

Chapter 4. Mixtures and Mixing (Tadmor Chapter 7)

Tadmor, Chapter 7 deals with the basic approaches to the description and understanding of mixing in continuous and batch processes. Many of these ideas are critical to design and use of polymer and chemical process equipment and the purpose is to make you familiar with the terminology and approaches which are commonly used. These include statistical descriptions of mixing, and various distribution functions which are used to calculate average features from a process. Of particular importance are strain distribution functions (**SDF**) and residence time distribution functions (**RTD**).

Mixing is often the critical step of polymer processing and is the least understood. Consider an extruder as a model. Mixing of pellets involves solid/solid distributive mixing in the early stages of extrusion or in a mechanical mixer such as a V-mixer. This might involve mixing of a color concentrate or foaming agent concentrate. If filler is mixed such as carbon black, silica or titania mixing proceeds to Solid/Liquid mixing in the extruder barrel. Mixing of two immiscible polymers in an extruder is common (LDPE and LLDPE) which occurs mostly in the high shear parts down stream in the extruder. Mixing also can occur in down stream parts such as in a calander or film blowing apparatus.

Basic Ideas:

For low-viscosity liquids mixing is commonly by molecular diffusion or eddy diffusion such as milk in coffee. For high viscosity liquids mixing is by convection (bulk diffusion). There are two types of mixing which can occur in such high viscosity systems: (**FIGURE 7.1 pp. 199**)

- 1) Increase in Surface Area usually caused by shear. This is what happens in laminar flow mixing in an extruder. This is typically an ordered rearrangement. Since surface area is related to strain, the strain distribution function is needed which is related to the residence time distribution function. (**FIGURE 7.2 pp. 200**)
- 2) Distributive mixing: Randomization of Particle distribution. This is what happened in the Brabender mixer lab. This is common for solid/liquid mixing.

For 1) the strain needs to be calculated from the residence time and the strain rate. The viscosity's of the two phases being mixed are important parameters. For mixing of a solid and a liquid the yield stress for the particle to break-up is important.

We can distinguish between *Intensive* mixing where domains or particles break-up and *Extensive* Mixing due to convective flow.

Either of these can be Distributive (rearrangement of parts) or Laminar, increase of surface area as occurs in shear stretching or squeezing of a fluid.

Parameterization of a Mixing Process.

The first question is to consider what "goodness of mixing" means in a quantitative way.

To do this you need to consider the sample concentration of minor components at "points" in the mixture.

The phrase "Concentration at a point" involves defining what a "point" is. Continuum mechanics defines a point as a very small volume from a macroscopic sense which can be described using thermodynamic properties, i.e. a point contains many particles, and can be describe with thermodynamic parameters, T,P,

velocity, concentration etc., i.e. can be describe with bulk properties so is **not** an atom.

In the absence of molecular diffusion and eddy diffusion each point is a pure phase, e.g. Carbon black or polymer. For a larger volume of a "point you need to define a concentration, i.e. a point is larger than a single ultimate particle

Because of these issues involved in describing what a "point" is for quantitative descriptions of mixing, you should consider materials in terms of the scale of observation. Ultimately, the size and description of a "point" depends on the application you are interested in.

Gross Uniformity: Average concentration for whole sample and the randomness of the samples, e.g. the percent blue in a blue shopping bag. For Gross uniformity the scale of observation is very large compared to the domains being mixed, "r" is big. Typically Gross uniformity is judged at the size scale of the article being produced, i.e. the shopping bag.

Texture: Correlations between domains, e.g. streaks in the shopping bag. Typically "r" for Texture is smaller than "r" for Gross Uniformity.

Scale of Segregation:

The scale of segregation is the size scale of the domains. (Texture can be a larger size scale but not a smaller size scale.) The Scale of Segregation can be described by a correlation function, $p(r)$, for the domains. ($p(\mathbf{r})$ can be a vector as in the case of streaks in a shopping bag.) Typically you desire the scale of segregation to be smaller than some specific value for a given product. Usually, the scale of segregation is larger than the ultimate particle size, r^* .

Pairwise correlation functions for mixing:

Tadmor discusses the "needle method" for calculation of $p_c(\mathbf{r})$. (This is identical to the calculation of a correlation function for diffraction or scattering.) Throw needles (of length "r") in a material at random, $p(r)$ is the probability that a needle will have both ends in a minor phase, i.e. in the domains. This process is repeated for needles of different sizes "r" to construct $p(r)$ as a continuous function.

At large distances, "r" the probability is just the square of the concentration. At smaller distances the probability becomes larger due to preferred distances of separation. Since $p(r)$ is an arbitrary function, it is often described as a power-series of indeterminate length:

$$p(r) = A + Br + Cr^2 + D r^3 + \dots$$

The first term, A reflects the gross uniformity, and the concentration of the minor phase. (Volume)

The second term, $B = dp(r)/dr$ reflects the Surface Area.

The third term, $C = d^2p(r)/dr^2$ reflects the shape of the domains

The higher order terms can also be described in a structural approach.

How good is a mixture Mixed?

In considering how well mixed a mixture is we are immediately confronted with the *definition of a random mixture*. This is a question which can only be quantitatively answered using statistics.

Mixing attempts to make a **random mixture**. We should be careful to consider the features of a random mixture. First, a random mixture contains some clusters. That is, a highly dispersed mixture such as a suspension of charged particles which repel each other is not random. Your first inclination to draw a "random" mixture is to draw dots separated from each other. Consider how this drawing would compare with a drawing made by randomly drawing dots on a sheet of paper, i.e. with your eyes closed and the paper moving randomly about the table. *In this sense it is possible to make a mixture which is more dispersed than random!*

A random mixture is defined by the **binomial** distribution. The binomial distribution describes a system composed of a lattice of N boxes which contain two distinguishable components, i.e. x's and o's. Consider the x's to be the minor components. $N = N_x + N_o$, and p , the volume fraction of minor components is $p = N_x/N$. (p reflects how much of the x component you have added to your Branbury mixer for instance.)

We consider a subset of this system composed of n boxes. "**n**" is the size of **observation** and the size of a box is the size of a base unit of the system which can not be broken down further. The binomial distribution gives the probability of finding **k boxes filled with x's** in a system of n boxes with a bulk volume fraction p , **$b(k; n, p)$** :

$$b(k; n, p) = \frac{n!}{k!(n-k)!} p^k (1-p)^{n-k}$$

p^k is the probability for k boxes to have x's and $(1-p)^{n-k}$ is the probability for the remaining boxes to have o's. This situation can be constructed $n!$ ways so this probability must be multiplied by the number of ways it can happen. Some of these ways can not be distinguished from each other since moving one x to replace another leads to an arrangement which can not be distinguished from the original. There are $k!(n-k)!$ of these indistinguishable duplicates so this number must be used to reduce the overall probability.

The mean number of x's in a sample of n boxes for a binomial distribution is obtained by summing k times the probability b given above for all k 's from 0 to n . This yields

$$\bar{k} = np$$

as might be expected.

The variance, σ^2 , for the binomial distribution reflects the average deviation from the mean for the distribution and is obtained by summing $(k - \bar{k})^2$ times the probability b for k , which yields:

$$\sigma^2 = np(1-p)$$

The standard deviation is the square-root of this.

Several other distribution functions are spin-offs from the binomial for certain conditions.

Poisson distribution: Very low probability for an x appearing (radio-active decay) $p \ll 1$, $\bar{k} \ll n$.

$$P(k, \bar{k}) = \frac{\bar{k}^k}{k!} e^{-\bar{k}}; \quad \sigma = \sqrt{\bar{k}}$$

This is the distribution used for an intensity counting system where counts are recorded and the error is the square-root of the number of counts.

The **Gaussian** distribution is the binomial for number of observations n is infinite and the probability is finite so np >> 1. This is good for random systems with a large number of samples like a large class grade distribution plot or the conformation of a polymer coil. Here:

$$G(k, \bar{k}) = \frac{1}{\sqrt{2\pi}} \exp \left[-\frac{1}{2} \frac{(k - \bar{k})^2}{\bar{k}} \right]$$

Here we will only use the Binomial distribution but it is useful to consider the other 2 distributions which are closely related to it.

Mixing Index, M

The mixing index, M, is calculated from the sample variance observed (for a sample size n) and the binomial variance,

$$M = \frac{S^2}{\bar{k}}$$

For a "random system" as defined by the binomial distribution, M = 1. For a completely unmixed system, M = n. It is possible for M to be less than 1 as discussed above.

Other statistical methods for describing the goodness of mixing such as the t-test are also available and you should refer to pp. 208 table 7-1.

Scale of Segregation:

The mixing index, M depends on the sample size, n in a part of size N. This means that there is some size-scale at which we can consider a sample is segregated, s.

This **Scale of Segregation**, s, can be directly obtained from the samples correlation function, R(r), by integration,

$$s = \int_0^{\infty} R(r) dr$$

where s is a size scale beyond which there is no correlation of domains (it is mixed beyond this size scale), i.e. R(r >= s) = 0

R(r) can be calculated from observation of the sample,

$$R(r) = \frac{\sum_{i=1}^N (x'_i - \bar{x})(x''_i - \bar{x})}{NS^2}$$

R(r) goes from -1 to 1, -1 is desegregated, 1

is totally segregated, 0 is no correlation (random).

$$S^2 = \frac{\sum_{i=1}^N (x_i - \bar{x})^2}{2N - 1}$$

Coefficient of Correlation for an arbitrary 2-phase system:

$R(r) = \frac{1}{2} \left(\frac{r-1}{L_1} + \frac{r-1}{L_2} - \frac{r-1}{L_1+L_2} \right)$ where $\frac{1}{2}$ is the probability of a rod falling with both ends in the "1" phase and $\frac{1}{2}$ is the volume fraction of phase 1.

Consider a striped texture such as might occur in an extruded sheet. Consider correlations perpendicular to the stripes as in figure 7.10. In problem 7.6 you will derive the coefficient of correlation from the volume fraction rule above,

$$R(r) = 1 - r \frac{L_1 + L_2}{L_1 L_2}$$

which is a straight line which crosses $R(r) = 0$ at $r = L_1 L_2 / (L_1 + L_2) = L/2$, where L is the harmonic mean of the two phase sizes.

since $R(r)$ goes to 0 at $L/2$, the integral for the scale of segregation, s , goes from $r=0$ to $L/2$, and $s = L/4$.

For this striped texture, if $L_1 = L_2 = L$ then $s = L/4$
If $L_1 \ll L_2$,

The scale of segregation may depend on the range over which the integral of the coefficient of correlation is taken reflecting different frequencies of segregation as shown in figures 7.11 and 7.12 on pp. 214.

Intensity of Segregation:

The scale of segregation only reflects the size of segregation and does not comment on the intensity of segregation as shown in figure 7.7 on pp. 209.

The Intensity of segregation similarly, has not association with size and only reflects the concentration difference between "Phases".

$$I = S^2 / \bar{x}^2,$$

For a simple 2-phase system,

$\bar{x} = x_1 v_1 + x_2 v_2$, where v is the volume fraction and x is the composition.

$$S^2 = v_1 (x_1 - \bar{x})^2 + v_2 (x_2 - \bar{x})^2$$

using v_1 for p : $v_2 = v_1(1 - v_1) = v_1 v_2$
and

$$I = S^2 / \bar{x}^2 = (x_1 - x_2)^2$$

Mixing Processes and Their Relationship to a Statistical Analysis:

For the stripe texture analyzed above we have determined that:

$$s = L/4$$

where s is the scale of segregation and L is the harmonic mean of the layers L_1 and L_2 .

For thin stripes this reduces to

$$s = L_1/2$$

where L_1 is the stripe thickness.

The stripe thickness is given by the total volume divided by half of the interfacial area:

$$L_1 = V/\{A/2\}$$

This shows that the scale of segregation, at least for this simple case, is directly proportional to $1/A$ where A is the interfacial area of the two phases.

For Laminar Mixing Tadmor shows through a tensor analysis that the interfacial areas for two mixing phases is proportional to the cumulative strain which has been applied to the sample, equation 7.9-16 on page 219.

This is convenient since we have measures of strain rate using constitutive equations for many flow situations.

Strain Distribution Functions:

In most processing situations the cumulative strain applied to the sample is not single valued. (This should be clear from the extruder lab where we measured the limiting residence times for the extruder.) This means that strain in processed samples will be described by continuous functions which relate to the amount of material from a process which has been exposed to a certain value of strain, $g(\epsilon)$.

BATCH MIXERS

For batch mixers all fluid elements are considered to have experienced the same residence time in the mixer. This means that the residence time distribution is single valued.

$g(\gamma) d\gamma$ is the fraction of the liquid in a mixer which has experienced a shear strain from γ to $\gamma + d\gamma$.

Often it is of interest to know how much fluid has experienced a strain of less than some value γ . For example when a certain value of γ is associated with a critical strain for mixing to be achieved or for a certain scale of segregation to be observed. $G(\gamma)$ is defined in this way,

$$G(\gamma) = \int_0^{\gamma} g(\gamma) d\gamma$$

The mean strain from a batch mixer is given by:

$$\bar{\gamma} = \int_0^{\gamma_{\max}} \gamma g(\gamma) d\gamma$$

CONTINUOUS MIXERS

For continuous mixers fluid elements are subjected to different strain rates and to different residence times due to the velocity distribution. A new function, $f(\gamma) d\gamma$ is defined which reflects the fraction of exiting flow rate that experiences a strain from γ to $\gamma + d\gamma$. Similarly, a cumulative strain distribution function can be defined in terms of exiting flow rate,

$$F(\gamma) = \int_0^{\gamma} f(\gamma) d\gamma$$

The mean strain from a continuous mixer (extruder) is given by:

$$\bar{\gamma} = \int_0^{\gamma_{\max}} \gamma f(\gamma) d\gamma$$

Residence Time Distribution

Similar to the strain distribution functions we can describe residence time distribution functions which are convenient terms for calculation of strain distributions and mixing statistics.

We can consider the volume fraction of fluid in the processing machine in terms of the internal RTD, $g(t) dt$, or in terms of the exiting stream function as with SDF's, $f(t) dt$. Both have cumulative functions $G(t)$ and $F(t)$. Similarly, a mean residence time can be calculated as the mean strain was calculated. Tadmor relates all of the RTD functions in a table on pp. 230.

Examples of Calculation of Strain and Residence Time Distribution Functions and Their Use.

Consider the SDF for a batch mixer consisting of three concentric cylindrical chambers as in Example 7.5, of radius R_1 , R and R_2 .

The middle cylinder rotates at v_0 , while the inner and outer cylinders remain stationary. Consider the total strain at some time "t" when the batch mixer is dumped.

If you ignore curvature effects, the two regions are parallel plate laminar flow regions. The rate of strain is constant across both gaps and the strain in zone 1 (inner gap), $\epsilon_1(t)$ is given by:

$$\epsilon_1(t) = \frac{v_0 t}{x(R_2 - R_1)}$$

where x is R_1/R_2 and $v_0 t$ is $V_0 t/R_2$. ϵ is the distance traveled normalized by R_2 and x is the normalized ratio of radii for the inner and outer cylinder. x is the normalized distance from the middle, $x = (R - R_1)/(R_2 - R_1)$.

The rate of strain in the outer gap is:

$$\epsilon_2(t) = \frac{v_0 t}{(1 - x)(R_2 - R_1)}$$

The fraction of the two zones is given by ratios of the unitless numbers:

$$f_1 = \frac{x^2 + x(2 - x)}{1 + x}$$

$$f_2 = 1 - f_1$$

$$G(\epsilon) = f_1 G_1(\epsilon) + f_2 G_2(\epsilon)$$

a plot of $g(\epsilon)$ versus ϵ will have two spikes at the two strains, and a plot of $G(\epsilon)$ versus ϵ will have two steps as shown on pp. 224.

Continuous Mixer: Parallel Plate Flow, Example 7.6

Figure 7.17 shows this continuous mixer. Strain is accumulated between $x=0$ and $x=L$ where L is the length of the mixer. Residence time varies across the gap with the lowest residence time near the moving plate and the longest at the fixed plate. We assume a linear velocity distribution, $v_x = yV_0/H$ where H is the gap distance and V_0 is the top plate velocity.

We need to consider the amount of flow, q , for volume elements of different strain. The total flow is $q=V_0H/2$. The fractional flow between y and $y+dy$ is:

$$f(y)dy = \frac{dq}{q} = \frac{2ydy}{H^2}$$

The cumulative distribution of flow is the integral of this from y to H :

$$F(y) = \int_y^H f(y)dy = 1 - \frac{y^2}{H^2}$$

The shear rate is V_0/H , the residence time at L is $t = L/v_x(y) = HL/(V_0y)$, the shear strain is the time times the rate of strain at y , or $\gamma(y) = L/y$. The minimum strain is at $y=H$, $\gamma_{\min} = L/H$.

The conversion from y to γ can be used to convert f and F to SDF's:

$$F(\gamma) = 1 - (L/(H\gamma))^2$$

$$f(\gamma)d\gamma = 2L^2d\gamma / (H^2\gamma^3)$$

The mean strain is $2L/H$ by integration of these functions in terms of y from 0 to H .

The Mean strain is proportional to the L/H ratio