

# Heterogeneous Polymeric Reaction Under Shear Flow

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**ABSTRACT:** The effects of different shear flows on polymeric reaction between poly(styrene/maleic anhydride) (SMA) and polyamide 6 (PA6) in heterogeneous blending system were investigated. FTIR, SEM, rheometry, and GPC were used to qualitatively analyze the reaction, and the reaction apparent activation energy was determined as 75.7 kJ/mol by a rheological method. To study the effects of different shear flows on heterogeneous polymeric reaction, a more practical technique was developed to select the data that only responds to the reaction without the effect of different shear flows. Avrami's equation was employed to analyze the reaction process under

shear flow and the results showed that the half period ( $t_{1/2}$ ) of reaction process decreased with the increase of the shear rate in this study. Moreover, the decrease rates were different in the different shear modes as follows: the half period decreased slightly under the oscillatory shear, whereas it decreased strongly under the steady shear. The possible reasons for these phenomena were discussed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2737–2745, 2008

**Key words:** shear flow; reaction kinetics; rheological method

## INTRODUCTION

Producing polymer blends with small-scale and stable microstructure is an important research goal. One of the most popular methods currently used in industry is reactive blending, which can result in immiscible polymers blending well after a few minutes of mixing.<sup>1–6</sup> When the polymer chains with complementary functional groups meet at an interface during mixing, they can react to form block or graft copolymers that can greatly reduce the interfacial tension and suppress the coalescence, and then result in a stabilized blend.

During the past decades, there have been studies of effectiveness of these copolymers in fortifying morphology and improving the properties of the polymer blends.<sup>4–6</sup> Many aspects of the reaction have been investigated, including reaction kinetics, interfacial morphology development, and interfacial adhesion. However, basic knowledge of the kinetics of the coupling reaction at the interface is still lacking. Moreover, research of the shear flow effects on the coupling reaction at the interface is especially limited, which may be attributed to the complexity of the flow. Yang and Lin<sup>7</sup> qualitatively studied the influence of shear flow on the SEBS-g-MA/PCL reac-

tive blending and concluded that the reaction rate was strongly affected by both the intensity and the pattern of flow. Macosko and coworkers<sup>8,9</sup> suggested that the external flow in the mixer during polymer blending process accelerated the interfacial coupling rate to a great extent from that of the static flat interface by increasing the interfacial area. But they also found that the reaction conversions under dynamic shear were also significantly increased as compared with that under static annealing when the total interfacial area was kept the same. Clearly, more work is needed to experimentally study the effects of shear flow on the polymeric reaction.

Recently, Bousmina et al.<sup>10,11</sup> reported that the interdiffusion coefficient between two polymer chains with a planar interface could be measured by monitoring the changes of rheological properties under a small-amplitude oscillatory shear which does not affect the diffusion mechanism. Once the rheological properties are related to the amount of *in situ* formed graft (or block) copolymers for a reactive blend, the reaction kinetics might be evaluated if the temporal rheological properties are monitored. Based on the earlier inference, the coupling reaction of functional polymers at flat, immiscible polymer–polymer interfaces has been studied using bilayer samples as a model system.<sup>12,13</sup> Kim and coworkers<sup>14,15</sup> evaluated the kinetics of the reaction between the PS-mCOOH/PMMA-GMA reactive polymer–polymer interface by putting the samples under a small-amplitude oscillatory shear. Although this method brings much convenience to the study of

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reaction kinetics and interfacial morphology development, the form of bilayer samples with a planar interface limits the study of effects of shear flow.

In this study, we aimed at investigating the reaction between SMA and PA6 in a heterogeneous melt blending and the effects of shear flow on the reaction. A reactive PA6 was selected for the study. The end groups of this PA6 are not blocked, and each long chain has an amino end group. The amino end group can react with the maleic anhydride group on SMA in melt and produce long chain branched copolymer, which stay at interface acting as compatibilizer. Firstly, we presented the experimental results of the interfacial reaction by rheological method combining with GPC, and got the reaction kinetic parameter. Secondly, we studied the effects of different shear flows on the polymeric reaction in heterogeneous melt. By comparing the half period of reaction processes obtained under different shear flows, we investigated the effects of shear flow on coupling reaction in heterogeneous blend and tried to give a reasonable explanation.

## EXPERIMENTAL

### Materials

The molecular characteristics of the polymers employed in this study are listed in Table I. Polystyrene (PS) are commercial grade and was supplied by Chevron (The Woodlands, TX). Poly(styrene/maleic anhydride) (SMA) containing 18 wt % maleic anhydride was supplied by SINOPEC Shanghai Research Institute of Petrochemical Technology. The polyamide 6 used in this study were supplied by Jinlun Group, China, having an average of one  $-NH_2$  end group per chain.

### Melt blend

Before processing, all materials were dried overnight under vacuum at 80°C. Then, SMA and PA6 were blended by Haake at 230°C with a rotor speed of 45 rpm. The weight ratio between SMA and PA6 was 80 : 20. After mixing for a given time, the blends were removed from the mixer quickly and quenched to freeze in the existing phase morphol-

ogy. The same process was performed on the PS/PA6 blend. The weight ratio between PS and PA6 was also 80 : 20.

### Characterization

Samples for the FTIR study were prepared by separating the SMA and PA6 components from the blends after processing. Before chemical characterization blends removed from the mixer were milled to little particles and subsequently dried overnight at 60°C under vacuum. Then, tetrahydrofuran (THF) was used to dissolve the blended material, resulting in a PA6 precipitate and a solution of SMA in THF. The solution of SMA could be separated by a centrifuge. FTIR spectra were recorded on a Paragon 1000 (Perkin-Elmer, USA) spectrometer after drying of the solution at 60°C under vacuum. Data were reported as an average of at least 20 scans. A Series 200 GPC (Perkin-Elmer) was also used for molecular weight characterization as well as for monitoring the progress of the reaction in polymer blend.

### Rheological measurements

For rheological analysis, blends from mixer were hot-compression molded under 10 MPa at 230°C for 3 min to form plate. The thicknesses of plates were about 1 mm. After that, the blend plates were cut carefully with a razor blade to form discs with a diameter of 25 mm. Then the discal blending samples were dried at 80°C under vacuum for 1 day and stored under vacuum to minimize the moisture sorption.

After the samples were put into a rotational rheometer (Gemini 200 HR, Bohlin Instruments, UK), the rheological properties of the samples were monitored at 240°C. To study the effects of the different shear flows, oscillatory shear mode and steady shear mode were employed. When samples were under the oscillatory shear, the strain amplitude was 0.01, which lies in the linear viscoelastic region, and the angular frequency was varied from 0.3 to 30 rad/s. When samples were under the steady shear, the shear rate changed from 0.1 to 10  $s^{-1}$ .

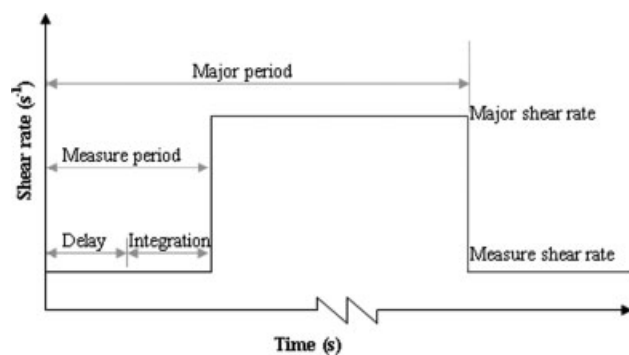
The rheological properties of the samples under different shear rates were monitored. To correlate the apparent rheological properties with the progress of the reaction, a new measure technique was employed to eliminate the shear effects on the materials. The measure method employed here is illustrated in Figure 1. Firstly, the samples were sheared under a low shear rate (namely measure shear rate) for a measure period, then, the shear rate was raised to a high shear rate (namely major shear rate). It should be noticed that the major period was much longer than the measure period. After that, the shear rate was decreased to the low shear rate again to

TABLE I  
Molecular Characteristics and Properties of  
the Polymers Used in This Study

Polymer	$M_n$ (kg/mol)	$M_w/M_n$	$T_g$ (°C) <sup>b</sup>	$T_m$ (°C) <sup>b</sup>
PS	58.31 <sup>a</sup>	1.636 <sup>a</sup>	133	–
SMA	55.99 <sup>a</sup>	1.782 <sup>a</sup>	134	–
PA6	22	1.9	–	222

<sup>a</sup> By GPC.

<sup>b</sup> By DSC.



**Figure 1** Schematic description of the measure method for rheological measurement in this study.

measure the temporal rheological properties, and raised to high shear rate again. Then, the rheological properties obtained under the low shear rate can reflect the progress of reaction which happens mostly under the high shear rate. Changing the major shear rate (high shear rate) and maintaining the measure shear rate (low shear rate), the data of rheological properties under different shear rates can be obtained in same conditions. So, this experimental method gives us possibility of investigating the effects of different shear rates on the reaction.

It is shown in Figure 1 that the measure period was divided into delay section and integration section. On the one hand, as there is a relaxation for the polymer to reach a new equilibrium after a sudden change of the shear rate, delay section should be set longer than the maximum relaxation time of polymer. Experimental data proved that the relaxation times of our materials are no more than 20 s at 240°C. On the other hand, the measure period should be much shorter than the major period. Because the measure period is much shorter than the major period, it can be regarded that the measure period has less effect on the reaction that happened under high shear rate. The experiment parameters are shown in Table II.

### Morphological measurements

The phase morphology of the blends has also been characterized by a S-2150 (Hitachi, Japan) SEM. The microstructure was revealed by examining surfaces

produced by freezing in liquid nitrogen and subsequent fracture.

Image analysis on the obtained SEM micrographs was performed using image analysis software (Image Tool, UTHSCSA). The morphological parameters of the blends were quantified as follows. For the systems with a droplet/matrix structure, the average size and the size distribution of the dispersed particles were determined. About three SEM photographs (each containing about 100 particles) were analyzed for each blend. The number-average particle diameter ( $D_n$ ) was calculated from

$$D_n = \frac{\sum_i n_i d_i}{\sum_i n_i} \quad (1)$$

with  $n_i$  as the number of particles having diameter  $d_i$ . Data were expressed as means  $\pm$  standard deviation (SD) and were analyzed using standard analysis of Student's  $t$ -test. Differences were considered significant when  $P < 0.05$ .

## RESULTS AND DISCUSSION

### Characterization of SMA-g-PA6 copolymers

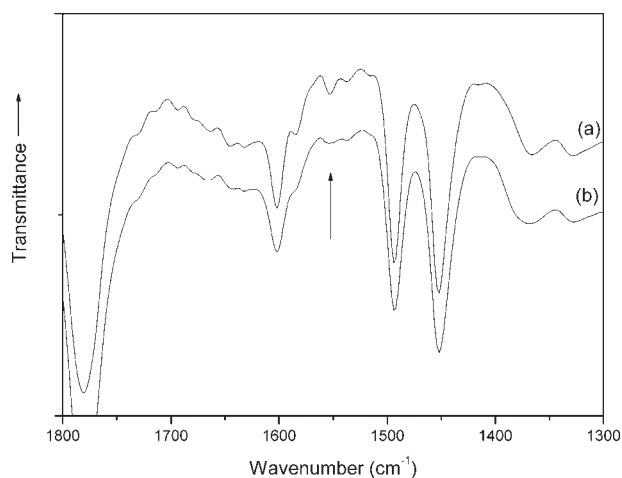
The *in situ* reaction between SMA and PA6 during melt mixing may form graft copolymers at the interface. The nature of the compatibilizing reaction was investigated using FTIR spectroscopy, with the aim of directly confirming the generation of copolymers. Unfortunately, it was not possible to confirm the reaction mechanisms directly in SMA/PA6 blends owing to overlap of the absorption bands of the reactive groups. However, the reactivity of SMA with PA6 has been previously verified.<sup>16,17</sup>

An extraction technique was employed to prepare samples for FTIR which used to verify copolymer formation.<sup>18</sup> After the solvent separation, the SMA was examined. Figure 2 shows FTIR spectra of pure SMA and SMA extracted from the melt blend. Comparing the spectrum of pure SMA with that of SMA extracted from the melt blend shows the presence of amide group as evidenced from the N–H bending at about 1550  $\text{cm}^{-1}$ . Therefore, it is clear that SMA-g-PA6 copolymer was formed via chemical reaction between SMA and PA6.

**TABLE II**  
Experiment Parameters for Rheological Method

	Major shear rate	Measure shear rate	Major period	Measure period	
				Delay	Integration
Steady shear	0.1–10 $\text{s}^{-1}$	0.1 $\text{s}^{-1}$	300 s	20 s	20 s
Oscillatory shear	0.3–30 rad/s	0.3 rad/s	About 300 s	20.9 s <sup>a</sup>	20.9 s

<sup>a</sup> A period time in 0.3 rad/s is about 20.9 s.



**Figure 2** FTIR spectra of (a) SMA dissolved from blending of SMA/PA6 and (b) pure SMA.

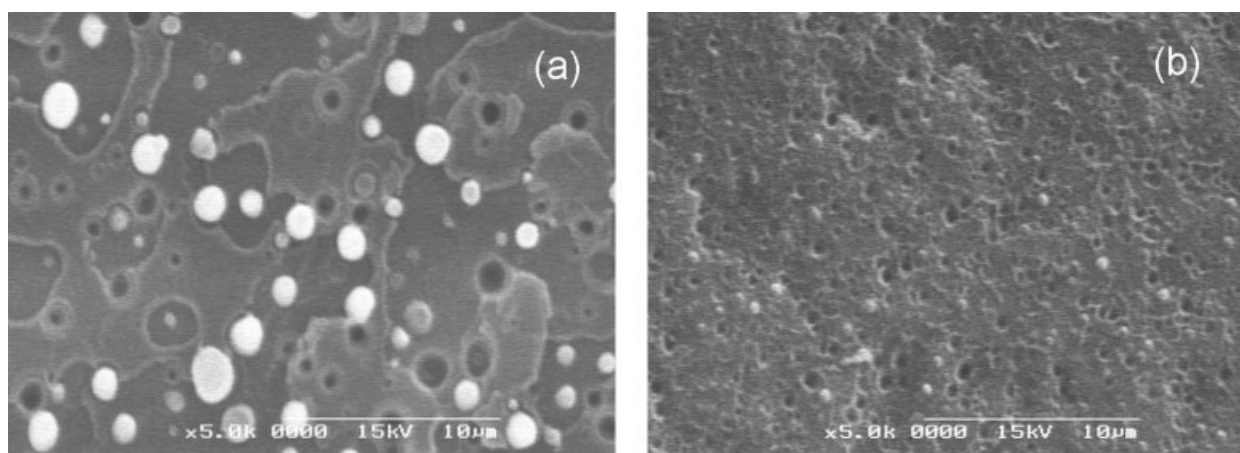
The fracture surfaces of blends of PS/PA6 and SMA/PA6 are shown in Figure 3. In the SEM micrograph of the 80/20 PS/PA6 blend, PA6 domains have a well-defined spherical shape and a very broad size distribution. Also, the fracture surface of this blend appears to be very smooth. This is a typical morphology of an incompatible blend. When, instead of PS, SMA is blended with PA6, the domain size of the dispersed phase is significantly reduced and its distribution becomes sharper. These are expected results since the reactive system may generate the SMA-PA6 graft copolymer, which would play a role of emulsifier to prevent particle coalescence during blending and to reduce the interfacial tension.<sup>19</sup> Figure 4 shows the average diameters of dispersed particles from SEM as a function of reaction time in mixer. It can be seen that there is a significant decrease of the particle size in the unreactive system with the residence time in the mixer and more fast size reduction in the reactive system. Even

less than 5 min of mixing is sufficient for the reactive system to reach the final particle size. Many studies<sup>20</sup> have shown that most of the size reduction of dispersed particle in compatibilized system occurs very rapidly during mixing. The particle size in the reactive system is slightly smaller than that in the unreactive system.

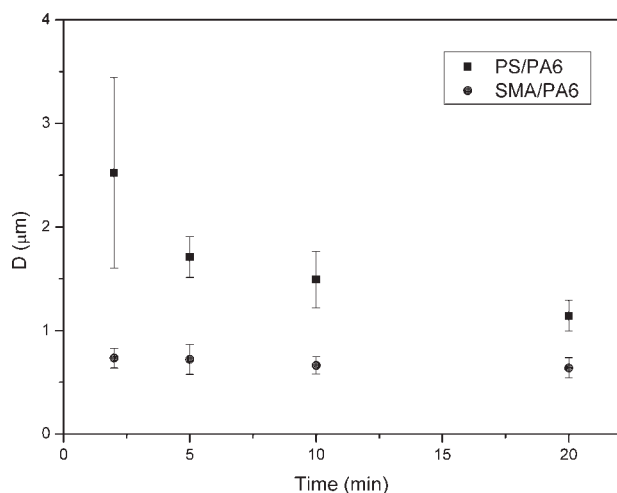
The application of  $G'$  versus  $G''$  plots is a useful method for rheological characterization. It has been reported<sup>19</sup> that such plots are very slightly affected by temperature and molecular weight, but strongly dependent upon the molecular weight distribution and side-chain branching. Figure 5 shows the  $G'$  versus  $G''$  plots for the PS/PA6 and SMA/PA6 blends. When SMA was used as a blend component, the curve shifted from the viscous-dominant region to the elastic-dominant region. This phenomenon suggests that SMA reacts with PA6 resulting in some branching and molecular weight broadening.<sup>21,22</sup>

### Reaction kinetics analysis

As the plot of  $G'$  versus  $G''$  is sensitive to the amount of long-chain branched copolymer *in situ* formed, the reaction kinetics might be evaluated by monitoring temporal changes of  $\tan \delta$  of reactive system. SMA (or PS) and PA6 were firstly blended by Hakke at 230°C in 2 min, and then removed for sample molding quickly. After the sample was put into the rotational rheometer,  $\tan \delta$  of the system was monitored at 240°C under a small-amplitude oscillatory shear and the angular frequency was 0.3 rad/s. Figure 6 shows the plots of  $\tan \delta$  with time for SMA/PA6 blend. Those plots of immiscible blend of PS/PA6 were added. It can be seen from Figure 6 that  $\tan \delta$  SMA/PA6 blend could be divided into two different stages.  $\tan \delta$  decreases with time and gradually reaches a steady value in the Stage I. After the transition time ( $\tau_{\text{tran}}$ ),  $\tan \delta$  maintains a steady value



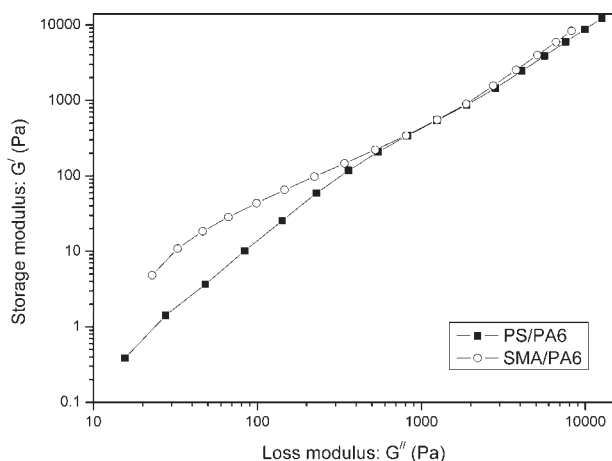
**Figure 3** SEM micrographs of fractured surfaces for (a) PS/PA6 blend and (b) SMA/PA6 blend.



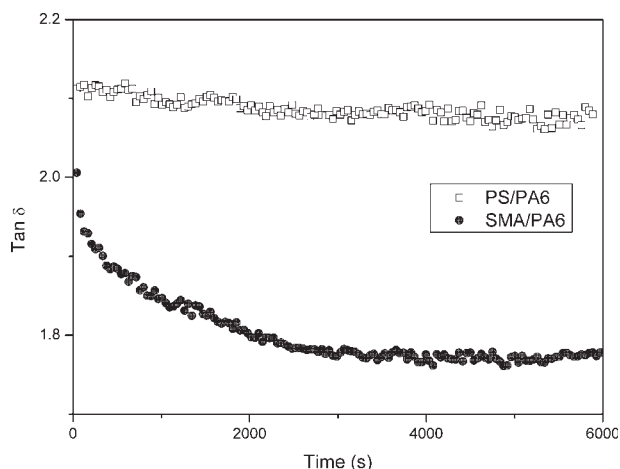
**Figure 4** The average diameters of dispersed particles in mixing versus time.

( $\tan \delta_{ste}$ ) in the Stage II. This is attributed to the coupling reaction between amino end group on PA6 and maleic anhydride group on SMA.<sup>23</sup> The long-chain branched copolymer *in situ* formed increases the elastic response of the system leading to the decreases of the loss angle. As the reaction proceeds, functional groups near the interface become less and less, and the interfacial layer becomes saturated gradually. The saturated copolymer layer prevents the meeting of the reactive chains and the reaction enters into stagnant stage, which corresponds to the steady value of  $\tan \delta$ . However, there is almost no change in  $\tan \delta$  of PS/PA6 system during the whole process, which is quite different from that of the SMA/PA6 system. As PS has no reactive group, there is no reaction and no copolymer produced, and then  $\tan \delta$  of the system has no change.

As the end groups of PA6 are not blocked, polycondensation reaction may happen in melt and pro-



**Figure 5** Log-log plot of storage modulus against loss modulus for PS/PA6 and SMA/PA6 blends.

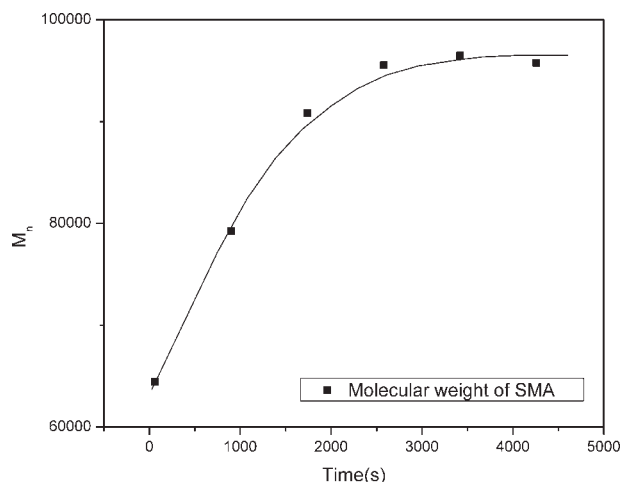


**Figure 6** Plots of  $\tan \delta$  with time for PS/PA and SMA/PA6 blends.

duce longer chain that also increases the elastic response of the system. The polycondensation reaction in PA6 can be ignored as expected since the reaction rate of polycondensation is much lower than that of the reaction between amino group and anhydride group and the weight fraction of PA6 is as low as 20%. This also can be proved in Figure 6 as there was almost no change in  $\tan \delta$  of PS/PA6 system during the whole process.

As a blend containing two immiscible polymers, the loss angle of system is also affected by the morphology of the dispersed phase. Results from SEM indicate that the average diameter of dispersed particle hardly changed in an hour in the rheological experiment. This suggests that the morphology of phase made no contribution to the change of  $\tan \delta$  of the system. Therefore, it can be concluded that the change of  $\tan \delta$  was mostly because of the reaction between SMA and PA6. As mentioned earlier<sup>20</sup> that a little copolymer produced at the interface can greatly reduce the size of the dispersed particle in the heterogeneous system, no change of dispersed phase in our rheological experiment indicates that a little reaction have occurred during the sample preparation though we decrease the temperature of preparing process from 240 to 230°C. Nevertheless, the little amount of reaction occurred during the sample preparation facilitates our following rheological experiments for keeping morphology unchanged.

Figure 7 shows the GPC measurement results of the samples removed from the rheological experiments in different time. It can be seen that the molecular weight of the SMA increased with the reaction time and reached a steady value gradually. However, the molecular weight of PS shows no change because of unreactive system. This result also suggests that the change of  $\tan \delta$  is closely relative with the reaction process.



**Figure 7** Plots of molecular weight of SMA dissolved from SMA/PA6 blend and PS dissolved from PS/PA6 blend with time.

Similar to the study of Kim et al.,<sup>15</sup> the conversion  $X(t)$  of the *in situ* formed copolymers can be obtained by the change of  $\tan \delta$  as follows:

$$X(t) = \frac{[\tan \delta(t) - \tan \delta_0]}{[\tan \delta_{ste} - \tan \delta_0]} \quad (2)$$

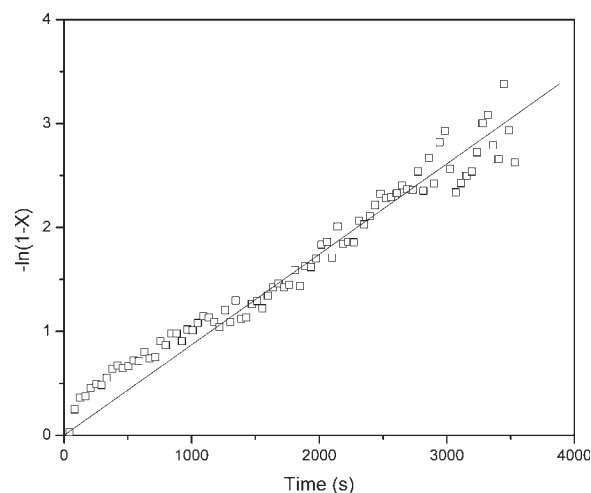
where  $\tan \delta_{ste}$  is the steady value of  $\tan \delta$  of reactive blend and  $\tan \delta$  is the maximal initial value. There have been experimental and theoretical studies of the interfacial reaction kinetics, and the results have indicated that the first-order kinetics dominates the interfacial reaction.<sup>24,25</sup> Figure 8 shows the plots of conversion ratio of the reaction at the interface with reaction time, which were calculated according to the following equation for the first-order reaction kinetics:

$$kt = -\ln(1 - X) \quad (3)$$

It can be seen that the reaction kinetics can be described by the first-order reaction kinetics. The results at other temperatures (245 and 250°C) were the same to that at 240°C as shown in Table III. From the Arrhenius plot (the reaction constant versus inverse temperature), it can be obtained that the apparent activation energy ( $\Delta E$ ) for the reaction of SMA and PA6 was 75.7 kJ/mol on the basis of first-order reaction.

### Effects of shear flow on polymeric reaction

As mentioned earlier that the loss angle ( $\delta$ ) of system might also be affected by the morphology of dispersed phase, and the strong external shear flow may result in the change of the morphology in the



**Figure 8** Plots of conversion versus time by eq. (3).

system, then  $\delta$  of system may also change with time even there is no reaction. Although the possible change of morphology disable us from estimating the reaction kinetic parameters by using change of  $\tan \delta$ , other approximation can still help us observe the process of reaction. As same as  $\tan \delta$ , the primary normal stress coefficient ( $\psi_1$ ) is also firmly relative to the elastic property of the system. The results obtained in steady shear mode shows that the plots of  $\psi_1$  with time has two similar stages: decreases in the first stage and maintains a steady value in the second stage. This gives a possibility to study the shear flow on polymeric reaction in steady shear mode as same as in oscillatory shear mode. The conversion  $X(t)$  of the *in situ* formed copolymers in steady shear mode can be obtained by the change of  $\psi_1$  as follows:

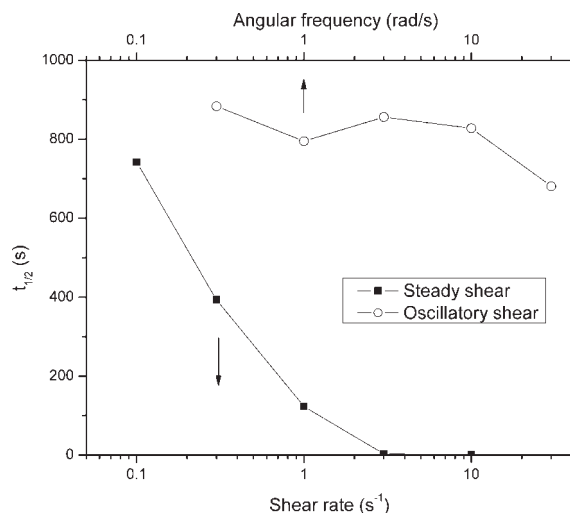
$$X(t) = \frac{[\Psi_1(t) - \Psi_{1,0}]}{[\Psi_{1ste} - \Psi_{1,0}]} \quad (4)$$

where  $\Psi_{1ste}$  is the steady value of  $\psi_1$  of reactive blend and  $\psi_{1,0}$  is the initial value.

Avrami's theory is a classical theory over all transformation kinetics theories. It is a simple approximation and widely used to analysis transformation in many fields. It also appears to give reasonable results even when its restrictive assumptions are not well satisfied. Here, Avrami's equation was used to analyze the process of reaction as follows:

**TABLE III**  
Reaction Constants at Different Temperatures

Temperature (°C)	Reaction constant (s <sup>-1</sup> )
240	$8.71 \times 10^{-4}$
245	$8.89 \times 10^{-4}$
250	$1.22 \times 10^{-3}$



**Figure 9** Plots of half period in different shear rates for steady shear mode and in different angular frequencies for oscillatory shear mode.

$$1 - X(t) = \exp(-Kt^n) \quad (5)$$

where  $X(t)$  is the conversion in eqs. (2) and (4),  $K$  and  $n$  are special constants. The half period of process ( $t_{1/2}$ ) can also be given as follows:

$$t_{1/2} = \left(\frac{\ln 2}{K}\right)^{1/n} \quad (6)$$

So, the half period ( $t_{1/2}$ ) can help us observe the process of reaction.

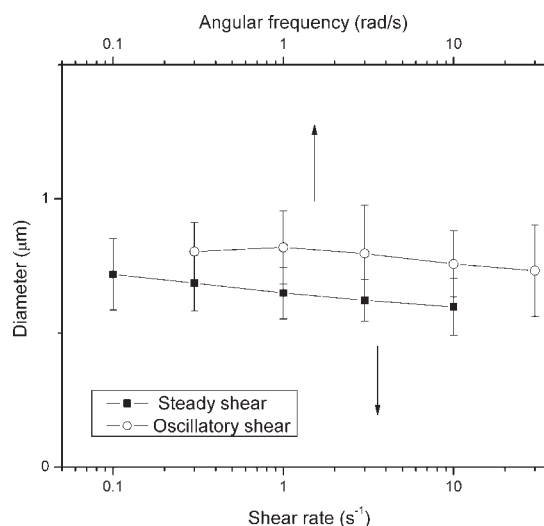
The half period ( $t_{1/2}$ ) in different shear modes are shown in Figure 9. It is obvious that the half period decreased with the increase of the shear rate. This indicates that the external shear flow can accelerate the reaction at the interface. As an immiscible system, the functional groups are located primarily in the different bulk phases, respectively, and are highly segregated. The interfacial regions between both the phases are only locations where the two functional groups can meet, collide, and react. This leads to the fact that the rate of reaction is entirely controlled by the collision frequency of the functional groups at the interface. Many workers<sup>26,27</sup> have studied the reactions in mixing and have proposed that the shear flow greatly accelerates the reactions in heterogeneous systems by increasing interfacial area. However, the diameters of dispersed particles have no much change after transition time under shear flow as shown in Figure 10, which indicates that the conclusion reported previously is not fit for our experiments. When external shear flow performs on the polymer system, the movement of macromolecules is accelerated. This increases the collision probability of complementary functional groups at the interface and shortens the time needed

for the saturated interface. In addition, the external shear flow can also lead to the deformation of dispersed droplet, which increases the interfacial area. This also contributes to the increasing reaction rate.

Yang and Lin<sup>7</sup> proposed that the oscillatory shear was more effective in promoting the reaction rate than the steady shear. But in our study, when the results obtained under the oscillatory shear were compared with that obtained under the corresponding steady shear, it could be seen that the decrease of the half period ( $t_{1/2}$ ) under the steady shear was much greater than that under the oscillatory shear as shown in Figure 9. This indicates that the steady shear is more effective than the oscillatory shear in accelerating reaction in our study. It seems that the conclusion we obtained is contrary to that previously reported. But as the strain amplitude of oscillatory shear in our study is small as 0.01 and the small-amplitude oscillatory shear do not affect the macromolecule diffusion mechanism,<sup>10</sup> the results we obtained are acceptable.

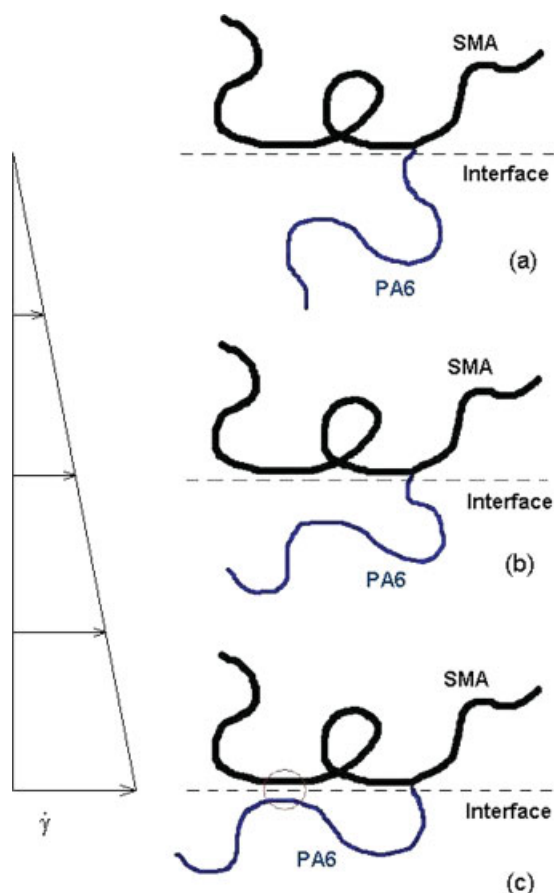
Figure 10 shows the average diameters of dispersed particle after transition time under different shear modes. It can be seen that the value hardly change with the increase of the frequency in oscillatory shear mode because the experiments being in the same low strain amplitude. The values were lower after transition time in steady shear mode compared with that in oscillatory shear mode and decreased slightly with the increase of shear rate. These results confirmed that the steady shear was more effective than the oscillatory shear in this study.

Under the external shear flow, the long chains in the blend are orientated and stretched easily. So does the copolymer which produced at the interface. As the long-chain branched copolymer locates only

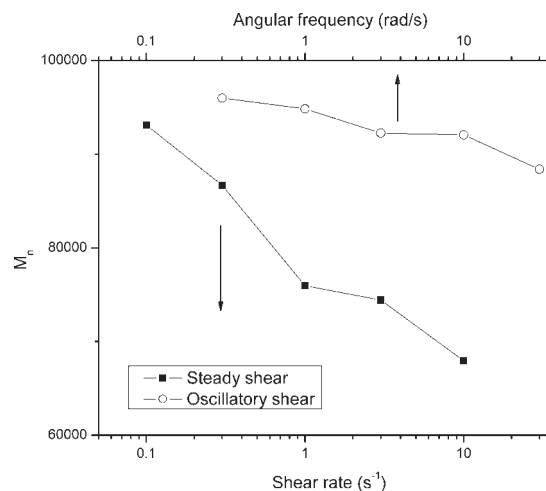


**Figure 10** The average diameters of dispersed particles after rheological experiment in different shear modes.

at the interface, the orientation and stretch of branched long chain make it more close to the interface. This gives amide functional group in grafted PA6 chain more opportunity to meet, collide, and react with maleic anhydride group in SMA as illustrated in Figure 11. Duin et al.<sup>21</sup> experimentally studied the reaction between PA and maleic anhydride containing polymer. They concluded that the grafted PA chains close to the PA/(MA-containing polymer) interface can react with maleic anhydride again in the existence of water molecule released from previous graft reaction, and led to the decrease of the molecular weight of grafted PA chains. Similar results were obtained in our study that the molecular weight of SMA in blend after transition time decreased with the increase of the shear rate as shown in Figure 12. This can be attributed to the more reaction between amide group in grafted PA6 chains and maleic anhydride group in SMA. When the results obtained from different modes were compared, it can be seen that the decrease of the molecular weight of SMA in blend after transition time under steady shear is greater than that under the oscillatory shear as shown in Figure 12. This result



**Figure 11** Illustration of branched copolymer (a) at static interface and (b, c) under shear flow. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 12** Plots of molecular weight of SMA dissolved from SMA/PA6 after transition time in different modes.

also indicates that the steady shear is more effective than the little amplitude oscillatory shear in this study.

## CONCLUSIONS

In this study, FTIR, SEM, rheology, and GPC were used to study the reaction between SMA and PA6 in heterogeneous blending system. A rheological method was used to estimate the reaction apparent activation energy. The value is 75.7 kJ/mol. To study the effects of different shear flows on the heterogeneous polymeric reaction, a more practical technique has been employed to select the data that only responds to the reaction without effect of different shear flows. The reaction process under different shear flows were analyzed by Avrami's equation and the results were compared. Investigation of half period of reaction process under different shear flows showed that the reaction was accelerated with the increase of shear rate. This phenomenon may be attributed to the increase of the collision probability of functional groups at the interface when the interfacial areas have no much change. In addition, the experiments also showed that the steady shear is more effective than oscillatory shear in accelerating reaction. This is attributed to the small-amplitude oscillatory shear employed in our study which does not affect the macromolecule diffusion mechanism.

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