Capturing the Efficiency of a Melt-Mixing Process for Polymer Processing

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Polymer blends and composite materials are often produced by a melt-mixing process using equipment specially designed to mix high-viscosity fluids during laminar flow. The melt-mixing process can be classified into distributive and dispersive mixing. Distributive mixing includes stretching and folding of fluid elements and rearrangement of dispersed materials. Dispersive mixing is the size reduction of filler aggregates and/or liquid droplets in a matrix fluid. In order to optimize the design of a melt-mixing equipment, the evaluation of distributive and dispersive mixing is essential. In this paper, we consider fundamental aspects of melt-mixing, and experimental and computational approaches that have been reported in the literatures. Experimental observation of melt-mixing, by and large, provides rather limited information on the mixing process inside of equipment. Although a mixed material can be obtained under specified conditions and its physical properties can be directly measured, it is difficult for the mixing mechanism behind the final result to be inferred. Computational fluid dynamics complements this situation. Numerical simulation of a mixing process provides a non-invasive and detailed data in a equipment so that the quantitative measures for distributive and dispersive mixing can be obtained. We consider various quantitative measures that have been previously proposed to characterize distributive and dispersive mixing.

Introduction

Melt mixing is an important operation that determines the material properties of polymer composite materials manufactured using batch-type mixing machines, twin-screw extruders, or single-screw extruders in the mixing functions. Mixer and extruder design is important for achieving effective mixing. Technological development of melt-mixing equipment has progressed based on the accumulated experimental data, development of visualization and measurement techniques, and the application of numerical simulations. In this paper, we explain the theoretical aspects of melt-mixing, characterization of mixing processes, and tasks remaining for understanding melt-mixing processes.

1. Mixing/Kneading Mechanisms

The mixing/kneading effects in an extruder can be classified as distributive or dispersive mixing based on the influence of the flow field on the dispersed phase or the interface between the components (e.g., Tadmor and Gogos, 2006; Kajiwar and Nakayama, 2008). The two mechanisms are explained below; the mixing of polymer

blends and polymer composites are discussed separately to facilitate understanding of the mechanisms by capturing detailed images of each type.

1.1 Polymer blends

Melt mixing of polymer materials generally involves high-viscosity fluids. Therefore, diffusion between different polymer components can be neglected. **Figure 1** shows a schematic illustration of distributive and dispersive mixing in a polymer blend. First, a miscible liquid–liquid system is considered. Distributive mixing is a mixing process in which the strain field is created by flow-induced deformation and extension of the component interface. In this process, the interfacial area between components increases and the distribution of each component is promoted. Here, the strain direction plays an important role in the effective increase of the interfacial area. Strain parallel to the interface does not contribute to increasing the interfacial area, and strain perpendicular to the interface is the most effective. However, it is impossible to control the strain direction in the actual machine. Therefore, it is important to create a complex flow field that has strain in every direction.

Next, we consider the deformation and breakup behavior of dispersed droplets in the matrix liquid in an immiscible liquid–liquid system. As droplets are deformed during matrix flow, interfacial tension simultaneously acts to reform the droplets into spheres. Here, the application of stress is essential to overcome the interfacial tension in the dispersion droplet and initiate its

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Fig. 1 Schematic of distributive and dispersive mixing in a polymer blend

breakup. This is dispersive mixing, defined as a mixing process in which the extended dispersed droplet is broken up by the action of a stress field. Since the strain rate and stress always exist in the flow field, both distributive and dispersive mixing processes generally contribute to a mixing/kneading process. When the size of a dispersed droplet of an immiscible polymer blend system is large, mixing proceeds by an initial distributive mixing followed by a size reduction in the dispersed droplets by dispersive mixing. Distributive mixing then distributes the small droplets uniformly throughout the matrix.

Generally, liquid viscosity and flow type are important in the mixing process. For example, under the application of a given stress, a higher viscosity results in a smaller strain rate. This corresponds to the fact that a larger ratio of dispersed droplet viscosity to matrix viscosity, η_D/η_M , makes dispersive mixing more difficult. In dispersive mixing, the flow regime is also important, in addition to the viscosity.

Grace (1982) studied the static breakup condition for a single droplet in a matrix liquid in a Newtonian fluid system. To break up the droplet, the matrix liquid viscous stress, $\eta_M \dot{\gamma}$, must be greater than the interfacial tension, σ/ρ . Here, $\dot{\gamma}$ is the strain rate, ρ is the droplet curvature, and σ is the interfacial tension. In this case, the stress in the matrix liquid is also affected by the viscous stress in the droplet. The breakup condition is determined by two dimensionless numbers given by three quantities: the hydrodynamic stresses of matrix and droplet, and the interfacial tension. The static breakup condition is determined jointly by the capillary number,

$$C_a = \frac{\eta_M \dot{\gamma} \rho}{\sigma} \quad (1)$$

and the viscosity ratio, η_D/η_M (Grace, 1982; Bentley and Leal, 1986). It was proven that breakup does not occur in simple shear flow with a viscosity ratio greater than about 5. In simple shear flow, as the viscous stress increases, the rotation of the droplet increases corre-

spondingly, effectively avoiding breakup. Conversely, in simple elongation flow, droplet breakup occurs regardless of the viscosity ratio, and the critical Ca is smaller than the one in simple shear flow. This is because droplet rotation does not occur in simple elongational flow, such that the stress acts more effectively to break up the droplets. As a result, the importance of flow type in dispersive mixing was recognized. Melt mixing equipment was accordingly designed to promote dispersive mixing by elongational flow with good results.

Inside the actual equipment, the flow type is not homogenous; the strain rate varies along with flow. Consideration of the non-stationary property in droplet breakup is required. In one study, data were evaluated including the time needed to achieve breakup when a stress higher than the critical Ca was applied (Grace, 1982). In addition, obtaining a high strain rate in elongation flow is normally very difficult. In practice, it is important to design the equipment so as to realize a high stress and to pump droplets into the high stress region efficiently.

Additionally, polymer blends are viscoelastic fluids. Droplet deformation, which serves as a reference in considering droplet breakup, is determined not only by the viscous stress, but also by the difference in pressure distribution, including the elasticity effects around the droplet. Therefore, the deformation and breakup of droplets in a viscoelastic fluid are significantly different from those in a Newtonian fluid system (Utracki and Shi, 1992). It has also been proven in an experimental study (Gauthier *et al.*, 1971) that the critical Ca is higher for a droplet in a viscoelastic liquid than in a Newtonian fluid. Additionally, droplet coalescence must be considered when discussing polymer blend mixing. The conditions here include not only the conditions for breakup, but also the dispersed phase concentration and droplet collision frequency. Since the conditions for coalescence are more complex than those for droplet breakup, they have not been sufficiently characterized.

1.2 Polymer composites

Palmgren (1975) divided a polymer and filler mixing process into four phases: 1) the polymer is plasticized and melted as large aggregate filler is crushed, 2) small crushed aggregate filler interfuses into the matrix of melted polymer, 3) aggregated filler in the polymer is further reduced in size when passing through the high-stress region, and 4) miniaturized filler is mixed into the matrix completely to achieve homogenization of the material. Here, distributive mixing in melt mixing corresponds to Phase 3, and dispersive mixing occurs in Phase 4. **Figure 2** shows a schematic illustration of distributive and dispersive mixing in a polymer composite.

In polymer composites, a stress higher than the cohesive force of the filler (adhesive force, viscous force, and electrostatic force) operates on the material and miniaturizes the aggregate; this is the dispersive mixing mechanism. This cohesive force corresponds to the in-

Fig. 2 Schematic of distributive and dispersive mixing in a polymer composite

terfacial tension acting to reform the droplets into spheres, as in a polymer blend. Regarding the mechanism of dispersive mixing, the basics are the same in both cases. However, in the case of a polymer composite, the cohesive force depends on a combination of many factors, such as the size and shape (particle, fiber, or plate) of the filler inclusions and their surface characteristics. Particularly, in dispersive mixing theory, it is stress that promotes dispersive mixing. However, in the cohesion of an irregularly shaped filler, the dispersive mechanism technically should vary depending on the shape. The task remains to expand the theory further in this respect.

2. Melt Mixing in a Single-Screw Extruder

In melt mixing using a single-screw extruder, differently shaped mixing elements than a pumping screw are used in the melt transport zone, where these are roughly classified into three types based on differences in the mixing method: the place-exchanging method, the barrier-slit method, and the elongational deformation method.

The place-exchanging method is distributive mixing using a relatively weak shear flow. Since breakup is less likely to occur, this method is most extensively used for homogenization of temperatures and materials. Dulmage-type, DIS-type, and pin-type mixers use this method. All are designed to cause distributive mixing by complicating the flow field so as to promote material place exchange.

The barrier-slit method is dispersive mixing using a strong shear force. This method entails the breakup of the dispersed phase and is used for polymer blends, additive blends, and polymer composites. The mixer elements used for this method include ring-type, Maddock-type, Unimelt-type, and double-flight type. The elonga-

tional deformation method uses the effect of elongational flow in dispersive mixing. The CRD mixing screw (Rauwendaal, 2008) uses this method. It has slits of different widths on several flights. The dispersed phase enters at the wider slits and is elongated by the tighter slits to facilitate breakup. The wave-type, CTM-type, barrel-pin-type, HM-type, and Spirex-type elements use this method.

Single-screw extruder elements have been developed based on the concept of dispersive mixing by strong shear and/or elongational flow. A single-screw extruder is more economical on the facility capital investment side compared with twin-rotor mixers or twin-screw extruders. However, the stress initiated is relatively small, and the degree of dispersive mixing is limited.

3. Melt Mixing in a Twin-Rotor Mixer or Twin-Screw Extruder

Twin-rotor mixers and twin-screw extruders achieve higher stress and more complex flow by using two screws of varied shapes, arrangement, and operating conditions than single-screw extruders. The dispersive mixing in melt mixing is achieved both by applying shear stress to the material when it passes through the tightest locations between screw barrels or between two screws. By passing through such a tip clearance repeatedly, a high shear stress is repeatedly applied to the material to promote dispersive mixing. Tightening the tip clearance increases the shear stress level; however, it decreases the amount of material passing through the tip clearance and degrades the uniformity of the material due to differences in mixing history. In other words, tip clearance affects dispersive mixing significantly and can degrade dispersive mixing performance when it is either too wide or too tight.

In distributive mixing, as in the single-screw extruder, a complex shape element is used to induce a complex flow. The difference here is that material is transported unfilled except for a part of the mixing zone. Therefore, a part of the material is transported in a direction opposite to the extrusion direction, promoting place exchange.

Dispersive mixing requires a large stress, which causes the problem of viscous heating. The temperature rise of a polymer due to viscous heating can cause not only thermal degradation of the material, but also influence mixing performance by decreasing fluid viscosity. Cooling of the barrel is essential to limit the temperature rise. However, if molten polymer forms a film on the barrel wall, it becomes a cooling obstruction due to the low thermal conductivity of polymers, an undesirable phenomenon. To solve this problem, tip clearances are tightened to achieve a self-cleaning function (i.e., scraping plastic off of the barrel wall). As stated above, tip clearance is related to the amount of material passing

through the extruder. Therefore, an element consisting of different tips corresponding to barrel scraping and material passage functions is created by reducing tip clearance at a few screw tips in some areas (Inoue, 2004).

4. Experimental Mixing Evaluation

Mixing/kneading performance can be determined by evaluating the extrudate. Structural evaluations from observation of optical/electron microscopy images or evaluations of material properties such as mechanical strength are often performed. However, the mixing mechanism—the reason behind the result—cannot be inferred from observation of the final structure. An evaluation based on the mixing mechanism itself is required if the mixing is being evaluated to improve the equipment and/or process.

Observation of flow patterns inside hot (typically 200–300°C) and highly pressurized equipment is not easy; however, a workable experimental study aimed at evaluating mixing in situ has been reported (Cassagnau *et al.*, 2007; White and Kim, 2010). Visualization of flow patterns was performed at a room temperature and near atmospheric pressures using a test fluid simulating a mixing material, e.g., a high-viscosity oil, in an extruder constructed with a transparent plastic barrel, such as an acrylic. This enabled velocity field measurement using laser Doppler velocimetry (LDV) or particle image velocimetry (PIV) (Jaffer *et al.*, 2000) and flow observation using a tracer. However, the measurement of intermeshing region between two screws or tip clearance, i.e. the regions most affecting mixing, remains difficult.

The following methods were used in the experiments using the actual extruder: 1) a transparent window was placed on the barrel to allow observations inside 2) mixer operation was suddenly stopped and the material cooled rapidly and was extracted along with the screw to observe the interior pattern 3) several sampling ports were placed at different axial locations on the barrel to extract material for structural observation. These methods allowed the observation of mixing under normal operating conditions; however, each method has its limitations. It is impossible to observe a portion of the interior such as the intermeshing region through the window, and the time elapsed between suspension of mixer operation and sample observation in the sudden cooling extrusion experiments may pose a problem. Additionally, although material extracted from a sampling port can indicate the material's status at a certain point, it also reflects the cumulative mixing effects from the mixer entrance to the port. Therefore, the pointwise information remains unknown. A measurement of residence-time distribution can also be performed by monitoring the concentration of an injected tracer at the extruder exit. This measurement can reflect not only mixing characteristics but also characteristics of the whole mixing equipment. See the textbook of White and Kim (2010) for the details of each

experiment. Generally, the importance of experimental observation is to obtain information using actual shapes during operation. It is difficult to obtain pointwise information of parts of the process, such as the intermeshing region and tip clearance, affecting mixing. Therefore, a theoretical consideration combining experiments and numerical simulation is necessary.

5. Mixing Evaluation by Numerical Simulation

Since the mixing process occurs due to flow that is, in turn, controlled by the equipment configuration, a fluid dynamic simulation was performed for a three-dimensional shape. In reality, the material is a multi-component, multi-phase system, but it is assumed to be a homogeneous fluid in the simulations. The mixing process is mainly controlled by equipment configuration; therefore a well-characterized fluid is used to clarify the equipment characteristics. Additionally, using a multi-phase system to perform a three-dimensional simulation faithful to the equipment shape is practically impossible with existing computational capacity. Applicability of the simulation result with a homogeneous fluid has its limitations. In other words, the results with a homogeneous fluid can be applied if the flow of the target material is under shape control. However, if the flow pattern is significantly different from that of a homogeneous fluid due to the inhomogeneity of the mixture material, then experimental analysis is necessary.

Keeping in mind the above points, numerical simulation can offer detailed physical information such as the velocity field in the whole mixer, including intermeshing regions and tip clearances, the stress field, and the temperature field. Additionally, case studies with different equipment shapes, operating conditions, and/or material properties can easily be performed. Simulation is thus essential in constructing the theory of mixing phenomena. In particular, numerical tracer experiments can provide a visual understanding of the overall picture and details of the flow field; this technique is highly effective in facilitating our understanding of the phenomena. Nonetheless, applying simulation results to the actual problem still requires the use of an evaluation index to quantitatively determine mixing capability, as explained in the next section.

6. Mixing Evaluation Index

The characteristics that can be used to determine the effectiveness of a mixing operation are extensive and are, therefore, difficult to evaluate with one index. Additionally, mixing evaluation essentially requires fundamental understanding of the morphology control of multi-component systems. Therefore, the construction of a practical and effective index from numerical data determined under various assumptions requires many careful comparisons of numerical simulation and experimen-

tal results. Using the previously developed distributive/dispersive mixing evaluation index, an effective case will be explained in the following (Kajiware and Nakayama, 2008). The mixing index can in principle be applied to the experimental data in essentially the same way, if the whole flow field is measured experimentally. It is important to understand the mixing mechanism because considering the mixing index entails considering the mixing mechanism.

6.1 Distributive mixing index

Distributive mixing is a kinematic mixing process. A local factor that causes distributive mixing is the strain rate. Therefore, an index can be created based on the strain magnitude and flow type. Usually, the high-strain-rate region is at a limited part of the mixing equipment. Material distributions elongated by strain rate are rotated and folded to promote mixing. It is desirable that the low-strain-rate region in the mixing equipment creates a flow pattern whereby all the fluid element repeatedly passes the high-strain-rate region. Therefore, distributive mixing capability cannot be characterized simply by looking at the spatial distribution of strain rate; flow pattern must also be considered. Alternatively, an index can be created by quantifying the distribution of mixed material by the flow. The former example is a quantification based on distributive mixing mechanisms, and the latter is a quantification based on mixing results. What is important here is to achieve a desirable mixture state in the final material distribution. Therefore, global information processing is essential to quantify mixing. It is also important to quantify the phenomenon multilaterally using different indices.

First, quantification based on distributive mixing mechanisms will be explained. Distributive mixing can be quantified by solving material transport equations (e.g., for concentration field or discrete particles) based on the velocity field. The method is classified roughly into two types; the first method is to examine the time variation of the inhomogeneity of a concentration distribution. This method requires a characterization of the inhomogeneity of the concentration field.

The most basic measures of mixture inhomogeneity introduced by Danckwerts (1952) are the intensity of segregation (IoS)

$$\text{IoS}(t) = \frac{\sigma^2(t)}{\sigma_{\max}^2} \quad (2)$$

$$\sigma^2(t) = \frac{1}{V} \int d\mathbf{x} [c(\mathbf{x}, t) - \bar{c}]^2 \quad (3)$$

which is a normalized variance of concentration fluctuation c , where $\bar{c}$, V , and $\sigma_{\max}$ are the mean concentration, the system volume, and the maximum possible variance, respectively, and scale of segregation (SoS)

$$\text{SoS}(t) = \int_0^\infty dr R(r, t) \quad (4)$$

which is an integral length of correlation coefficient, where $R(r, t)$ is a two-point correlation coefficient of the concentration fluctuation. IoS is a measure of inhomogeneity of the spatial distribution of a component, whereas SoS is, roughly speaking, a measure of agglomerate size. To characterize a mixing process, the way of reduction in IoS and SoS as time evolves is utilized.

In order to study a mixing process by kneading disks in the melt-mixing zone of a twin-screw extruder, Lawal and Kalyon (1995b) computed the IoS from the time evolution of point tracers which were initially set to be localized. Bigio and Stry (1990) used alternative measures instead of the IoS and/or SoS, which are the homogeneity of the interface distribution and its correlation function. Instead of SoS, Bothe *et al.* (2006) used

$$\Phi^{-1}(V) = \left[\frac{1}{V} \int d\mathbf{x} \left\| \nabla \frac{c}{c_{\max}} \right\|^2 \right]^{-1} \quad (5)$$

as a length scale for the concentration distribution $c(\mathbf{x}, t)$. In contrast to the SoS, which shows a rather large segregation scale, this quantity reflects concentration fluctuations over a short distance. When the target is an immiscible system, Φ indicates the interfacial area per unit volume.

As an index of heterogeneity, an entropy rate based on the probability measure induced from the concentration field can be used instead of the IoS (Wang *et al.*, 2003; Alemaskin *et al.*, 2005; Camesasca *et al.*, 2006; Camesasca and Manas-Zloczower, 2009; Guida *et al.*, 2010). There is no essential difference between entropy rate and IoS in terms of expressing the heterogeneity of a mixture. Additionally, a method to obtain a segregation scale from the scale dependence of the entropy rate has been discussed (Camesasca and Manas-Zloczower, 2009). However, the length scale obtained from the entropy rate generally does not yield segregation scale (Nakayama and Kajiware, 2011).

Yang *et al.* (1994) and Yang and Manas-Zloczower (2009) proposed another measure of inhomogeneity based on the pair distribution function used in the statistical physics, called the cluster distribution index. The cluster distribution index is defined as the integral of the difference between the observed pair distribution function and that of the homogeneous distribution. Concerning the characterization of inhomogeneity, the cluster distribution index has no essential differences from the IoS or entropy rate, again.

To consider inhomogeneity at various scales, a measure called the Mix-Norm has been proposed (Mathew *et al.*, 2005). The IoS and/or entropy rate can be used to represent inhomogeneity at a given single scale, and fluctuations at smaller scales are averaged out. In contrast, Mix-Norm considers inhomogeneity at all scales to define and global inhomogeneity of a mixture. Mix-Norm can be used as a measure of mixture inhomogeneity like the IoS and entropy rate, but it does not re-

quire the selection of an observation scale. Polymer blends and polymer composites as mixing targets in polymer processing are immiscible systems in most cases. The mixture state of an immiscible system cannot be evaluated simply by the homogeneity of concentration fluctuations at a single scale, but requires characterization of the filler morphology and corresponding inhomogeneity in multiple scales. Nakayama and Kajiware (2011) have proposed a way for simultaneous characterization of inhomogeneity in multiple scales and homogeneity at a macroscopic scale.

For batch mixers, the time evolution of a mixture state is sufficient to characterize the mixing process. Conversely, characterization of the mixing process in a continuous mixer requires observation of the development of the mixture state in the extrusion direction. To characterize mixing in the axial cross-section, the fraction of opposite volumetric flux, Q_b , to the net flux, Q , $G = |Q_b|/Q$ have been used. This is called the mixing coefficient or Werner coefficient (Szydlowski *et al.*, 1987), and has been used in one-dimensional model calculations as a simple evaluation index for distributive mixing. The Werner coefficient has also been used in three-dimensional calculations for twin-screw extruders (Ishikawa *et al.*, 2002). However, the magnitude of the strain rate is not considered in the mixing coefficient. To represent the mixing capability in a cross-section, a quantity based on the velocity gradient, $\nabla_{//} v_z \equiv (\mathbf{I} - \mathbf{e}_z \mathbf{e}_z) \cdot \nabla v_z$, must be considered, where $\mathbf{I}$ is the unit tensor, and $\mathbf{e}_z$ is the unit vector in the z -direction. Lawal and Kalyon (1995b) and Nakayama *et al.* (2011) have discussed mixing processes in the axial direction of a twin-screw extruder in relation to the temporal evolution of material distributions.

Another method to describe distributive mixing is to quantify the line-stretching ability of the velocity field. A naive method is to trace the time evolution of a distance between tracers (Funatsu *et al.*, 2002; Stone and Stone, 2005).

$$m(t) = \frac{1}{N} \sum_{i=1}^N \min_j d^2(x_i, s_j \in \text{Opp}(x_i)) \quad (6)$$

where m , N , $d(x_i, x_j)$, and $\text{Opp}(x_i)$ are the average squared distance between the closest tracers, the number of tracers, Cartesian distance between x_i and x_j , and the set of tracer positions other than x_i , respectively. This method does not represent the folding of line elements; therefore, it describes only the short-time process of mixing kinetics.

Line-stretching ability can be quantified by the Lyapunov exponent, λ , which measures the expansion rate of two nearby fluid elements as time evolves (Ottino, 1989; Funakoshi, 2008). The Lyapunov exponent is computed based on the velocity gradient, $\nabla \mathbf{v}$, and Lagrangian history. Lawal and Kalyon (1995a) calculated the Lyapunov exponent for single-screw and twin-screw extruders. Ishikawa *et al.* (2001, 2002) calculated

the area stretching rate in the melt-mixing zone of a twin-screw extruder. To find the Lyapunov exponent, time evolution of the line element is traced along the trajectory of a fluid element. Instead of computing the kinetics of the line element, the largest eigenvalue of the strain rate, λ_1 , was utilized to evaluate the line elongation ability of velocity field (Nakayama *et al.*, 2011).

Apart from the magnitude of the line-stretching ability characterized by the Lyapunov exponent, the efficiency of line-stretching in different flows by different mixers can be compared by using the mixing efficiency defined as

$$e_\lambda(\mathbf{x}, \mathbf{n}, t) = \frac{\mathbf{D} : \mathbf{n} \mathbf{n}}{\sqrt{\mathbf{D} : \mathbf{D}}} \quad (7)$$

where $\mathbf{n}$ is a direction vector in which the elongation is considered (Ottino, 1989). The mixing efficiency is the ratio of the stretching component of the strain rate, $\mathbf{D} = (\nabla \mathbf{v} + \nabla \mathbf{v}^T)/2$, in the $\mathbf{n}$ -direction to the magnitude of the strain rate. The Lagrangian average of the mixing efficiency can be used to distinguish flows with or without re-orientation (Ottino, 1989). The Lagrangian average of the mixing efficiency has also been used to quantify mixing in the pin-mixing section of a single-screw extruder (Yao *et al.*, 2001) and mixing in the melt-mixing zone of a twin-screw extruder (Connelly and Kokini, 2007; Zhang *et al.*, 2009).

6.2 Dispersive mixing index

Generally, high stress is required to miniaturize aggregated filler and/or droplets. Therefore, mixing equipment normally contains sections designed to produce high stress. The other sections generating low stress are designed to repeatedly send the fluid to the high-stress region. The stress or work history during the flow of a fluid element is utilized to evaluate dispersive mixing. Here, the dispersive mixing performance of the mixing equipment is evaluated by calculating the statistical distribution of the Lagrangian average of stress or work. Moreover, if the miniaturization mechanisms of a target including filler and droplets are well understood, the dispersion process of the target component can be predicted by combining the Lagrangian work history and miniaturization mechanisms.

Nakayama *et al.* (2011) used the second invariant of stress $s = \sqrt{\boldsymbol{\tau} : \boldsymbol{\tau}}$, the Lagrangian average of:

$$\overline{s_\alpha}^{T_\alpha} = \frac{1}{T_\alpha} \int_0^{T_\alpha} ds \int d\mathbf{x} \delta(\mathbf{x} - \mathbf{X}_\alpha(s)) s(\mathbf{x}, s) \quad (8)$$

to evaluate dispersive mixing performance of the pitched-tip kneading disks in a twin-screw extruder. Here, T_α and $\mathbf{X}_\alpha(t)$ are the residence time and trajectory of the α th tracer, respectively. Kajiware *et al.* (2006) used a Lagrangian average of some unknown quantify from the stress tensor to evaluate the dispersive mixing performance of multiclearance kneading disks and a grooved barrel in a twin-screw extruder.

The miniaturization of aggregated filler and droplets requires high stress, and the stress needed for miniaturization depends on the flow type. If the flow regime deviates from simple shear flow, the stress required for droplet breakup is significantly reduced (Grace, 1982; Bentley and Leal, 1986). The dispersion efficiency is the highest when the flow is simple elongational flow. Several indices for flow type have been proposed to evaluate the efficiency of dispersion mixing. Deviation of the flow type from simple shear flow has two effects: a reduction in the vorticity component and an increase in the elongation component. The fraction of the vorticity component in the strain rate can be utilized to describe the flow type indirectly. Along this line, two quantities are proposed such as the flow strength parameters (Larson, 1985)

$$S_f = \frac{2(\mathbf{D} : \mathbf{D})^2}{\mathbf{D} : \mathbf{D}} \quad (9)$$

where $(\cdot)$ represents the steady-state corotational derivative, and the flow number (Yang and Manas-Zloczower, 1992)

$$\lambda_{MZ} = \frac{\sqrt{\mathbf{D} : \mathbf{D}}}{\sqrt{\mathbf{D} : \mathbf{D}} + \sqrt{\mathbf{\Omega} : \mathbf{\Omega}^T}} \quad (10)$$

S_f is zero when the flow is purely rotational, unity when it is simple shear flow, and ∞ when there is no rotation (elongation flow). λ_{MZ} is zero when the flow is purely rotational, 1/2 when it is simple shear flow, and unity when there is no rotation (elongation flow). λ_{MZ} has been calculated for the shearing disks of a twin-screw extruder (Li and Manas-Zloczower, 1994), a twin-rotor mixer (Yao and Manas-Zloczower, 1998), the conveying element of a twin-screw extruder (Cheng and Manas-Zloczower, 1998), and the kneading disks of a twin-screw extruder (Cheng and Manas-Zloczower, 1997).

Nakayama *et al.* (2011) derived a strain-rate type identifier

$$f_D(\mathbf{x}, t) = \frac{\max_{n, |n|=1} \mathbf{D} : \mathbf{n}\mathbf{n}}{\sqrt{\mathbf{D} : \mathbf{D}}} \quad (11)$$

which uses the invariant of the strain-rate tensor instead of using the vorticity tensor to determine the flow regime. Although λ_{MZ} and S_f cannot differentiate between uniaxial elongational flow and bi-axial elongational flow, f_D can. f_D is used in dispersive mixing evaluation for pitched-tip kneading disks in a twin-screw extruder (Nakayama *et al.*, 2011).

7. Perspectives

In general, the characterization of a mixing process requires study of the overall flow field in space and time. High-stress and high-strain-rate regions themselves are important, but more important matters are their distribution in the flow field in mixing equipment. Low-stress

regions in the mixing equipment are also important since the fillers and/or droplets are transported by the flow of low-stress regions. Analyzing the overall flow pattern is essential in the evaluation of a mixing process. Therefore, local or point-wise observation has its own limitation in the study of mixing processes.

Although numerical simulations solve a model system of a mixing process, they provide us overall information on the flow pattern in space and time. Qualifying a mixing process by the numerical simulation is becoming more important and indispensable. However, it is still difficult to compress volumes of data from the numerical simulations into a small number of qualifiers on a mixing process. At this point, this approach is still far from being a standard in the handling of data in the chemical engineering community. A dynamical system approach is fundamental in analyzing mixing processes, in which the Lyapunov exponent as an invariant of a process and statistics of Lagrangian-history quantities are the basic tools. To extract relevant information from the volumes of data from numerical simulations, more applications of qualifiers based on the dynamical system approach are required.

In addition to the data from numerical simulations, direct measurement and visualization of an experimental mixing process should prove to be more important. Although experiments with actual equipment and target materials under the target conditions is desired, it can hardly extract information on the whole flow pattern and mixture states. Alternative options would be local samplings from the actual process, model experiments under mild conditions, and designing experiments with common characteristics of actual equipment, which would make the visualization of the flow pattern and mixture state possible. A primary concern in experimental observation is the relationship between a mixing process and mixture state. Combining numerical simulations and experimental observation with the above theoretical viewpoints should lead to systematic understanding of this relationship and underlying melt-mixing mechanism.

Concluding Remarks

The evaluation of melt-mixing efficiency has been discussed. Although the theories presented herein capture the essential phenomena, many unknown factors remain regarding the details of the melt mixing mechanism. A systematic study is crucial for the optimization of equipment design. Even at this point, various problems at the production level may be mostly solved by consideration of the phenomena from both experimental and computational viewpoints. Based on the achievements to date, further development of mixing theory and its systematization in the future will prove to be highly desirable.

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Nomenclature

Ca	= capillary number of a droplet	[—]
c	= concentration field	[1/m ³]
$\bar{c}$	= average of concentration field	[1/m ³]
$c_{\max}$	= maximum concentration	[1/m ³]
$\mathbf{D}$	= strain-rate tensor	[1/s]
$d(\mathbf{x}_i, \mathbf{x}_j)$	= Cartesian distance between $\mathbf{x}_i$ and $\mathbf{x}_j$	[m]
$\mathbf{e}_z$	= unit vector in z-direction	[—]
e_λ	= mixing efficiency	[—]
f_D	= strain-rate type identifier	[—]
G	= mixing coefficient of Werner coefficient	[—]
$\mathbf{I}$	= unit tensor [—]	
IoS	= intensity of segregation	[—]
m	= average square distance of nearby tracers	[m ²]
N	= number of point tracer	[—]
$\mathbf{n}$	= director vector	[—]
Opp($\mathbf{x}_i$)	= set of all points except $\mathbf{x}_i$	[m]
Q_b	= backward volumetric flow rate	[m ³ /s]
Q	= net volumetric flow rate	[m ³ /s]
$R(r, t)$	= correlation coefficient of concentration fluctuation	[—]
S_f	= flow strength parameter	[—]
SoS	= integral scale of segregation	[—]
T_α	= residence time of α th tracer	[s]
V	= volume of the system	[m ³]
$\mathbf{v}$	= velocity	[m ³ /s]
v_z	= z-component of velocity	[m/s]
$\mathbf{X}_\alpha$	= position of α th tracer	[m]
$\dot{\gamma}$	= strain rate	[1/s]
η_D	= shear viscosity of a droplet	[Pa · s]
η_M	= shear viscosity of a matrix	[Pa · s]
λ	= Lyapunov exponent	[1/s]
λ_{MZ}	= flow number	[—]
λ_1	= maximum strain rate of $\mathbf{D}$	[1/s]
ρ	= curvature of a droplet	[m]
σ	= interfacial tension	[Pa · m]
σ^2	= variance of concentration fluctuation	[1/m ⁶]
$\sigma_{\max}^2$	= maximum possible variance of concentration fluctuation	[1/m ⁶]
$\boldsymbol{\tau}$	= deviatoric stress tensor	[Pa]
Φ	= specific contact area	[1/m]

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