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Study on the reaction kinetics between PBT and epoxy by a novel rheological method

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Abstract

In the present study, the reaction kinetics of polybutylene terephthalate (PBT) and epoxy system was studied by a novel rheological method. The reaction process was determined by rheological test and the results showed that there were three stages in the reaction between PBT and epoxy, which were reaction-controlling stage (stage I), reaction-stagnation stage (stage II) and diffusion-controlling stage (stage III). In addition, the stage I was selected to study the reaction kinetics by the rheological method. The results showed that the reaction between PBT and epoxy could be classified as a pseudo-first-order reaction due to the excessive amount of epoxy group. Furthermore, the reaction apparent activation energy of the stage I determined by the rheological method was 143 kJ/mol. To confirm these results, the reaction kinetics was also evaluated by the endgroup determination method, and the results showed that the reaction could also be classified as a pseudo-first-order reaction. Moreover, the apparent activation energy of the reaction was 116 kJ/mol, which was similar to that of the value obtained by the rheological method.

Keywords: PBT; Epoxy; Reaction kinetics; Rheological method

1. Introduction

Polybutylene terephthalate (PBT) is well known as a commercial thermoplastic material with various applications because of its some special properties, such as thermal resistance and chemical resistance. However, a number of problems limit its extensive application. The most important one is that the product made of the PBT has poor impact strength due to its brittleness. Many methods have been tried to solve this problem. One of the most effective and feasible methods is to blend it with other tough polymers, which is often called polymer–polymer alloying technique. However, the incompatibility between the PBT and the tough polymer is still a problem when using this method to obtain improved impact strength. In order to improve compatibility of the immiscible blends, reactive compatibilizers were selectively applied in many studies [1–11] because they could react with each polymer phase. Among these reactive compatibilizers, epoxy resin was usually chosen for PBT blend systems since it is commercially available.

In recent years, the compatibility of epoxy in blends of PBT and other components has been studied in some previous literatures [6–11]. However, most of these studies just focused on the improvement of physical

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properties of the blend systems and the compatibility of two polymer phases. Few studies were reported on the examination of the reaction kinetics between PBT and epoxy, which was probably due to the complexity of the reaction and restricted methods for monitoring the process of the reaction.

Reaction kinetics of many other systems has been studied in previous literatures. Recently, Oyama et al. [12,13] investigated reaction kinetics of the reactive PA6/PSU-MAH blends with a planar interface and Kim et al. [14] evaluated the reaction kinetics in the reactive polymer–polymer (PS-COOH/PMMA-GMA) planar interface through determining the complex viscosity (η^*) of the system. All of these results suggested that the reaction kinetics might be evaluated by the rheological method as the temporal changes of rheological properties, which were related to the amount of in situ formed graft (or block) copolymers for a reactive blend, could be monitored.

Therefore, in the present study, the epoxy resin was chosen to react with PBT and the reaction kinetics of PBT/epoxy planar interface was evaluated by the rheological method. In order to confirm the results determined by the rheological method, the endgroup determination method was used to investigate the reaction kinetics of the system [15].

2. Experiments

2.1. Materials

Polybutylene terephthalate (PBT), 1097A (density:1.31 ± 0.02 g/cm^3; intrinsic viscosity:0.97 ± 0.02 cm^3/g; melting point:222–226 °C), is a natural grade product from Nantong Synthetic Materials Co. Ltd., China and the content of carboxylic acid in it is 0.06 mol/kg. The epoxy resin, E51 (low molecular weight), was obtained from Shanghai Resin Factory Co. Ltd. and its epoxy value is 5.1 mol/kg.

2.2. Rheological analysis

For rheological analysis, PBT plates were prepared by hot compression molding method under 10 MPa at 230 °C for 5 min. After that, the PBT plates were cut carefully with a razor blade to form discs with a diameter of 25 mm. Then, the epoxy, which was colloidal under room temperature, was sandwiched between two PBT plates. The surface of the PBT plates was very smooth, which was necessary for investigating the interface properties. A kind of paraffin, which has same molecular weight without reactive group, was selected to blend with PBT to form a non-reaction system.

As soon as samples were put into a rheometer (Advanced Rheometrics Expansion System, Rheometrics Co.), the complex viscosity (η^*) of the blend system was monitored with time at three different temperatures (230, 235, 240 °C). The strain amplitude was 0.01 and the frequency was 0.1 Hz, which lies in the linear viscoelastic region.

2.3. Carboxyl endgroup determination

To confirm the results determined by the rheological method, the reaction kinetics of this system was also evaluated by a modified carboxyl endgroup determination method. For the determination of carboxyl endgroup, PBT and epoxy were blended by Haake at 230 °C with a rotor speed of 45 rpm. During the mixing, a small amount of mixed melt was picked up by pincette at appropriate intervals and was quickly quenched. Thus, we prepared a series of mix-and-quenched specimens with various residence times in the mixer. These specimens were dissolved in mixture solution of chloroform and phenol (3:2 in weight ratio) for 12 h at room temperature. Then, the pH values of mixture solution were monitored by an electrolyte-type pH meter instead of by titration [15] with NaOH in benzyl alcohol against a phenol red indicator and the concentrations of the carboxyl endgroup were obtained.

3. Results and discussion

3.1. Reaction evolution measured by rheological test

The changes of complex viscosity (η^*) of the PBT/epoxy system as a function of time at 230 °C are shown in Fig. 1. It can be seen from the Fig. 1 that the process of the PBT/epoxy system could be divided into three

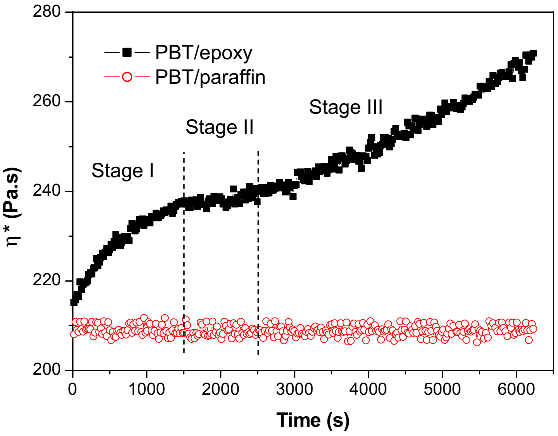

Fig. 1. Plots of η^* at 230 °C vs time for PBT/epoxy (■) as well as non-reactive blend system of PBT/paraffin (○).

different stages. η^* increased within short time during the stage I and then maintained at a steady value showed in stage II (1500 s < t < 2500 s). After that, η^* increased slowly again during the stage III. However, there was almost no change in η^* of PBT/paraffin system during the whole process, which was quite different from that of the PBT/epoxy system. As the paraffin has no reactive group with PBT, there was no reaction and no copolymer produced, and then the complex viscosity of the system kept no change. Therefore, it can be concluded that the change of the complex viscosity was mostly due to the reaction between PBT and epoxy.

In addition, the sharp increase of the complex viscosity before 1500 s (stage I) was attributed to the reaction between carboxyl group of PBT and epoxy group at interfacial region [8,16]. Since the diffusion rate of epoxy group was faster than the reaction rate, the process was reaction-controlled. As the reaction proceeded, epoxy group near the interface became less and less, and the interfacial layer became saturated gradually. The saturated copolymer layer prevented the meeting of the reactive chains and the reaction entered into a stagnant stage, which corresponded to the plateau curve in stage II. However, when the epoxy group penetrated through the copolymer layer, the reaction could proceed again, resulting in the increase of η^* again, which was shown in the stage III. These results were in accordance with the conclusion reported by Kim [14].

It is also shown in Fig. 1 that the increase in η^* with time during the stage III was much reduced compared with that during the stage I. The difference in slopes of the curves during the stage I and the stage III might be due to the fact that the process was reaction-controlled during the stage I while became diffusion-controlled during the stage III as the interfacial layer becomes saturated with in situ formed copolymers. This conclusion was in accordance with the results reported by Fredrickson [17] and O'shaughnessy [18,19].

3.2. Evaluation of the reaction order by rheological method

While the copolymer produced by the coupling reaction between carboxyl groups and epoxy groups, η^* increased rapidly with reaction time in stage I. Therefore, we correlated the change of η^* with the conversion $X(t)$ of the in situ formed copolymers as follows:

$$X(t) = [\eta^*(t) - \eta^*_0]/[\eta^*_{\text{pla}} - \eta^*_0] \tag{1}$$

where η^*_{pla} is the plateau value of η^* of reactive blend at stage I, and the η^*_0 is the minimal initial value.

The following reaction rate equation was applied [20]:

$$k_1 t = \ln\left\{\frac{[A]_0}{[A]_0 - x}\right\} \tag{2}$$

for the first-order reaction kinetics and

$$k_2 t = \left\{\frac{1}{[B]_0 - [A]_0}\right\} \times \ln\left\{\frac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}\right\} \tag{3}$$

for the second-order reaction kinetics. Here, k_1 and k_2 are the reaction constants, and $[A]_0$, $[B]_0$ are initial concentrations of carboxyl group and epoxy group, respectively. x presents the concentration of copolymer produced at time t. Setting $X_A(t) = x/[A]_0$, and the following formulas could be obtained:

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

$$k_2 t = \left\{\frac{1}{[B]_0 - [A]_0}\right\} \times \ln\left\{\frac{[B]_0 - [A]_0 X_A}{[B]_0 - [B]_0 X_A}\right\} \tag{5}$$

However, the concentration of reactive group in PBT is 0.06 mol/kg, which was significant lower than that of the reactive group in epoxy resin (5.1 mol/kg). Then we can have that $[A]_0 \ll [B]_0$ and the right-hand side of expression in Eq. (5) became same to that in Eq. (4). Therefore, this reaction could be classified as a pseudo-first-order reaction.

Fig. 2 shows plots of conversion ratio of the reaction between PBT and epoxy at 230 °C with reaction time, which were calculated according to the Eq. (4). It was obvious that the reaction kinetics in stage I at 230 °C was well described by the first-order reaction kinetics. The results at other temperature (235 and 240 °C) were same to that at 230 °C (data not shown). From the Arrhenius plot (the reaction constant vs inverse temperature), it could be obtained that the apparent activation energy (ΔE) for the reaction of PBT and epoxy was 143 kJ/mol on the basis of pseudo-first-order reaction.

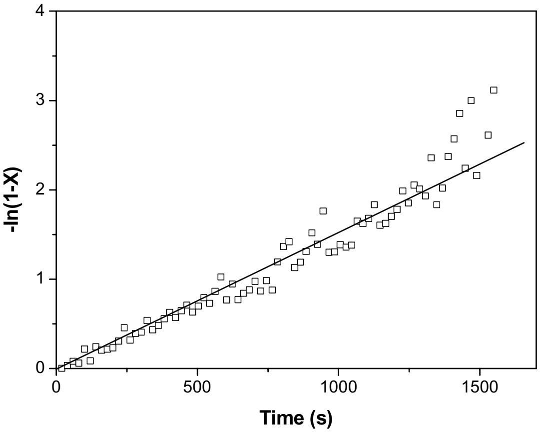

Fig. 2. Plots of conversion vs reaction time given by Eq. (2) for PBT/epoxy using rheological method.

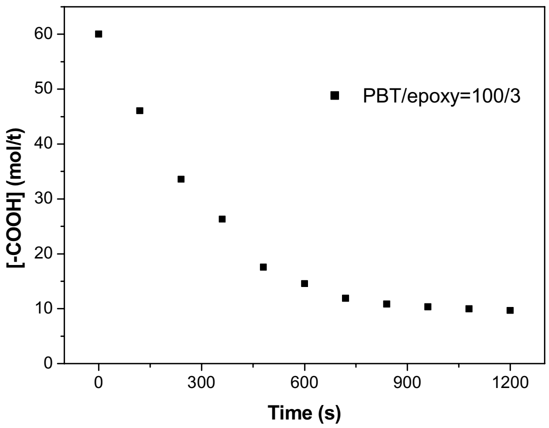

Fig. 3. Plots of concentration of the carboxyl group in reactive system at 230 °C vs reaction time.

3.3. Evaluation of the reaction order by endgroup determination method

As the reaction between carboxyl group and epoxy group dominated in the stage I, the concentration change of carboxyl group in the blend was a direct indication of the reaction progress. Since the concentration of carboxyl group in planar interface was difficult to monitor, we blended PBT and epoxy in mixer and the concentration of reactant group in blending system was determined at different time. It can be seen from the Fig. 3 that the concentrations of the carboxyl endgroup decreased with the reaction time at the previous stage, while maintained a steady balance value at the post stage of the reaction. This result suggested that the conversion ratio of the carboxyl endgroup increased with the reaction time in the previous stage, and then maintained a balance value. The conversion ratio of the carboxyl endgroup achieved to 83% at 230 °C. In addition, Fig. 4 shows that the final conversion ratio of the carboxyl endgroup increased with the rising of the reaction temperature (91% at 235 °C and 93% at 240 °C).

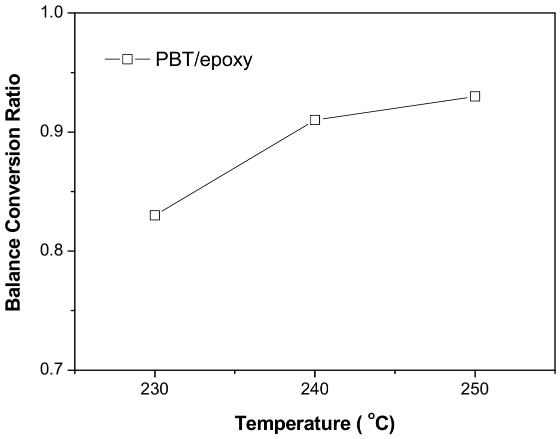

Fig. 4. Balance conversion ratio for reaction of PBT/epoxy in blending system at different temperatures.

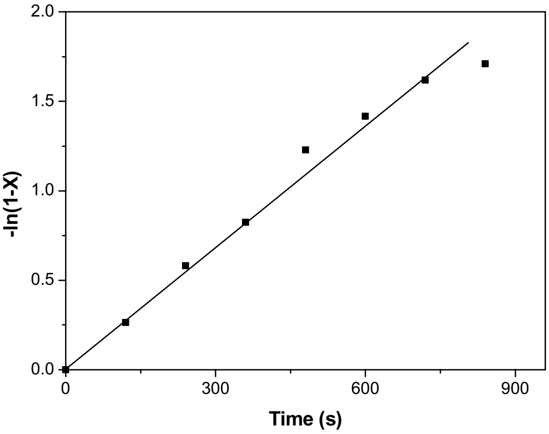

Fig. 5. Plots of conversion vs reaction time given by Eq. (2) for PBT/epoxy using endgroup determination method.

Fig. 5 shows that a straight line was obtained after fitting the conversion ratio to a pseudo-first-order reaction and the apparent activation energy (ΔE) was 116 kJ/mol by calculating the reaction constants at different temperatures. The value was slightly lower than that obtained by the rheological method.

4. Conclusions

In the present study, the reaction kinetics of polybutylene terephthalate (PBT) and epoxy were studied by the rheological method. The results showed that the reaction between PBT and epoxy could be classified as a pseudo-first-order reaction due to the excessive amount of epoxy group and the reaction apparent activation energy of the stage I determined by the rheological method was 143 kJ/mol. Evaluated by the endgroup determination method, the reaction kinetics of this system was found to be consistent with pseudo-first-order kinetics and the apparent activation energy of the reaction was 116 kJ/mol, which were in accordance with the results determined by the rheological method.

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