Development of a Novel Microcompounder for Polymer Blends and Nanocomposite

Younggon Son

Division of Advanced Materials Science and Engineering, Kongju National University, Kongju, Chungnam 314701, South Korea

Received 6 December 2006; accepted 9 June 2008
DOI 10.1002/app.28890
Published online 13 January 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this article, we introduce a new type of small scale compounder. The compounder developed is for mixing of polymeric samples of 0.5–10 g. It consists of a heated cylindrical metal having two cylindrical cavities connected through a narrow channel and two cylindrical pistons, which squeeze molten polymers from one cavity to the other cavity through the narrow channel. During mixing procedure, the molten polymers flow from one cavity to the other cavity, repeatedly, and this operation generates the extensional flow in the converging and the diverging geometry. Because the compounder has mixing chamber of very simple geometry, the cleaning is very easy and the material lost is very small. We evaluated the mixing efficiency of the compounder by comparing with the commercialized small-scale mixers including a cup and rotor batch mixer, an internal batch mixer, and a recirculating conical twin-screw extruder. It was found that the compounder developed has many advantages over the existing small-scale mixers.
 J Appl Polym Sci 112: 609–619, 2009

Key words: microcompounder; extensional batch mixer; polymer blends

INTRODUCTION

Polymer blends and composites are the most efficient way of obtaining new materials having improved properties.[1] The increasing researches on polymer blends and composites have lead to demand for an appropriate mixing facility. Even though most polymer blends and composites are manufactured in twin-screw extruders, a small scale mixing equipment is essential in research and development stage because typical compounding conditions are initially optimized on laboratory-scale equipment. This is indeed true for very expensive materials such as high performance engineering plastic, polymer composite containing carbon nanotube, etc. Additionally, many new materials are available in limited quantities because they are initially synthesized in small amounts. Therefore, a laboratory-scale mixing device is essential.

Several small-scale mixers have been developed[2–5] and some of them are commercially available at present. One of them is a cup and rotor batch mixer (CRBM),[6] shown in Figure 1. It consists of a heated metal cup and a cylindrical rotor, which rotates on the top of the polymer melt to mix the materials. This mixer is normally operated with small amount of material (less than 0.5 g) to have better mixing quality (i.e., the smaller gap size, the higher shear rate). Because this mixer has the Couette geometry and provides only pure shear flow, the mixing efficiency, especially the distributive mixing, is very poor even after long mixing time. Several efforts were devoted to improve the mixing quality of this mixer by incorporating the extensional flow.[5,7] The authors added rigid spheres to the CRBM to improve the mixing efficiency. Mixing efficiency by the modification is much improved, but it still needs long mixing time, which may deteriorate the materials. Moreover, the modification of the CRBM produces additional problems; the cleaning of the mixer is difficult and the material lost is increased.

An internal batch mixer (IBM) has been most widely used as a laboratory-mixing device.[8] It consists of two roller blades that rotate within a dual-cylinder cavity as shown in Figure 2. The IBM is commercially produced by several manufacturers with volume of the mixing chamber of 30 or 60 cc. Mixing efficiency of the IBM is affected by the amount of sample loaded in the mixer as demonstrated by Moon.[9] When the volume of sample is less than half of the mixing chamber, the mixing efficiency is very poor in the IBM. Thus, it cannot mix very small amount of material. It provides a complex flow and relatively good mixing efficiency. However, removing samples from roller blades and cleaning of the blades after mixing operation is very

Correspondence to: Y. Son (sonyg@kongju.ac.kr).
Contract grant sponsor: RIC/NMR program of MOCIE in Kongju National University.

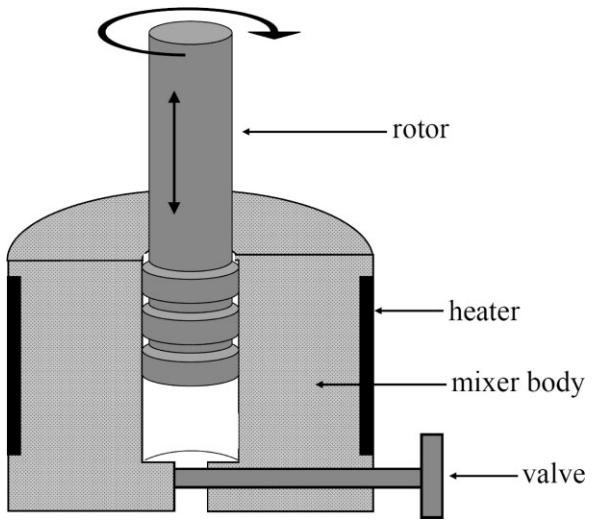


Figure 1 Schematic of a cup and rotor batch mixer.

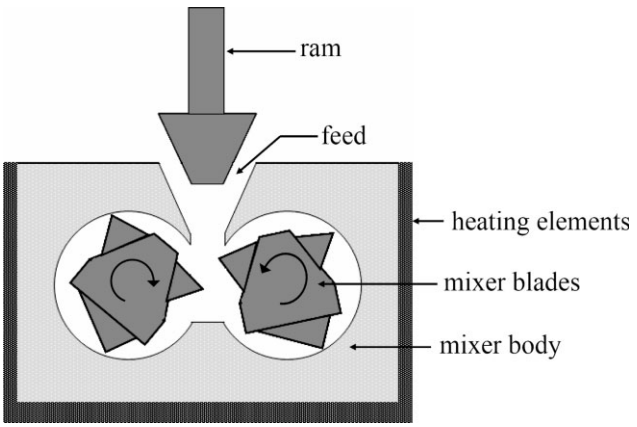


Figure 2 Schematic of an internal batch mixer.

awkward for most materials. Even well-trained operator spends at least 30 min for the sample-removing and cleaning. Furthermore, because the sample contacts air directly during the sample-removing procedure, the thermal oxidation cannot be avoidable. It is frequently observed that a compression-molded specimen blended in the IBM shows spotted appearance because of the oxidation.

Most recently, a recirculating conical twin-screw extruder (RCTSE) was introduced.[10] The RCTSE is based on a conical twin-screw extruder with an incorporated recirculating channel as shown in Figure 3. Because of the recirculating channel and a bypass valve, this mixer is operated as a batch mixer rather than a continuous mixer. Typical volume of the mixing chamber is 5 or 15 cc in the DSM machine and 7 cc in the ThermoHaake machine. During the mixing period, the recirculating channel connects a screw exit and entrance so that the polymer melts circulate through the recirculating channel for certain period of time. After the mixing is completed, a bypass valve is adjusted to disconnect the recirculating channel and open an outlet channel so that the melts come out from the mixing chamber. As this mixer provides relatively good mixing efficiency and easy operation (cleaning and removing sample), it is gaining more popularity replacing the IBM. However, as will be shown in the later section, it is observed that when the volume of material is less than that of the recirculating channel, the circulation of the polymer melts does not occur and the mixing is impossible.

In this study, a new type of microcompounder is developed and evaluated with respect to both dispersive and distributive mixing efficiency for polymer blends. The performance of the mixer developed was evaluated by comparing the microstructure of PS/PE blends compounded in a CRBM, an IBM, and a RCTSE.

EXPERIMENTAL

Materials

Polymers used are polystyrene (PS) from Cheil Industries (trade name: HF2660, M_n = 120,000 g/mol), polyethylene (PE) from the Dow Chemical Company (trade name: EG8150, Melt Flow Index = 0.5 g/10 min), and polypropylene (PP) from SK corp. (trade name: R900Y). Viscosities of PE and PS investigated in this study are shown in Figure 4. The shear viscosity was measured by a capillary

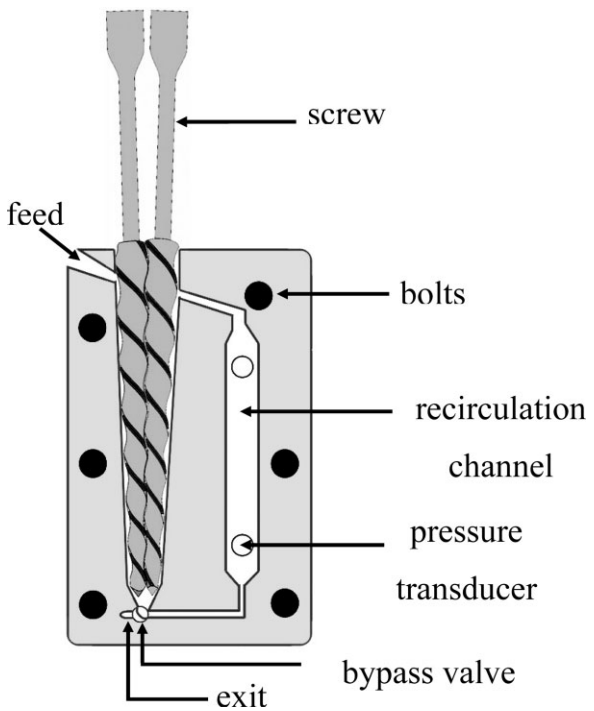


Figure 3 Schematic of a recirculating twin-screw extruder.

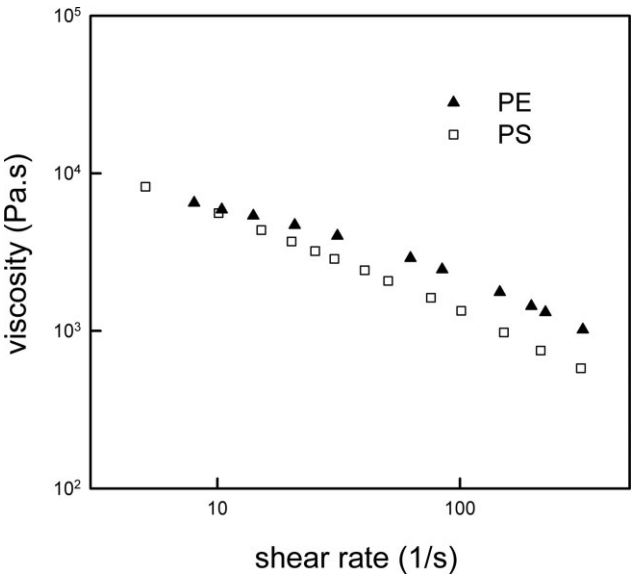


Figure 4 Viscosities of PE and PS investigated in this study.

rheometer with a steel capillary die of 1.0 mm in diameter and 20 mm in length at 180°C.

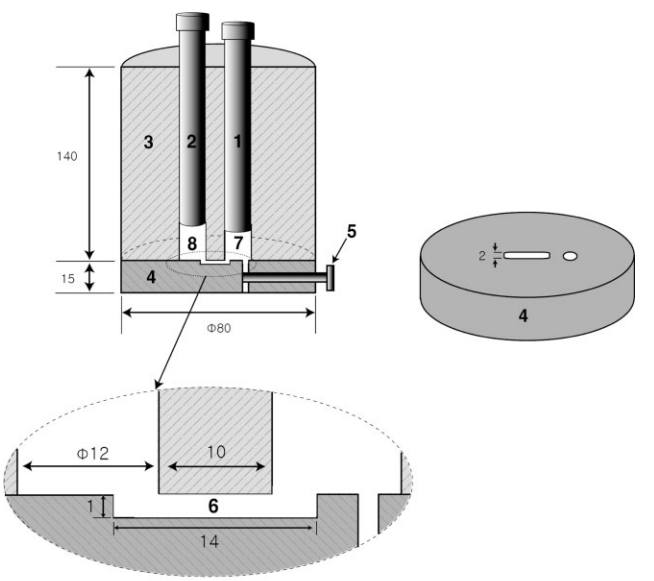
Design of the microcompounder

We tried to design a microcompounder which has the following advantages: (1) cleaning of the mixer and removing sample are easy. (2) The size of mixing chamber varies from 0.5 to 10 cc and the mixing efficiency is still excellent even when it is operated with small amount of sample. To accomplish the target (1), we designed the compounder having a very simple geometry and being operated mainly under an extensional flow, because the extensional flow is much effective for the dispersive mixing.[11] One of main drawbacks of the IBM is that it is very awkward to clean up and remove sample from the rotors. This is mainly because the geometry of the rotor is very complex though this complexity produces good mixing efficiency. Thus, the design with simply reduced mixer (in size) resembling the IBM was excluded. There are several ways to produce the extensional flow. However, to meet the target, "simple geometry for easy cleaning and removing sample" the contraction geometry found in the entrance region of the capillary rheometer is thought to be the only solution.

A schematic design of the compounder is shown in Figure 5. It consists of a heated cylindrical metal (No. 3 in Fig. 5) having two cylindrical cavities (Nos. 7 and 8 in Fig. 5, hereafter denoted as a reservoir) connected through a narrow rectangular channel (No. 6, hereafter denoted as a shear channel, because the shear flow is dominant in this channel.) and two cylindrical pistons (Nos. 1 and 2).

The devise itself is not novel because Mackley et al. also used a double piston arrangement in their so-called "multipass rheometer" to measure the rheological properties of polymer melts.[12] This double piston arrangement has been used by Westover more than four decades ago to measure the pressure dependence of the viscosity of polymer melts.[13] Kadijk and Van Den Brule also used similar device.[14] In this study, we mainly focus on the mixing performance of the double piston type device for the polymer blends. Novelty of our study lies here because no one evaluates the mixing performance for the double piston type rheometer.

To improve the mixing efficiency of the multipass rheometer and the convenience of operation, we modified the existing double piston type equipment as follows. The length of the midsection (shear channel in this study) between the reservoirs is very short compared with the other double piston type device. This enables to generate higher portion of extensional flow, maintaining lower operating pressure in the hydraulic pump. Arrangements of two pistons differ from the multipass rheometer, where pistons are aligned. In our equipment, two pistons are positioned in parallel way in a heated metal cylinder. The arrangements are somewhat similar with the device used by Kadijk and Van Den Brule.[14] A short shear channel is built when a bottom plate is assembled to a cylindrical metal block with six bolts. The bottom plate has an exit channel and a valve



1 & 2 : pistons
3: heated cylindrical metal block
4: bottom plate
5: exit valve
6: shear channel
7 & 8: reserviors

Figure 5 Schematic of an extensional batch mixer.

TABLE I
Characteristics of Small-Scale Mixers Investigated in this Study

Mixer	Instrument name	Capacity	Mixing efficiency	
			Distributive	Dispersive
Cup and rotor batch mixer	MiniMax	<1.0 g	Bad	Marginal
Internal batch mixer	Brabender Plasticorder	~30 g	Good	Good
Recirculating conical twin-screw extruder		2–5 g	Good	Good
Extensional batch mixer		0.5–10 g	Good	Excellent

(No. 5). After a mixing operation, the exit valve opens and the mixed polymer blends can comes out through the exit channel. Details will be discussed later on.

Two pistons move up and down in turn by a hydraulic pump to generate a converging and diverging flow repeatedly. The size of the reservoir is 12 mm in diameter and 140 mm in height. Distance between axes of the reservoirs is 22 mm. The piston can move with maximum distance of 100 mm. Therefore, the mixing capacity in volume is about 11 cc.

The operation of this compounder is straightforward. At first, one piston is inserted into an empty reservoir and the compounder is heated to a preset temperature. Then, desired amounts of polymers and additives are loaded into the other reservoir and the other piston is inserted in the reservoir containing the polymers. After a few seconds, constant pressure is applied on one piston by a hydraulic pump, whereas the other piston is free from the pressure. As the materials melt, the piston under pressure begins to move down to the bottom of the reservoir, squeezing the polymer melt into the other reservoir through the shear channel. The other piston is moved upward by the pressure which is built by squeezed polymer melts. When the piston reaches the bottom of the reservoir, the motions of the pistons are switched by position detectors and a controller. During the mixing period, the materials flow between two reservoirs through the narrow shear channel in a reciprocating manner and experience a periodic extensional force by the converging flow. This extensional flow is known to be very efficient for the mixing of immiscible fluids. Thus, hereafter we denote the mixer developed as an extensional batch mixer (EBM). After preset number of cycles is completed, the pistons stop, an exit valve is open, and both pistons move down to the bottom by a hydraulic pump, squeezing out the polymer melts.

Temperature of the mixer is controlled by a band heater and a PID temperature controller within 0.5°C. Temperature in the mixing chamber was checked by the following procedures. PE sample of 10 g was loaded into the one reservoir followed by a packing. After 5 min for complete melting, a thermocouple of a portable electrical temperature indicator was inserted into the reservoir. Temperature at every 1 cm along the vertical direction was recoded by moving the thermocouple.

Mixers

To evaluate performance of the EBM developed, mixing experiments with various mixers commercially available were carried out for comparison. The characteristics of the mixers are summarized in Table I. The mixing efficiencies of various mixers assessed in Table I are summaries of other studies[10,15] and this study. The CRBM was operated at a rotor speed of 128 rpm, with 0.5 g of polymer. Given a gap of 3.3 mm and the cup diameter, D, 13 mm, the maximum shear rate can be estimated:

$$\dot{\gamma}_{\max} = \frac{\pi DN}{\text{gap}} = 26\ \text{s}^{-1}$$

At this shear rate, the viscosity ratio of the blends is estimated to ~ 2. The IBM is Brabender Plasticoder with a mixing volume of 30 cc. It was operated at a rotor speed of 100 rpm, with 20 g (22 cc) for 7 min. The CRTSE is DSM Research 5 mL Microcompounder. It was operated at a rotor speed of 100 rpm, with 1, 2, 3, and 4 g, respectively, for 7 min.

Blend preparation and morphology observation

Mixtures of PS and PE were melt-blended at 180°C in all mixers. In all case, the composition of PS was 80 wt %. Blended samples were quenched immediately in liquid nitrogen after cessation of mixing operation. Fracture surfaces of the blend were prepared in liquid nitrogen and platinum-coated. Phase morphologies were studied with a JEOL JSM-6335F. ImageJ (which is a public domain Java image processing program inspired by NIH Image, http://rsb.info.nih.gov/nih-image/) was used to measure the diameter of PE domains. About 200 to 300 particles were averaged for each blend.

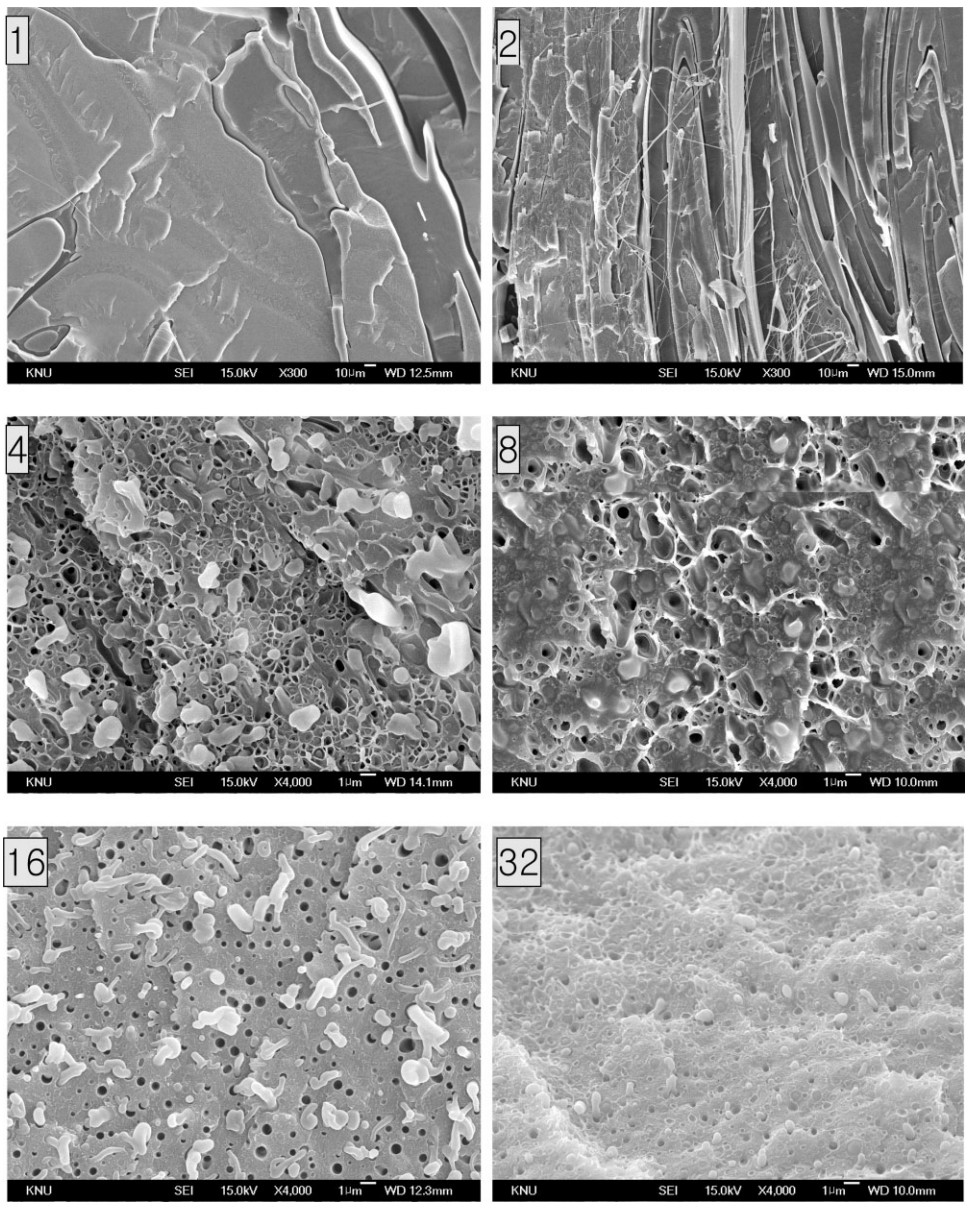


Figure 6 Morphology of PS/PE(8/2) blends extruded in the capillary rheometer. The number shown in each photograph corresponds to the number of extrusions. Apparent shear rate in the capillary die is 1000 s^{-1}. Temperature is 180°C.

RESULTS AND DISCUSSIONS

Before we fabricate the EBM, a simulation is performed with a capillary rheometer, which has a reservoir of the same diameter with the reservoir of the EBM. The capillary die used was 10 mm/1.5 mm in length/diameter, which is similar size of the shear channel of the EBM. PS and PE pellets with a predetermined ratio were loaded into the reservoir. After the melting was completed at 180°C, the piston was pushed down with speed of 197.7 mm/min equivalent to 1000 s^{-1} in shear rate. Extrudates were cut into small pieces and reloaded into the reservoir. This procedure was repeated several times. It is expected that this experiment simulates very well what occurs in the EBM. Figure 6 shows the morphological observation of the PS/PE (8/2) blend extruded various times in the capillary rheometer. Initially, the size of the dispersed phase decreases drastically with the number of extrusions, and the further size reduction of the dispersed phase is moderate. After extrusion of only eight times, the dispersed phase is already reduced to a micron-size scale. It is well known that the flow from a reservoir into and through a capillary combines shear and extensional components.[16] The extensional component, which dominates the flow in the entrance region, can cause the droplets to deform into fibrils. In the die there is heterogeneous shear flow. The fibrils that are formed in the entrance region can possibly break up as they flow through the die. Because the shear rate varies with the radial position,

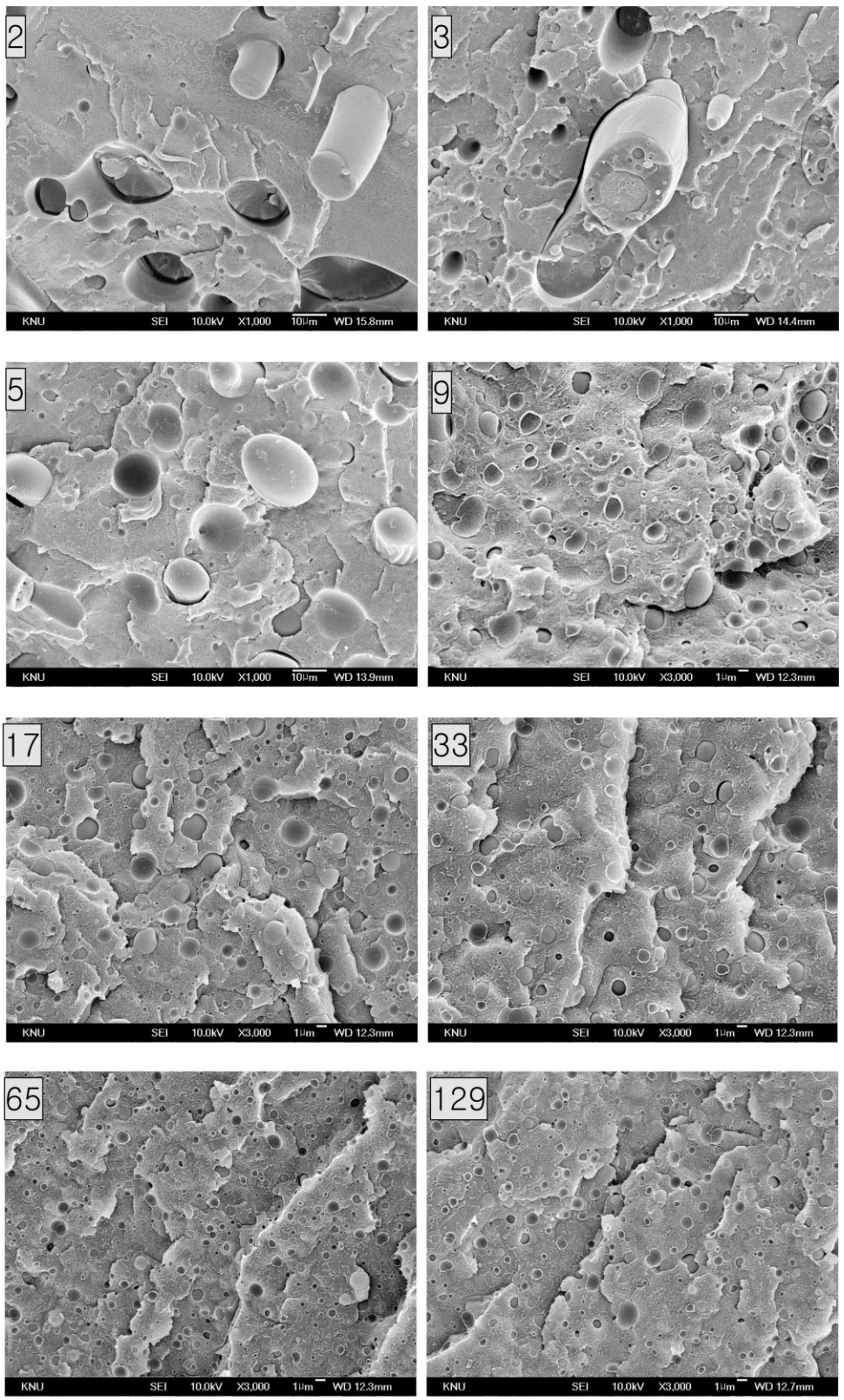


Figure 7 Morphology of PS/PE(8/2) blends compounded in the extensional batch mixer. The number shown in each photograph corresponds to the number of cycles. Peak pressure in the reservoir is 25 MPa. Temperature is 180°C.

the morphology might also be position-dependent and this could result in a size distribution of the dispersed phase.

After the successful simulation by the capillary rheometer, we fabricated the EBM as described in "Experimental section." Figure 7 shows the

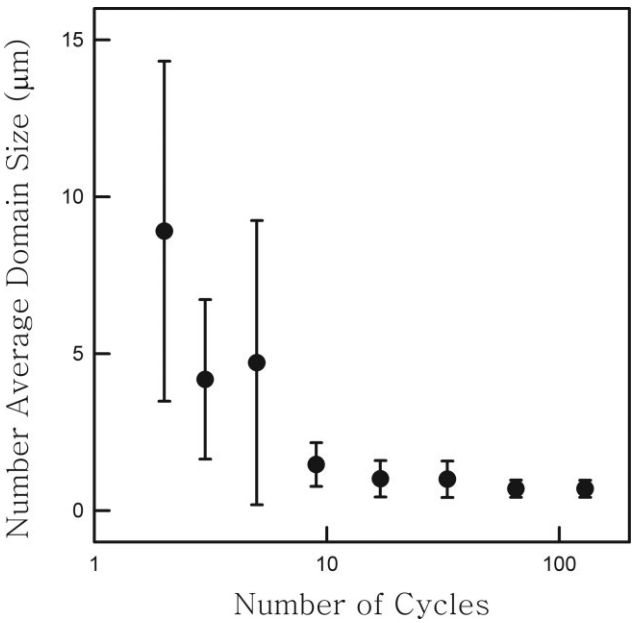


Figure 8 Number–average domain size as a function of number of cycles. Same experiment with Figure 6.

morphological observation of the PS/PE (8/2) blend compounded in the EBM at 180°C. Figure 8 shows average domain size obtained from micrograph in Figure 7. Figure 9 shows the volumetric flow rate, Q, as a function of cycles. Q was measured by analysis of motion pictures taken during the experiment. The flow rate increases rapidly up to five cycles which correspond to 20.3 s and then maintains almost a constant value. The increase of the flow rate is due to the temperature change of the polymer melts at early transient stage. Surprisingly, it takes only 20.3 s for complete melting. Initial millimeter-sized PE domains decrease to a submicron-size scale only after nine cycles which correspond to 24 s. This reduction of the PE domains is very fast compared with the other mixers investigated in this study as will be shown later. After 50 cycles which correspond to 76 s, no more change in morphology takes place. Thus, total mixing time of the EBM is much shorter than the other mixers. The EBM developed in this study has an advantage in mixing of heat sensitive materials. The fibrillar domains are found up to three cycles. The fibrils formed in the converging region by the extensional force can possibly break up in the shear channel and in the reservoir. According to the theory, the time to break up for the fibril is proportional to the diameter of the fibril.[17] When the fibrils are large at the initial period of mixing, there is not enough time for the fibrils to break up. Thus, the domains maintain cylindrical shape whereas smaller domains at the later period break up and/or relax to spherical shapes. The number–average diameter of the dispersed phase at the final stage is about 0.75 μm, which is the smallest among all mixers investigated in this study.

Figure 10 shows the morphological observation of PS/PE(8/2) blends compounded in various mixers. Table II shows the number–average domain size of the blends compounded in various mixers. Because the CRBM provides only pure shear flow, the mixing efficiency is poor as can be seen in Figure 10(a). The number–average domain size is 4.4 μm, which is the largest among all mixers investigated. Also, it is noteworthy that the size distribution is broadest, indicating that the coalescence process takes place during the mixing operation in the CRBM.

The morphology of the blends compounded in the IMB is finer than that of the CRBM. The size distribution of the dispersed phase is narrower, too. The number–average particle size of the blend compounded at 100 rpm is slightly smaller than that compounded at 50 rpm, which is consistent with the literature.[18]

The morphology of the blends compounded in the RCTSE is similar to that observed in the blend compounded in the IBM. We performed four different runs with samples of 1, 2, 3, and 4 g, respectively, equivalent to the volume of 1.1, 2.2, 3.3, and 4.4 cc. It was observed that the mixing is not possible when the sample of 1 g is loaded. When the volume of materials is less than that of the recirculating channel, the circulation of the polymer melt does not occur. Instead, the materials are stuck in the recirculating channel. When the volume of the material is slightly larger than that of recirculating channel, the

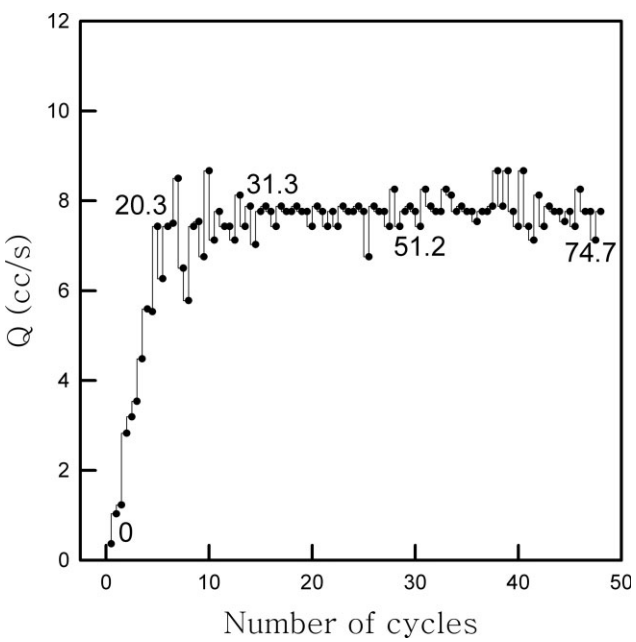


Figure 9 Volumetric flow rate as a function of cycles. Same experiment with Figure 6. The numbers shown in the graph correspond to time in second.

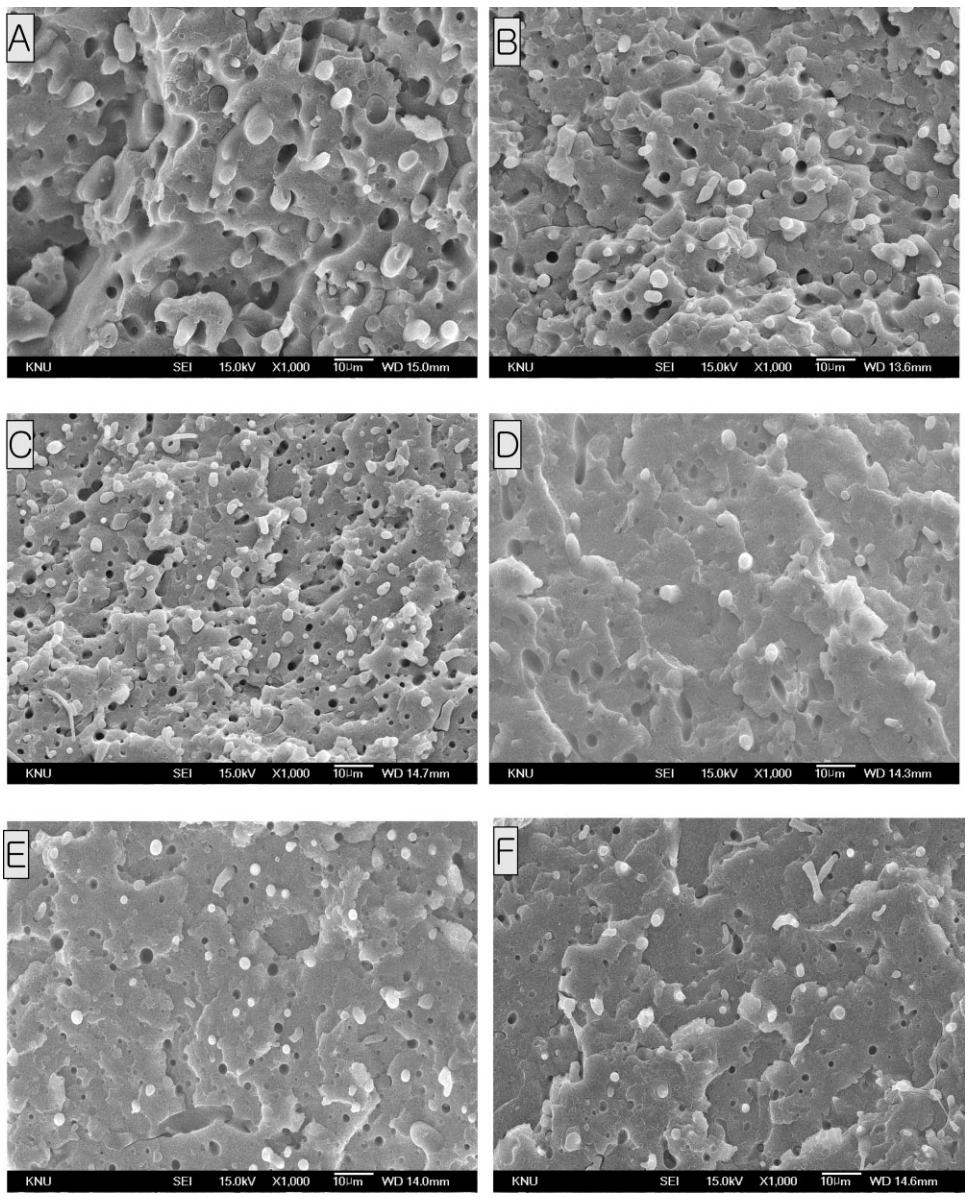


Figure 10 Morphology of PS/PE(8/2) blends compounded in various mixers investigated in this study. (A) Cup and rotor batch mixer; (B) internal batch mixer, rotor speed = 50 rpm; (C) internal batch mixer, rotor speed = 100 rpm; (D) recirculating twin-screw extruder, amount of sample loaded = 2 g; (E) recirculating twin-screw extruder, amount of sample loaded = 3 g; and (F) recirculating twin-screw extruder, amount of sample loaded = 4 g.

TABLE II
Number–Average Particle Sizes of the Blends Compounded in Various Mixers

Mixer	Mixing time (min)	Amount of the sample (g)	Mixing speed (rpm)	$<Dn>$ (μm)
Cup and rotor batch mixer	20	0.5	128	4.4 ± 1.8
Internal batch mixer	7	20	50	3.4 ± 0.92
	7	20	100	2.5 ± 0.79
Recirculating conical twin-screw extruder	7	2	100	2.5 ± 0.99
	7	3	100	2.2 ± 0.88
	7	4	100	1.9 ± 0.77
Extensional batch mixer	1.4	5	–	0.75 ± 0.27
	2.8	5		0.74 ± 0.29

mixing efficiency is good as shown in Figure 10(d). Average particle size does not vary much with the amount of the sample, once the circulation of the polymer melts occur. The volume of the recirculating channel varies with manufacturers. The volumes of the recirculation channel in the ThermoHaake and the DSM machines are 2.0 and 1.5 cc, respectively. Thus, the RCTSE cannot mix the materials when the amount of the materials is small (e.g., less than 2 cc). The average particle size and the size distribution of the blend from the RCTSE are similar to those from the IBM when the recirculation is possible.

Among all mixers investigated, the EBM provides finer morphology and the narrowest particle size distribution. It is most probably because of the fact that the EBM provides the most intensive extensional flow. The majority of flow is shear flow in the other mixers except the EBM. However, in the EBM, the majority of flow is extensional flow because of the contraction zone. As polymer melts flow from the reservoir to the shear channel, the polymer melts accelerate because cross-sectional area of the reservoir is larger than that of the shear channel. This contraction zone is known to provide intensive extensional flow.[16] Shear flow is provided only in a short shear channel. Therefore, the probability for coalescence to occur is lower than those of the other mixers, leading to finer and uniform morphology. This fact suggests that the EBM is efficient blending equipment.

So far, we mainly discussed the dispersive mixing efficiency. To assess the distributive mixing efficiency of the EBM, we employed a colored dual-layer technique. The experimental procedure is initiated by loading an unpigmented cylinder block (made of PP with 20 mm in length and 12 mm in diameter, white color) at the bottom of the reservoir and a pigmented block (PP cylinder incorporated with 0.5 wt % of carbon black) at the top. After several minutes, constant pressure was applied on the piston for mixing. After predetermined number of cycles was completed, the hydraulic pump and electric heater were turned off, followed by solidification of polymer. The solidified PP cylinder was taken out from the reservoir and split into half along the axial direction. Figure 11 shows the photographs of cross section as a function of number of cycles. Small white and black dots seen in the sample of 1.5, 2.5, and 7.5 cycles are cavities formed during the solidification, not an unmixed PP. Initially, separated white and black colored PP is gradually being mixed as a number of cycles increases. White color is barely seen on the sample after 2.5 cycles. It is noteworthy that the white PP originally loaded on the bottom is located on the bottom and surrounds the black PP in the 0.5 cycle. This is due to complex flow effect in the reservoir. As observed by Sombatsompop et al.,[19] a large fraction of material flows down along the center of the reservoir because the velocity profile is parabolic. As a consequence, black PP in the center of the reservoir penetrates, overtakes the white PP and is finally surrounded by white PP. It is also noteworthy that only one cycles of mixing generate multilayers of white and black materials. This multilayers are formed by folding effect generated by the flow near the piston. Materials adjacent to the surface of the piston tip are gradually being swept away from the reservoir wall across the face of the piston and into the center of the reservoir as observed by Sombatsompop et al.[19] Fundamental mixing mechanism of the EBM is a stretching by converging flow and folding by this complex flow near the piston tip. One of the most effective means of increasing interfacial area of polymer blends is a

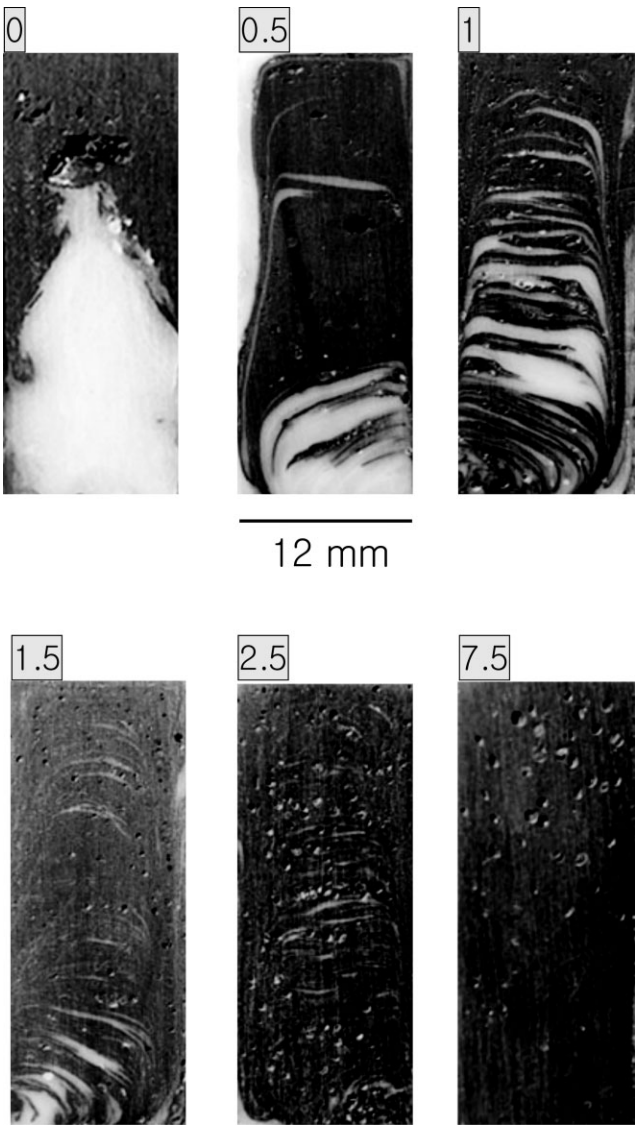


Figure 11 Flow visualization experiment in the extensional batch mixer. The number shown in each photograph corresponds to the number of cycles.

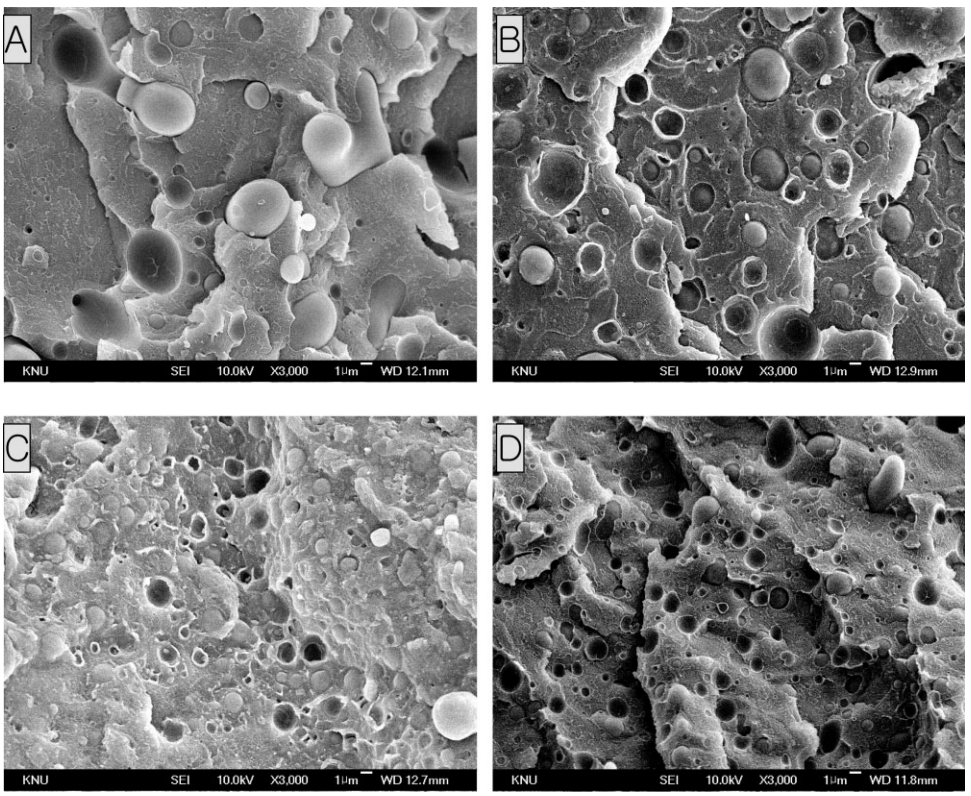


Figure 12 Morphology of PS/PP(8/2) blends compounded in the extensional batch mixer at various mixing speed. Numbers shown in each photographs correspond to average flow rate during the mixing. (A) Peak pressure in the reservoir = 10 MPa, flow rate = 0.2 cc/s, (B) peak pressure in the reservoir = 15 MPa, flow rate = 2 cc/s, (C) peak pressure in the reservoir = 20 MPa, flow rate = 7.5 cc/s, and (D) peak pressure in the reservoir = 25 MPa, flow rate = 7.9 cc/s.

stretching and folding of the interface. Thus, it is proved that the EBM provides both excellent distributive and dispersive mixing efficiency.

Figure 12 shows the morphology PS/PE(8/2) blends subjected to various pressure in the reservoir. The particle size is smaller in the blend subjected to higher reservoir pressure which implies higher flow rate, shear rate, and elongational rate. The particle size decreases continuously with the elongational rate. The occurrence of local minimum in particle size at the intermediate mixing speed found in other studies[15,18,20,21] and is not observed in this study. This local minimum in particles size might be attributed to coalescence, which is more intense at higher mixing speed. Therefore, it is inferred that the coalescences, which frequently occur in mixing equipment, seldom occur in the EBM.

One of several advantages of the EBM is minimizing material lost, owing to its unique simple design. Material lost is determined by the volume of the shear channel, outlet channel, and clearance between the piston and the reservoir wall. Material lost of the EBM is found to be $\sim$ 0.1 cc in 50 cycles at most.

The recirculating channel of the RCTSE manufactured by Haake is designed as slit capillary. (http://www.mcik.co.kr/product/pdf/MicroCompounderReactor.pdf) The pressure drop is measured with two pressure transducers mounted in the slit-shaped recirculating channel, and consequently the shear stress is obtained. To determine the shear rate, a volumetric flow rate should be measured. However, it is not possible to get an exact volumetric flow rate in the RCTSE. Therefore, the Haake RCTSE provides only relative shear rate and relative viscosity, which are function of screw speed. Another advantage of the EBM is that it can be used as a slit rheometer with a slight modification, similar to that reported by Kadijk and Van Den Brule.[14] With changing the narrow shear channel to a wide slit geometry and mounting pressure transducers on it, the mixer can provide rheological data. Unlike the RCTSE, an exact volumetric flow rate can be obtained by analysis of the piston motions in the EBM. Even the pressure dependency of the viscosity can be measured by controlling the pressures of two hydraulic pumps separately.

In this study, we study the mixing efficiency of the EBM with polymer blends. In many cases, dispersion of pigment powders is of great importance in industries. Preliminary test shows that mixing efficiency is not good for polymer and solid powder mixture such as polymer/clay nanocomposite especially at high loading of clay. This is probably due to the different mixing mechanism of two systems.

We are trying to improve the mixing efficiency for polymer/pigment powder system. This will be our next study.

CONCLUSIONS

A new type of microcompounder was successfully developed and the performance of the compounder was evaluated. The compounder was designed to utilize the extensional flow, which appears in the converging geometry. It was found that the compounder developed shows both excellent dispersive and distributive mixing efficiency. In addition, the operation of the compounder is very easy and material lost is very small, owing to its unique simple design.

References

1. Paul, D. R.; Newman, S. Polymer Blends; Academic Press: New York, 1978.
2. Covas, J. A.; Costa, P. Polym Test 2004, 23, 763.
3. Zumbrunnen, D. A.; Chhibber, C. Polymer 2002, 43, 3267.
4. Cassagnau, P.; Fenouillot, F. Polymer 2004, 45, 8019.
5. Maric, M.; Macosko, C. W. Polym Eng Sci 2001, 41, 118.
6. Maxwell, B. Soc Plast Eng 1972, 28, 24.
7. Yang, B.; Sato, M.; Kuriyama, T.; Inoue, T. J Appl Polym Sci 2006, 99, 1.
8. Inoue, K. In Mixing and Compounding of Polymers; Manas-Zloczower, I., Tadmor, Z., Eds.; Hanser Publishers: New York, 1994; Chapter 18, p 619.
9. Moon, D. Y. PhD Thesis, Korea Advanced Institute of Science and Technology, Daejeon, South Korea, 1998.
10. Scott, C. E.; Macosko, C. W. Polym Eng Sci 1993, 32, 1065.
11. Grace, H. P. Chem Eng Commun 1982, 14, 225.
12. Mackley, M. R.; Marshall, R. T. J.; Smeulders, J. B. A. F. J Rheol 1995, 39, 1293.
13. Westover, R. E. Soc Plast Eng Trans 1961, 1, 14.
14. Kadijk, S. E.; Van Den Brule, B. H. A. A. Polym Eng Sci 1994, 34, 1535.
15. Breuer, O.; Sundararaj, U. Polym Eng Sci 2004, 44, 868.
16. Han, C. D.; Funatsu, K. J Rheol 1978, 22, 113.
17. Elemans, P. H. M.; Janssen, J. M. H.; Meijer, H. E. H. J Rheol 1990, 34, 1311.
18. Sundararaj, U.; Macosko, C. W. Macromolecules 1995, 28, 2647.
19. Sombatsompop, N.; Tan, M. C.; Wood, A. K. Polym Eng Sci 1997, 37, 270.
20. Ghodgaonkar, P. G.; Sundararaj, U. Polym Eng Sci 1996, 36, 1656.
21. Hunealt, M. A.; Shi, Z. H.; Utracki, L. A. Polym Eng Sci 1995, 35, 115.