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Residence Time Distribution: An Old Concept in Chemical Engineering and a New Application in Polymer Processing

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Introduction

Polymer blending is a very important polymer processing process. It aims at preparing new polymer materials by blending existing polymers. However, most polymers are mutually immiscible, and their blends are thermodynamically unstable. Therefore, emulsifiers such as block or graft copolymers are often used for improving the adhesion of the interfaces and control the morphology of the resulting blends.[1] The efficiency of a copolymer as an emulsifier is often evaluated by a so-called emulsification curve.[2–4] The latter essentially follows the evolution of the dispersed phase domain size of the polymer blend as a function of the copolymer concentration.

Polymer blending processes use mainly batch mixers and continuous mixers of type screw extruder especially twin-screw extruders. The former are mainly used in the laboratory and the latter both in the laboratory and for production purposes. An emulsification curve in a batch mixer can be built up in the following manner. Given compositions of the polymer components of the blend as well as the copolymer are charged to the mixer. After a certain elapse of time, the process reaches a steady state and samples are then taken from the mixer. The size of the dispersed phase domains of the corresponding blend is measured. This makes up a point on the emulsification curve. The earlier process is repeated upon varying the copolymer concentration. An emulsification curve is then builtup for the said composition of the blend.

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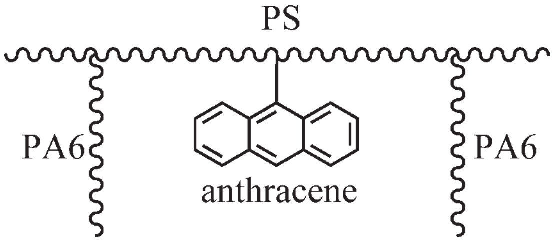


Figure 1. Schematic of the structure of the tracer emulsifier.

In the case of a screw extruder, the so-called steady-state experiments can also be carried out. They are similar to those in a batch mixer. Given compositions of the polymer components of the blend as well as the copolymer are charged to the hopper of the extruder. After a certain elapse of time, the process reaches a steady state and samples are then taken from the die exit for measurement.

Studies reported in the literature concerning emulsification curves often use batch mixers and not screw extruders. The main reason is that batch mixers are often more accessible in a laboratory than twin-screw extruders and that they are easier to operate too. More importantly, the amount of the copolymer required for building up an emulsification curve in a batch mixer is often much smaller than in a twin-screw extruder. This is especially true for a pilot or industrial-scale screw extruder of which the production rate can reach from a few dozens of kilograms to a few tones per hour. In such a case, the amount of the copolymer required may be too large to build up an emulsification curve.

This article aims at extending the residence time distribution (RTD), an old concept in chemical engineering, to polymer blending in order that a very small amount of copolymer still allows building up an emulsification curve in a pilot or industrial-scale screw extruder. The idea is based on RTD transient experiments.[5,6] Unlike a steady-state experiment in which given compositions of the polymer components of the blend and the copolymer are charged to the hopper of the extruder altogether, in a transient experiment the polymer components are first charged to the hopper of the extruder. When the process reaches its steady state, a given amount of the copolymer is then introduced to the hopper of the extruder as a pulse. Samples are taken at the die exit as a function of time. Both the evolution of the copolymer concentration and that of the morphology as a function of time can be obtained. The former provides the RTD and the latter the morphology distribution (MD) or the dispersed phase domain size distribution (DSD) for dispersed type polymer blends. From both distributions, the emulsification curve can be easily deduced.

Experimental

Materials

The blends were composed of polystyrene (PS) and polyamide 6 (PA6), both in the form of pellets. The emulsifier was synthesized in the laboratory, and its structure is depicted in Figure 1. It was a graft copolymer with PS as the backbone and PA6 as the grafts. The PA6 grafts were randomly distributed along the PS backbone. The graft copolymer also contained a very small amount of anthracene moieties along the PS backbone in a random manner. The presence of the anthracene moieties in the graft copolymer allowed in-line measurement of the copolymer concentration during the blending process. For that reason, it will be designated as tracer-emulsifier. Table 1 gathers selected characteristics of the PS, PA6, and the tracer-emulsifier.

Transient experiments and morphology characterization

Transient experiments were carried out on a standard twin-screw extruder of which the diameter and length-to-diameter ratio were 35 mm and 48, respectively. An in-line RTD measuring device with a bifurcated optical probe capable of exciting and emitting fluorescent light was installed in the die. It allowed measuring the tracer-emulsifier concentration.[9,10] The barrel temperature was set at 230°C. When the process reached its steady state, the tracer emulsifier was injected to the hopper as a pulse. At the same time, the in-line RTD measuring device started measuring the concentration of the tracer-emulsifier, and the corresponding extrudate was collected and then quenched immediately in liquid nitrogen to freeze-in its morphology. A scanning electron microscope of type JEOL JSM-T330A was used to measure the morphology of the extrudate. A semiautomatic image analysis method was used to determine the diameter of the dispersed phase domains. The latter was characterized by the volume average particle diameter, d_v, defined as follows:

$$d_v = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \tag{1}$$

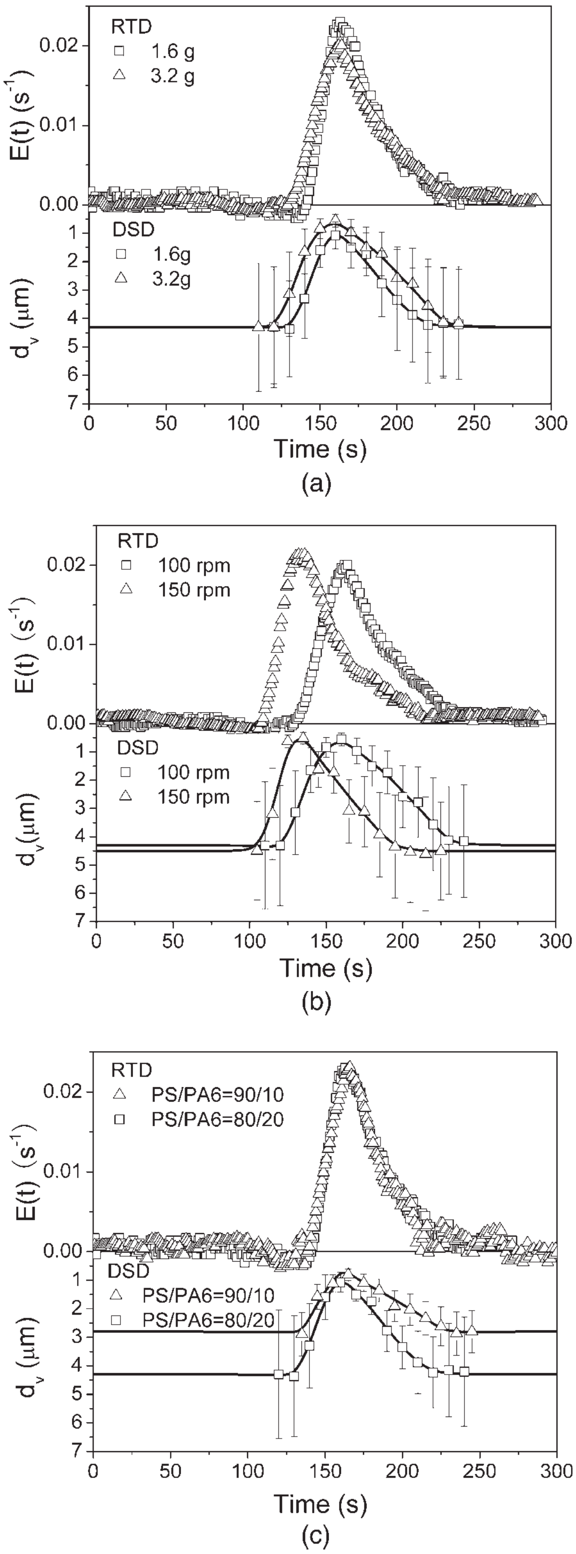
For each image analysis, at least 500 particles were counted.

Table 1. Selected Characteristic of the PS, PA6, and Tracer Emulsifier Used in This Work

	Number Average Molar Mass* (kg/mol)	Mass Average Molar Mass* (kg/mol)	Supplier
PS	101.3	228.8	Yangzi-BASF Styrenics Co. Nanjing, China
PA6	19.4	49.4	UBE Nylon Ltd., Thailand
Tracer emulsifier[†]	37.8	137.0	Our laboratory

*Molar masses measured by size exclusion chromatography.[7,8]

[†] The PA6 and anthracene contents in the tracer emulsifier were 35.3 and 0.1 wt %, respectively. The number of the PA6 grafts per PS backbone was 6.2, and the number average molar mass of a PA6 graft was 3.0 kg/mole.



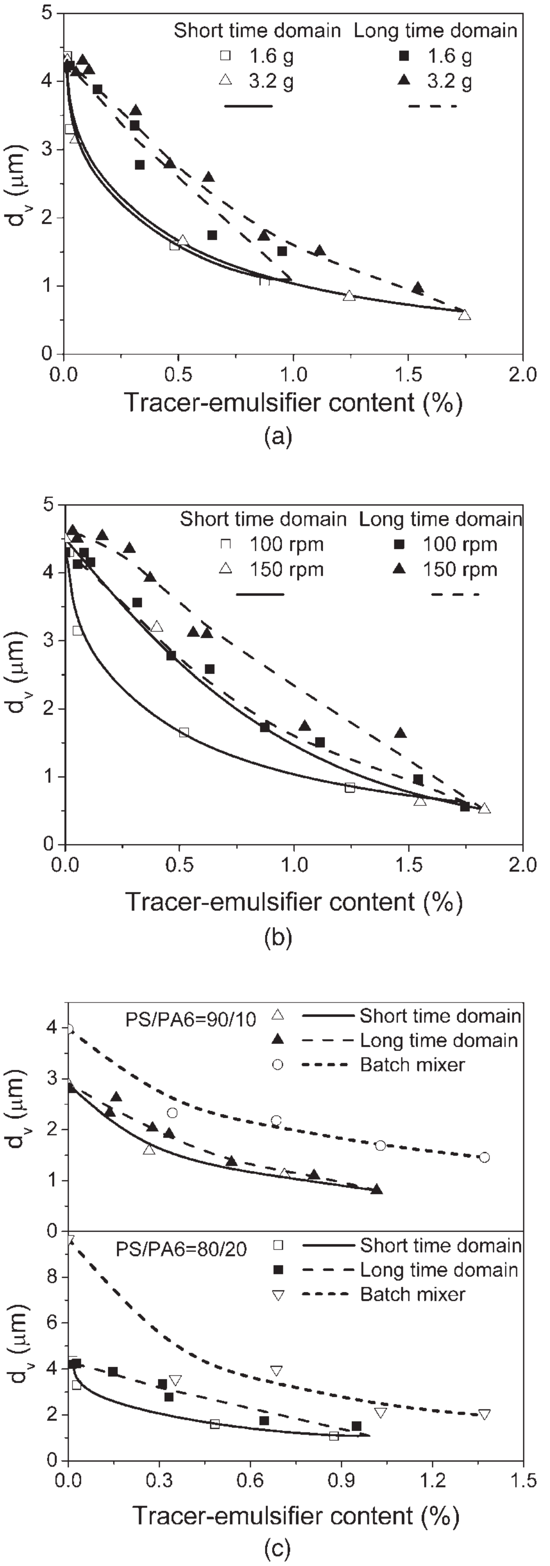
(a)

(b)

(c)

Figure 2. Effects of the amount of the tracer-emulsifier (a), the screw speed (b), and the PS/PA6 mass ratio (c) on the RTD and DSD curves of the PS/PA6 blend.

Feed rate = 13 kg/h. (a) PS/PA6 = 80/20, screw speed = 100 rpm; (b) PS/PA6 = 80/20, amount of the tracer-emulsifier = 3.2 g; (c) amount of the tracer-emulsifier = 1.6 g, screw speed = 100 rpm.



(a)

(b)

(c)

Figure 3. Effects of the amount of the tracer-emulsifier (a), the screw speed (b), and the PS/PA6 mass ratio and the type of mixer (c) on the emulsification curve of the PS/PA6 blend.

Data for the twin-screw extruder deduced from Figures 2a–c. Data for the batch mixer from the literature[4] using a Haake torque rheometer.

Results

Figure 2a shows the RTD and DSD measured using 1.6 and 3.2 g of the tracer-emulsifier. As expected, the two RTD curves almost superimpose. More interestingly, the DSD follows the overall trend of the RTD. A lower value of the DSD corresponds more or less to a higher value of the RTD. Although this is also expected, to the best of the authors' knowledge, it is the first time that such a curve is obtained upon doing RTD transient experiments. These results show that the use of a very small amount of a tracer-emulsifier does allow measuring the RTD and building up the DSD of a polymer blend at the same time.

The afore-mentioned statements are further confirmed by the results in Figures 2b,c. The latter show, respectively, the effects of the screw speed and the PS/PA6 mass ratio on the RTD and DSD. Again as expected, both the RTD and DSD shift to the shorter time domain, when the screw speed increases. The effect of the PS/PA6 mass ratio deserves comments. Both the PS/PA6 (80/20) and PS/PA6 (90/10) blends have almost the same RTD. However, their DSD are different, indicating that both RTD and DSD do not necessarily match each other. This will be further discussed later.

Discussion

Figures 3a–c shows the emulsification curves corresponding to the results in Figures 2a–c, respectively. For comparative purposes, Figure 3c also shows the emulsification curves reported in the literature using a batch mixer of type Haake torque rheometer.[4] The structures of the emulsifier used for the batch mixer was very similar to that of the tracer emulsifier used for the twin screw extruder. In the former, the content of the PA6 grafts and the number of the PA6 grafts per PS backbone were 30.3 wt % and 6.6, respectively. In the latter, they were 35.3 wt % and 6.2, respectively. The emulsification curves obtained from the twin-screw extruder are significantly below those from the batch mixer, likely because the twin-screw extruder had a much higher mixing capacity than the batch mixer.

The most striking feature is that unlike the emulsification curves obtained from the batch mixer, those from the twin screw extruder are no longer single curves but loops, regardless of the amount of the tracer-emulsifier, the screw speed, or the PS/PA6 mass ratio. These loops result from the fact that a RTD curve can be divided into short and long-time domains, which are demarcated by the maximum of the RTD density function $E(t)$. In the short-time domain, the tracer-emulsifier concentration increases with increasing residence time, and in the long-time domain it decreases with increasing residence time. In other words, a steady experiment leads to a single emulsification curve, a transient experiment results in two distinct emulsification curves.

The fact that the two curves of an emulsification loop do not superimpose implies that the emulsification curve of a polymer blend is controlled not only by the tracer-emulsifier concentration but also by other parameters such as the type of mixer, and processing conditions. Although this is expected, the literature has not yet paid enough attention to them. Closer inspection of Figures 3a–c reveals a second unique feature of the emulsification loops: the curves corresponding to the short time domain are all systematically below those corresponding to the long time domain. However, mechanisms responsible for this phenomenon remain poorly understood. Nevertheless, coalescence of the dispersed phase domains of the polymer blend could be one. For a given tracer-emulsifier concentration, coalescence is supposed to be more important at longer time or higher PS/PA6 ratio. This is consistent with the results in Figure 3b and especially those in Figure 3c. The differences between the curves at the short and long-time domains are indeed much more pronounced at the higher PS/PA6 mass ratio.

Conclusions

This article has reported on an original method for constructing the emulsification curve of a polymer blend in a continuous mixer such as a twin-screw extruder. It is based on transient experiments for measuring RTD, namely, the incorporation of a tracer molecule in the emulsifier in a low content and the injection of the resulting tracer-emulsifier to the continuous mixer as a pulse. In this manner, for the first time the use of a very small amount of a tracer emulsifier allows obtaining at the same time the tracer-emulsifier concentration distribution (i.e. the RTD) and the corresponding dispersed phase DSD of the blend system. From these two distributions, an emulsification curve can be easily obtained. More importantly, it reveals two unique features that have not yet been reported in the literature. First, a transient experiment leads to two distinct emulsification curves that form a loop. They correspond to the short and long residence time domains, respectively. Second, under the conditions studied in this work, the one corresponding to the higher time domain is always above the one corresponding to the long time domain. Coalescence could be an important mechanism responsible for this phenomenon. The method reported in this article opens up a new research field in polymer blending. Work is being undertaken.

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