion layer during the interfacial reaction. The undulated interface formed with reaction time is clearly seen in AFM images, which further proves the assumption that more interfacial reactions can result in the increasing of the interfacial area by formation of the undulated interface without increasing of the interfacial thickness.

## 4. Conclusion

Rheometry, ellipsometry and atomic force microscopy have been used to monitor the reaction at a SMA/PA6 interface at 200 °C for various period of time. The interfacial reaction as predicted by theory can be divided into three distinct stages by the results of complex viscosity ($\eta^*$). In the initial stage, the equal opportunities for the two reactants lead to a second-order reaction, which is controlled by the reaction rate. After a short time, the reaction is likely to become a first-order because of the slow diffusion rate of $NH_2$ groups. When the in situ formed copolymers are sufficient to inhibit the interfacial reaction, a reaction depletion layer forms, during which $\eta^*$ does not change with the reaction time. In the late stage, the two reactants again meet in the interface and the copolymers still can be formed, which make $\eta^*$ increase slowly again. However, the interfacial thickness increases with time in the early stage then keeps constant by building up the undulated interface. Moreover, for the interfacial reaction of SMA/PA6, there is an asymmetry interface which deeply develops into SMA layer as proved by ellipsometer.

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