ANALYSIS OF MIXING IN POLYMER PROCESSING EQUIPMENT

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Mixing is a key step in almost every polymer processing operation, affecting material properties, processability and cost. Polymers are blended with other polymers to combine their properties and sometimes to even synergistically increase their physical characteristics. Various additives and reinforcing agents are mixed with polymers to improve mechanical performance and impart specific properties to the mixture. The need for developing new materials with improved properties seems to rely nowadays more on blending and compounding than on the synthesis of chemically new polymers. Therefore the importance of a more fundamental understanding of the mixing process and its dynamics is clearly undeniable.

Modeling the mixing process in real mixing equipment through flow simulations is not an easy task. Major obstacles include, but are not limited to, the very complex geometry of the mixing equipment, the time dependent flow boundaries and the difficulties involved in selecting the appropriate "indexes" to quantify the mixing process. Yet modeling offers a means for understanding, designing and controlling the mixing process.

Key to a fundamental understanding of the mixing process and its optimization is the clear distinction between "dispersive" and "non dispersive" mixing mechanisms and identification of the important process characteristics enhancing realization of these mechanisms. In a multiphase system, dispersive mixing involves the reduction in size of a cohesive minor component such as clusters of solid particles or droplets of a liquid. Distributive mixing is the process of spreading the minor component throughout the matrix in order to obtain a good spatial distribution. In any mixing device, these two mechanisms may occur simultaneously or stepwise. Figure 1 depicts schematically these two mixing mechanisms.

The conditions under which dispersive mixing occurs are determined by the balance between the cohesive forces holding agglomerates or droplets together and the disruptive hydrodynamic forces. Quantitative studies of droplet breakup in simple shear and pure elongational flows [2-7] have shown that elongational flows are more effective than simple shear flows, especially in the case of high viscosity ratios and low interfacial tensions. Also, the magnitude of the applied stresses plays a decisive role in determining droplet size distribution. These studies have been supported by the experimental results reported by Powell and Mason [8] and the theoretical calculations of Manas-Zloczower and Feke [9] who point out that elongational flows enhance the process of agglomerate dispersion by comparison with simple shear flows. In mixing equipment, the complex flow geometry generates field patterns which represent a superposition of flows ranging from pure rotation to pure elongation. Thus, assessing dispersive mixing efficiency in mixing equipment in terms of elongational flow components as well as stress distributions seems appropriate.

Distributions of stress and elongational flow give only a global perspective on mixing efficiency in various types of equipment. A more accurate prediction of mixing efficiency would involve tracking the elements of the minor phase (droplets or agglomerates) during their entire residence time in the equipment and following the dynamics of their breakup / coalescence. Such an approach, if achievable, would be prohibitively expensive in terms of computing time and memory. However, the global approach of characterizing mixing efficiency provides one a means to discriminate between various designs and processing conditions for mixing equipment,

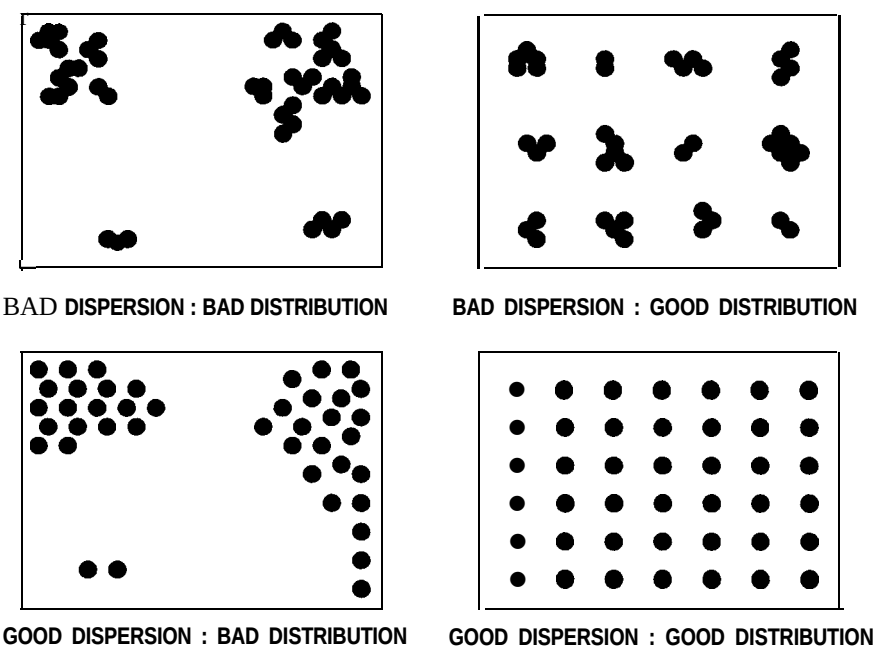

Figure 1 Schematic illustration of dispersive and distributive mixing mechanisms.

Besides its intrinsic limitations, this global approach poses additional problems. As mentioned previously, in most of the existing mixing equipment we face the problem of time-dependent flow boundaries. Take as an example the kneading discs in a corotating twin screw extruder. As the discs rotate, the overall geometry of the flow field changes. A simplified approach to solve for this problem is to select a number of sequential geometries / snapshots for a complete mixing cycle and solve the flow problem in each geometry [10,111. For polymer processing operations involving laminar flow of highly viscous materials, the overall effect caused by a changing geometry can be analyzed from the results obtained separately in selected sequential geometries. One can then proceed by solving the field equations for each sequential geometry. Shear stress distributions can be obtained for all sequential geometries and subsequently analyzed.

Another important characteristic of the flow field, relevant for dispersive mixing efficiency is the flow "strength". Steady flows can be classified according to the frame invariant concept of flow strength [12,13] in terms of the flow strength parameter, S_f, is defined as:

$$S_f = 2\frac{(tr\underline{D}^2)^2}{tr\mathring{\underline{D}}^2} \qquad (1)$$

where $\underline{D}$ is the rate of deformation tensor and $\mathring{\underline{D}}$ is the Jaumann time derivative of $\underline{D}$ (i.e. the time derivative of $\underline{D}$ with respect to a frame that rotates with the angular velocity of the fluid element). The flow strength parameter ranges from zero for pure rotational flow to infinity for pure elongational flow; its value is unity for simple shear flow. Determining the numerical value of this parameter requires second derivatives of the velocities. When using the finite element method in flow simulations, high density mesh designs are required in order to minimize the numerical error. This requirement is sometimes impeded by computational limitations, especially when considering processing equipment of very complex geometries.

A different way to quantify the flow strength is by considering the relative magnitude of the rate of deformation and vorticity tensors. A parameter λ can be defined as:

$$\lambda = \frac{|D|}{|D| + |\omega|} \qquad (2)$$

where $|D|$ and $|\omega|$ are the magnitudes of the rate of strain and vorticity tensors respectively. The above parameter assumes values between 0 for pure rotation and 1 for pure elongation, with a value of 0.5 for simple shear. Although not frame invariant, it can be used as a first approximation to discriminate between various equipment designs and processing conditions in terms of their dispersive mixing efficiency [14,151.

Aside from breaking clusters of fine particles or droplets of an immiscible fluid, the aim of any mixing operation is to reduce system nonuniformity. This is accomplished by a repeated rearrangement of the minor component into the major one. In this case, the mechanism of mixing is distributive.

In order to study distributive mixing, one has to track the position of the minor component elements (fluid elements or solid particles) at each instant of the process. This is not an easy task and is usually achieved only by introducing simplifying assumptions. In most cases the minor component elements are assumed to be massless points, such that their presence does not affect the flow field of the otherwise pure matrix. Furthermore, interactions among particles, such as Van der Waals attraction force, friction, and droplet coalescence are ignored. With these simplifications, the location of minor component elements can be found by tracking their motion in the mixing region, provided that their initial position is known. Figure 2 is an illustration of one particle trajectory in a single screw extruder. Due to computational limitations, usually only several thousand particles can be tracked simultaneously during their motion in the equipment.

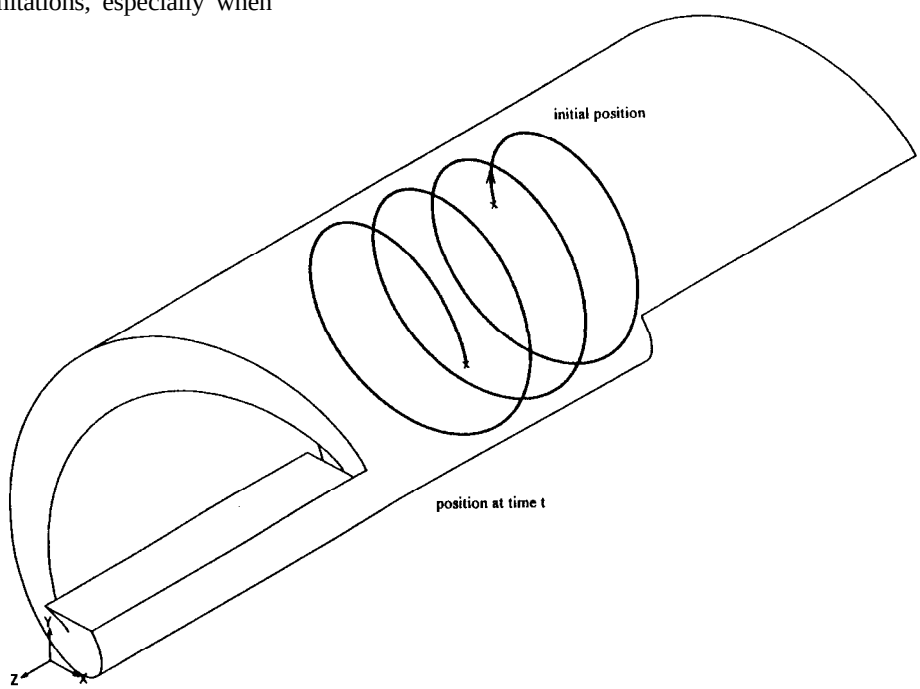

Figure 2 Particle trajectory in a single screw extruder.

In order to facilitate a quantitative analysis of the distributive mixing process, one needs to develop a framework which can provide the means to differentiate among various equipment designs or processing conditions. One index, frequently used for the characterization of distributive mixing efficiency, is the length stretch (distribution and average value) [16]. The length stretch l is defined as the ratio of the distance between two particles at any time t to the initial value of the distance between the same particles [17]:

$$l = \frac{|\underline{X}|}{|\underline{X}_0|} \tag{3}$$

where $|\underline{X}_0|$ is the magnitude of the vector defining the initial locations of two neighboring and distinct particles and $|\underline{X}|$ defines their locations at time t. For a system with N particles, the length stretch distribution $g(l,t)$ can be calculated from:

$$g(\ell,t) = \frac{2M(l,t)}{\Delta l N(N-1)} \tag{4}$$

where $M(l,t)$ is the total number of pairs of particles with a length stretch ranging from (l - A $l/2$) to (l + A f/2) at time t.

Using the length stretch distribution, the average length stretch $\bar{l}$ at any time can be obtained through the following relation:

$$\bar{\ell}(t) = \int_{(l=0)}^{(l=\infty)} l g(l,t)\, dt \tag{5}$$

Time evolution of length stretch distributions and average values can provide a quantitative measure of analysis for distributive mixing efficiency.

Another way of looking at the overall distribution of the minor component in the mixing region (usually in batch type mixing equipment) is by following the dynamics of pairwise correlation functions [18,19]. For a more local analysis of mixing in batch systems, one can search for regions of the mixer void of any minor component elements. Such regions are called islands and they represent an obstacle to efficient mixing [18].

The different indexes of distributive mixing, namely length stretch distributions, pairwise correlation functions or volume fraction of islands provide an objective framework to quantify distributive mixing and to discriminate between various operating conditions and / or various mixer designs. Distributive mixing is related to randomization of a minor component throughout the system and therefore chaotic features of flow will enhance the process. Ottino and coworkers [20-23] have presented the most systematic approach to the modeling of distributive mixing by combining the kinematical foundations of fluid mechanics with chaotic dynamics.

In polymer processing equipment, the origin of chaos is related to complicated, time-dependent flow geometry. In chaotic systems there is a rapid divergence of initial conditions

One way to quantify the divergence of initial conditions is by means of Lyapunov exponents. Positive values for the Lyapunov exponents indicate a more rapid divergence of the initial positions leading to better distributive mixing.

Simulating the mixing process in mixing equipment relies on the predictions of flow simulations. The computational schemes employed in most of the flow analyses in polymer processing are based on finite difference, finite element and boundary element methods. The purpose of these methods is to reduce the partial differential equations for the variables to a set of simultaneous equations for nodal variables at fixed points.

Most of the published literature on complex 3-D flow simulations in polymer processing equipment is based on either the Newtonian fluid or, at the next level of complexity, on the Generalized Newtonian Fluid model. Constitutive equations describing viscoelastic flow phnomena are generally numerically insoluble in multidimensional flows. One source of difficulty may arise from the singularity displayed in many of these constitutive equations when stress is plotted versus the rate of strain.

Larson [13] proposed constitutive equations for materials with a broad distribution of relaxation times using a power-law relaxation modulus. Such equations, although rigorously valid only for special flows (e.g. flows of constant stretch history) may represent a first step to a numerically tractable approximation of viscoelastic flows in complex flow geometries.

With today's rapid advancement in computer technology, there is hope of solving fluid-flow problems involving complex fluids in complex geometries. However, challenges still remain in selecting constitutive equations which describe material flow behavior realistically, yet are tractable in numerical solutions and in the interpretation of flow simulation results in tersms of process efficiency.

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