Reaction kinetics study of asymmetric polymer–polymer interface

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Abstract

In this study, the reaction kinetics of asymmetric polymer–polymer interface was experimentally and theoretically studied. A new rheological method correlating the change of rheological property of reactive system with the conversion of the in situ formed copolymers was applied to study the reaction kinetics of PBT/epoxy reactive system. Then, the new method was proved to be useful by comparing its results with that obtained from the conventional endgroup determination method. Moreover, the conversion of PBT/epoxy reactive system from rheological method could be well fitted by the numerical analysis, from which the kinetic constant and the diffusion constant of epoxy in PBT could be determined simultaneously.
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Keywords: Reaction kinetics; Rheological analysis; Numerical analysis

1. Introduction

Reactive blending of two or more polymers with in situ reactive compatibilizers has been extensively employed for developing new materials with desirable mechanical properties [1–11], which provided an attractive alternative to costly developments of new copolymer syntheses. However, most of the present studies were motivated principally by industrial applications and focused on the improvement of physical properties of the blend systems [5–11]. Only a few studies [12–15] were reported on the examination of the reaction kinetics in the reactive blend, which was probably due to the complexity of the reaction and restricted methods for monitoring the process of reaction.

Fredickson [16,17] and O'Shaughnessy [18–20] theoretically studied the reaction at a planar interface between two polymers. They showed that with increasing reaction time the reaction became mean-field type at initial time. As the interface became saturated with in situ formed copolymers, the reaction rate decreased markedly and the reaction became diffusion-controlled. Although the theoretical frameworks of the reactions were presented in these

reports, there were no experimental supports. Oyama and Inoue [21–23] proposed pseudo-first-order kinetics for PA6/PSU-MAH blends on a planar interface by employing the assumption that reaction rate was proportional to the area density change investigated by X-ray photoelectron spectroscopy (XPS). Since, they assumed that this reaction was similar to the kinetics of a gas/solid system in surface science, the reaction rate was dependent on the number of vacant sites available for the reaction at the interface. The first-order kinetics of reactive blends on a planar interface might be unexpected since the interface reaction was usually taken as second-order kinetics because of the reaction of two different reactive groups. As the rheological properties are related to the amount of in situ formed graft (or block) copolymers for a reactive blend, Kim and co-workers [24,25] evaluated the kinetics of the reaction between the reactive polymer–polymer interface by using PS-mCOOH/PMMA-GMA reactive system. The results showed that there were three distinct stages during the change of complex viscosity as a function of time and the apparent reaction kinetics in stage I was a first-order reaction. However, they did not give a very clear physical explanation for correlating the change of rheological property with the conversion of the in situ formed copolymers.

Other theoretical and experimental studies [26–28] have also addressed these interfacial reaction kinetics, but these studies focused on the reactions at the interface between two

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thermodynamically immiscible polymers. In the simplest situation, these authors considered a flat, symmetric interface between two polymer melts with same degree of polymerization *N*. However, the molecular weights of components of reactive systems were always different from each other in real industrial processes. In some situations, the added compatibilizers with relative lower molecular weights might be miscible with one of the components and the asymmetric polymer–polymer interface would be formed. These situations were much different from those assumptions for reactions at immiscible symmetric polymer–polymer interface. So, a number of basic questions are begged. How do the molecules diffuse and react at asymmetric interface? How rapidly do copolymers build up at the interface?

In this paper, experimental studies on the reaction kinetics of PBT/epoxy reactive system were carried out by a new rheological method. PBT is a kind of engineering thermoplastic polymer, and the epoxy resin with relative low molecular weight is often used as reactive modifier for the PBT blends. The reaction between the carboxyl acid in PBT and the epoxy group in epoxy resin occurs at the asymmetric interface easily, giving the in situ copolymers which usually as the compatibilizer for the PBT reactive blends [6,8,11]. Then, a theoretical study was presented and a simple numerical mode for reaction kinetics of asymmetric polymer–polymer interface was established.

2. Experimental

2.1. Materials

The poly(butylene terephthalate) (PBT, 1097, $M_n = 20,000$, density: 1.31 ± 0.02 g/cm^3; intrinsic viscosity: 0.97 ± 0.02 cm^3/g; melting point: 222–226 °C) used in this study was a natural grade product from Nantong XinChen Synthetic Material Co. Ltd, China, and the content of carboxylic acid is 0.03 mol/kg determined by potentiometric titration method. The epoxy resin used was E12, a bisphenol A diglycidyl ether-based resin made by Shanghai Synthetic Resin Co. Ltd, China. Its average molecular weight is about 1700 g/mol and the epoxy value of the epoxy resin is 1.2 mol/kg.

2.2. Rheological experiments

For rheological analysis, PBT plates were prepared by hot compression molding method under 10 Mpa at 240 °C for 5 min. After that, the PBT plates were cut carefully with a razor blade to form discs with a diameter of 20 mm. Then, the epoxy, which was ground into powder, was sandwiched between two PBT plates. The surface of the PBT plates was very smooth, which is necessary for investigating the interface properties.

As soon as samples were put into a rheometer (Rheo Stress 300, Thermo Haake Co.), the complex viscosity (η^*) of the blend system was monitored with time at 240 °C. The strain amplitude (γ_0) was 0.01 and the angular frequency (ω) was 0.5 rad/s, which lies in the linear viscoelastic region.

After the samples were reacted for a given time, the parallel plates, inside which the welded plates were located, were removed from the rheometer and then were quenched for the analysis of conversion by endgroup determination.

2.3. Endgroup determination

The weights of samples were tested before the experiments and the contents of carboxyl acid for PBT were obtained. Then, the specimens removed from the rheological experiments were dissolved in a mixture solution of chloroform and phenol (3:2 in weight ratio) at room temperature for 24 h. After that, the pH-values of mixture solution were monitored by an electrolyte-type pH meter instead of by titration [29] with NaOH in benzyl alcohol against a phenol red indicator. From pH-value the content of carboxyl acid retained could be obtained by simple calculation. Put these two values of contents of carboxyl acid before and after experiment, the conversion could be obtained.

3. Results and discussion

3.1. Rheological analysis of reaction conversions

The plot of complex viscosity (η^*) at 240 °C with time for PBT/epoxy blends is shown in Fig. 1. The changes of the storage and loss modules (G' and G'') with time are similar to the change of η^*. For a reactive system consisting of PBT and epoxy, η^* increased quickly, which is attributed to the coupling reaction between the carboxyl group of PBT and the epoxy group at interfacial region [9]. When the couple
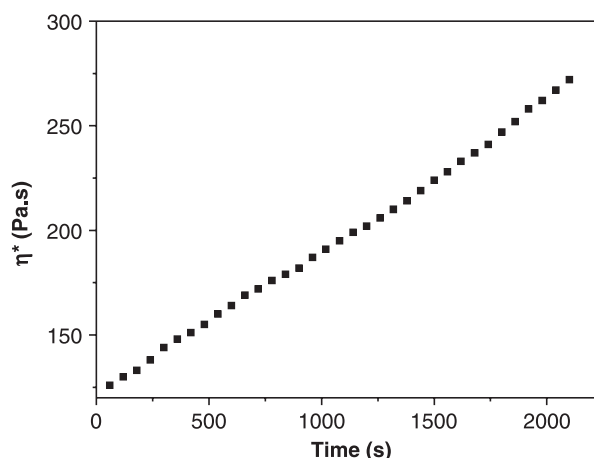

Fig. 1. Plots of η^* at 240 °C vs time for PBT/epoxy.

reaction occurs, copolymer, which have longer chains, is produced, which lead to the increase of η^*.

The viscosity of polymer/polymer blend with sandwich type planar geometry is given by [30]:

$$\frac{1}{\eta} = \sum_i \frac{\omega_i}{\eta_i} \tag{1}$$

in which ω_i and η_i are the weight fraction and the viscosity of the component i, respectively. At beginning of the reaction, there are two components, PBT and epoxy, in the blend. Then, the copolymers are produced and the amount of the copolymers increases with the reaction proceeding. Therefore, there should be three components in the blend. This leads to the following equation:

$$\frac{1}{\eta^*} = \frac{\omega_{PBT}}{\eta_{PBT}^*} + \frac{\omega_{ep}}{\eta_{ep}^*} + \frac{\omega_{co}}{\eta_{co}^*} \tag{2}$$

where ω_{PBT}, ω_{ep}, and ω_{co} are the weight fractions of PBT, epoxy and copolymer in situ produced in blend, respectively. η_{PBT}, η_{ep} and η_{co} are the complex viscosities of PBT, epoxy and copolymer in situ produced. As η^* is the function of time, it can be expressed as: $\eta^*(t)$. As the reaction goes on, ω_{PBT} and ω_{ep} decrease with time, and it can be expressed as:

$$\omega_{PBT} = \omega_{PBT,0} - \omega'_{PBT}(t) \tag{3}$$

where $\omega_{PBT,0}$ is the weight fraction of PBT in initial time, and $\omega'_{PBT}(t)$ is the weight fraction of PBT consumed from initial time to t time. Being similar to ω_{PBT}, ω_{ep} can also be expressed as:

$$\omega_{ep} = \omega_{ep,0} - \omega'_{ep}(t) \tag{4}$$

In addition, ω'_{PBT} can be correlated with ω'_{ep} by:

$$\frac{\omega'_{PBT}}{\omega'_{ep}} = \frac{M_{PBT}}{M_{ep}} \tag{5}$$

and ω'_{co} can be correlated as following:

$$\frac{\omega'_{co}}{\omega'_{PBT}} = \frac{M_{co}}{M_{PBT}} = \frac{(M_{PBT} + M_{ep})}{M_{PBT}} \tag{6}$$

Values of η_{PBT}^* and η_{ep}^* can be obtained from experiment, but η_{co}^* cannot. It could not be guaranteed that the pure copolymer of one PBT chain coupled with one epoxy chain could be obtained by blending stoichiometric amounts of two polymers. In the present study, as the chain of PBT is much longer than that of epoxy, the rheological properties of copolymer could be similar to that of PBT [31]. So the η_{co}^* can be estimated by:

$$\frac{\eta_{PBT}^*}{\eta_{co}^*} = \left(\frac{M_{PBT}}{M_{co}}\right)^{3.4} \tag{7}$$

So Eq. (2) can be transformed into an integral representation and manipulated into the following form:

$$\frac{1}{\eta^*(t)} = \frac{\omega_{PBT,0} - \omega'_{PBT}(t)}{\eta_{PBT}^*}$$
$$+ \frac{\omega_{ep,0} - (M_{ep}\omega'_{PBT}(t))/(M_{PBT})}{\eta_{ep}^*}$$
$$+ \frac{((M_{PBT} + M_{ep})\omega'_{PBT}(t))/(M_{PBT})}{\eta_{PBT}^*(M_{PBT} + M_{ep})/(M_{PBT})^{3.4}} \tag{8}$$

Therefore, the $\eta^*(t)$ can be related with ω'_{PBT} through Eq. (8). Moreover, the conversion of the PBT can be given as:

$$X(t) = \frac{\omega'_{PBT}(t)}{\omega_{PBT,0}} \tag{9}$$

So we can correlate the change of complex viscosity η^* with the conversion X of PBT by using Eqs. (8) and (9). The plots of conversion obtained from complex viscosity by this method with time are shown in Fig. 2.

It should be stressed that the conversion obtained here is the absolute one. This is completely different from the relative conversion obtained from the conventional rheological analysis [25], which only uses the linear difference between the instant value of viscosity (or modulus) and its initial to determine. The important assumption of the conventional method is that the final conversion should be 100%, and the instant conversion obtained base on it wholly. But the conversion obtained here by using the new rheological analysis method has clear physical content and is nothing with this assumption.

3.2. Conventional analysis of reaction conversions

As reaction between carboxyl group and epoxy group dominated in the process, the mass quantity change of carboxyl group in the sample was a direct indication of the reaction progress. Then, the reaction conversions could also be obtained by endgroup determination method. The plots of conversion obtained by endgroup determination method with time are also shown in Fig. 2. When the reaction
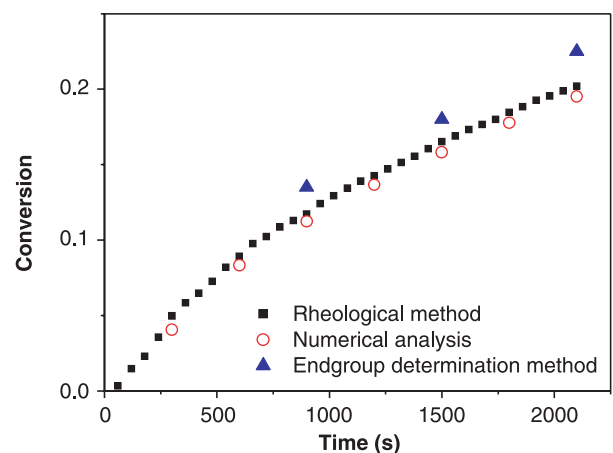

Fig. 2. Plots of reaction conversions vs time by different methods.

conversions obtained from the rheological method and that obtained from endgroup determination method were compared, there were just slight differences between the two results. This indicated that the above rheological analysis for the conversion of PBT/epoxy coupling reaction could be a useful method in the study of macromolecular reactions especially in the flow field.

3.3. Numerical analysis of reaction conversions

In principle, the kinetic constant of reaction between PBT and epoxy can be determined from the conversion. However, this is only possible when the reaction is the rate control process. If the transportation of reactions becomes a slower process, the convective or diffusion velocity can affect the evolution of conversion. In the case that studied here, the interfacial structure and morphology are not only dependent on the reaction kinetics, but also on the diffusion of epoxy in PBT. Therefore, the conversion is determined simultaneously by the kinetic constant of reaction and the diffusion constant of epoxy. Then we propose a one-dimensional analysis on this problem, with the geometry defined in Fig. 3. Moreover, the density of system is assumed to be invariable, which is convenient for the calculation.

As the molecular weight of epoxy is relatively lower than that of PBT, we proposed that the chains of epoxy penetrate into the matrix of PBT and react simultaneously. Then the equation for concentration of epoxy group, which is also the function of time and position, can be written as:

$$\frac{\partial c_{ep}}{\partial t} = \nabla \cdot (D \nabla c_{ep}) - k c_{ep} c_{-COOH} \tag{10}$$

where c_{ep} is the local concentration of reactive epoxy group, c_{-COOH} is the local concentration of the reactive carboxyl group on PBT, k is the kinetic constant of second order reaction. Here, a classical Fickian diffusion is adopted for epoxy, and D is the diffusion constant of epoxy in PBT. As PBT is assumed to be quiescent in the coordinates, the change of c_{-COOH} is only attributed to the chemical reaction:

$$\frac{\partial c_{-COOH}}{\partial t} = -k c_{ep} c_{-COOH} \tag{11}$$

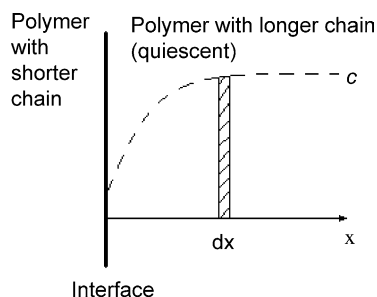Eqs. (10) and (11) establish simultaneous equations for the

PBT/epoxy reactive interface. The instant profile of c_{-COOH} and c_{ep} can be readily obtained by solving Eqs. (10) and (11) with proper initial and boundary conditions.

The parameters needed for the simulation are shown in Table 1. The boundary condition is given:

$$c_{ep}(0, t) = 1.2 \times 10^{-3} \text{ mol/g} \tag{12}$$

As the interface is planar and no external flow is imposed, the conversion of the carboxyl in the system can be obtained by equation:

$$X(t) = \frac{\pi r^2 l \rho c_{-COOH,0} - 2 \int_0^{l/2} \pi r^2 l \rho c_{-COOH}(t, x)}{\pi r^2 l \rho c_{-COOH,0}} \tag{13}$$

where r and l is the radius and the thickness of the specimen, ρ is the density and $c_{-COOH,0}$ is the initial concentration of the carboxyl group.

It is expected that the reaction conversion should depend on the value of rate constant k and diffusion constant D. The conversions under different k and D are shown in Figs. 4 and 5. It can be seen from Fig. 4 that the conversions in the same reaction constant were similar at the beginning of reaction although the diffusion coefficients were different by 2 orders of magnitude. The conversions increased with the process time and the conversions with different diffusion coefficients showed significant difference. The conversions with different reaction constants under same diffusion constant are shown in Fig. 5. It shows that the conversions were significantly different at the beginning of reaction with different reaction constants although the diffusion coefficients were same. With time being, the differences of conversion curves were not so much as that in Fig. 4 though they were still exist. These results indicated that the conversion of the reaction was strongly affected by the reaction constant at the beginning of the process and turned more sensitive to the diffusion coefficient with time. It was also to say that the process was reaction-controlled at the beginning and turned to the diffusion-controlled gradually. This conclusion was in accord with the results obtained

Fig. 3. Sketch map of one-dimensional coordinates for simulation.
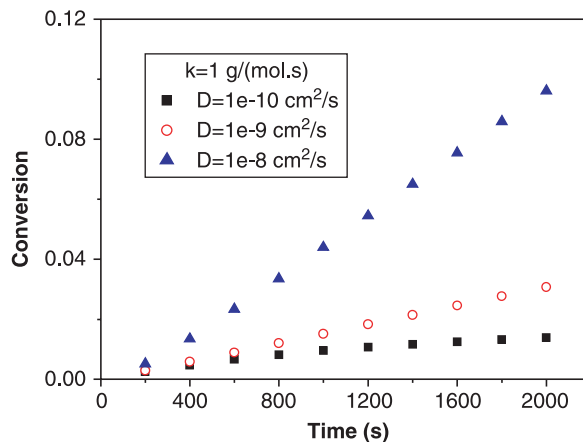

Fig. 4. Plots of reaction conversions vs time simulated by the numerical model in different diffusion coefficients.

Table 1
Values of the parameters used in the simulations

Parameters	Unit	Value
Initial concentration of epoxy group: $c_{ep,0}$	mol/g	1.2×10^{-3}
Initial concentration of carboxyl group: $c_{-COOH,0}$	mol/g	3×10^{-5}
Diffusion coefficient of epoxy in PBT: D	cm²/s	7×10^{-9}
Reaction constant: k	g/mol s	20
Thickness of specimen: l	cm	0.1

from symmetric polymer–polymer interfaces reported by Fredrickson [16,17] and O'shaughnessy [18–20].

It is possible then to determine the kinetic constant as well as the diffusion constant by fitting the numerical results with the conversion from eheological analysis. The best fit for the numerical result is also show in Fig. 2. It can be seen that the reaction conversions obtained from rheological method and numerical analysis presented same change profiles, which increased quickly at the beginning of the reaction and slowed down with the proceeding time. When two polymers are put together in melt, the reactive end groups react quickly at the interface and the conversion increases quickly. As the reaction proceeds, the reactive end groups near the interface become less and the polymer penetration slow down, which results in slow increasing of conversion. These results were in accord with the conclusion reported before [17,18]. The kinetic constant used is 20 g/mol s, the diffusion constant is 7×10^{-9} cm²/s. The kinetic constant is consistent with the kinetic constant between carboxyl group and epoxy group [32]. The diffusion constant of epoxy in PBT also agreed with previous studies [33]. Moreover, the results also suggested that the diffusion of the epoxy in PBT in melt could be predicted by the simple classical Fickian model.
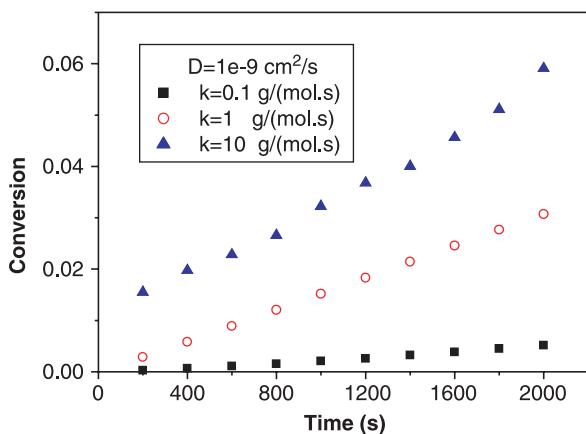

Fig. 5. Plots of reaction conversions vs time simulated by the numerical model in different reaction constants.

4. Conclusions

In the present study, a new rheological method, which correlates the change of rheological property of reactive system with the conversion of the in situ formed copolymers, was used to experimentally study the reaction kinetics of asymmetric polymer–polymer interface. This method was proved to be useful through studying the reaction kinetics of PBT/epoxy reactive system by conventional endgroup determination method. Then a simple numerical analysis was used to theoretically study the reaction kinetics of asymmetric polymer–polymer interface and the results suggested that the conversion of the system was strongly affected by the reaction constant at the beginning of the reaction and became more sensitive to the diffusion coefficient with the proceeding time. By comparing the results obtained by the experiments and the numerical analysis, it is possible to determine the kinetic constant of reaction and the diffusion coefficient simultaneously.

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