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Principles of Mixing Measurement

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1 INTRODUCTION

Mixing is such a common operation that newcomers to the field often wonder why mixing is so hard to measure. We all have an intuitive understanding of the difference between good mixing and bad mixing, but in practice it is quite difficult to assign numbers to the quality of mixing and even more difficult to understand what those numbers mean.

To get a better understanding of the problem, look at the mixture patterns in Figures 1 and 2 and then consider these questions:

1. Which is the best mixture?
2. Is there more interfacial surface area in Figure 2a or b?
3. How much mixing would be required to make Figure 2a as well mixed as Figure 1?
4. Suppose Figure 1 is a micrograph of a mixture of two different color polymers at a magnification of $\times 1000$. Is it well enough mixed to use on the dashboard of an automobile?

The goal of this chapter is to provide tools for answering these types of questions for polymer mixing operations. It will be necessary to define exactly what is the quality of mixing. This is because it is often easy to come up with a number related to the quality of mixing but difficult to

know what that number means. Also, there are several different definitions of quality of mixing, each subject to certain measurement techniques. To understand the measurements one must know what the definitions mean, when they may be applied, and what their limitations are.

2 DEFINING QUALITY OF MIXING

2.1 Mixtures, Mixing, and Composition in a Point

A *mixture* is simply a combination of two or more substances, and *mixing* is an operation whose purpose is to increase the spatial homogeneity of a mixture. Implicit in these definitions is the idea that any mixture can be examined on a fine enough scale to see the two different components. These may be visible to the naked eye in a coarse mixture, but a powerful

Figure 1 Mixture section similar to those observed in single-screw extruders.

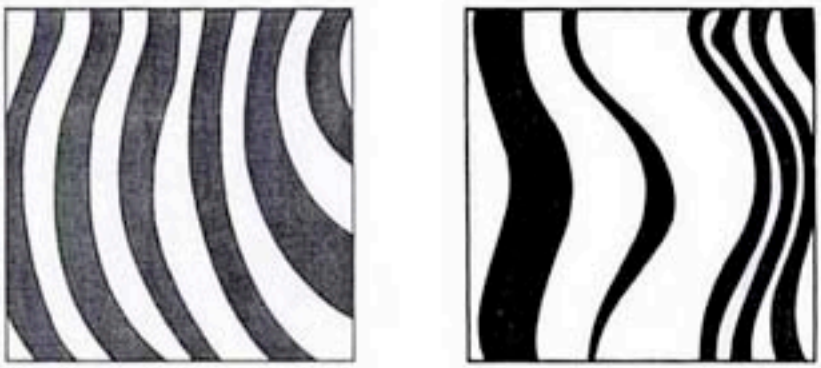

Figure 2 Sections of layered mixtures with (a) uniform striation thickness, and (b) wide distribution of striation thickness.

microscope may be required to see them in a fine mixture. However, for all mixtures there is some level at which segregation of the components of the mixture is visible.

In the best of mixtures, segregation of the components may exist only on the atomic or molecular scale. For example, the sodium and chlorine ions in a salt crystal are mixed on this scale. However, we deal here only with mixtures on a continuum scale. That is, we look at mixtures on a scale fine enough to see the differences in composition from point to point, but never on such a small scale that we see individual molecules.

This makes it possible to talk about "composition at a point" in a mixture, in the same sense as one talks of temperature at a point in heat transfer or stress at a point in mechanics. *Composition* measures the relative amount of one component present at that point in the mixture.

To see how we treat composition, consider the following analogy between a black-and-white photograph and a mixture. The photograph is actually made up of extremely small black dots on a white background (analogous to the molecules in our mixture), but we can look with our eyes at any spot of the photograph and assign a value to the gray level (analogous to the composition at that point). A value of zero would mean all white, a value of one would mean all black, and values between them would represent different shades of gray.

We consider only mixtures that have two components. Call the two components of the mixture A and B. The local concentrations of A and B are called a and b, so at some point located at $\mathbf{x}$, the composition is described by $a(\mathbf{x})$ and $b(\mathbf{x})$. (The bold type $\mathbf{x}$ denotes a vector quantity.) A value of $a(\mathbf{x}) = 1$ means that only A is present; a value of $b(\mathbf{x}) = 1$ means that only B is present. Obviously at every point we have

$$a(\mathbf{x}) + b(\mathbf{x}) = 1 \tag{1}$$

so that either $a(\mathbf{x})$ or $b(\mathbf{x})$ tells us the composition of the mixture at point $\mathbf{x}$.

The values of $a(\mathbf{x})$ and $b(\mathbf{x})$ averaged over all points in the mixture are called $\bar{a}$ and $\bar{b}$. Clearly they must also follow the relationship

$$\bar{a} + \bar{b} = 1 \tag{2}$$

Unless the mixture is completely uniform $a(\mathbf{x})$ is different from $\bar{a}$ and changes as $\mathbf{x}$ changes. The function $a(\mathbf{x})$ completely describes the distribution of the components in a two-component mixture. From this function we extract the statistics that describe the quality of mixing.

2.2 Intensity of Segregation and Texture

There are two different mechanisms of mixing in polymer processing: molecular diffusion and bulk deformation. We separate them because they have very different effects on the mixture pattern. Bulk deformation

changes the shapes of regions of the mixture with a given composition, but it can only move the points around, never change their composition. For example, consider a mixture consisting of round blobs of a black material surrounded by a white material. Deformation can smear the blobs out into streaks, make them into swirls, or change the pattern in many other ways, but the pattern is always black and white, never gray. On the other hand, molecular diffusion cannot change the shape of the blobs but instead produces gray wherever black meets white. Diffusion causes the gray areas to grow with time until the entire mixture is a uniform gray.

Intensity of segregation is the property of a mixture that is affected by molecular diffusion. It is determined by examining how the composition at each point differs from the average composition of the mixture. The variance in composition is a measure of how much concentration varies from the mean and is defined by

$$\sigma_a^2 = \langle (a(\mathbf{x}) - \bar{a})^2 \rangle \tag{3}$$

Here the angle brackets denote an average over the entire mixture. If $a(\mathbf{x})$ equals $\bar{a}$ at every point (i.e., the mixture is a uniform gray) then σ_a^2 equals zero. If $a(\mathbf{x})$ equals either one or zero everywhere (i.e., every point is either black and white, never gray) then σ_a^2 equals $\bar{a}\bar{b}$. This is used to normalize the variance, producing the intensity of segregation:

$$I = \frac{\sigma_a^2}{\bar{a}\bar{b}} \tag{4}$$

A value of I equal to zero means no intensity (complete uniformity of composition); a value of unity means maximum intensity (the mixture is black and white with no gray).

Intensity of segregation is not important in many polymer processing problems because the diffusivities of polymer melts are so small that no significant diffusion occurs during mixing and I is always very close to unity. When this is true, one can talk about a mixture with no diffusion. Most of the subsequent discussion concerns mixtures with no diffusion because they predominate in polymer processing.

Diffusion and changes in the intensity of segregation are important whenever intimate contact between molecules is needed. A prime example in polymer processing is reaction injection molding. Here two liquids must be mixed on a molecular scale so that they can react and form a polymer. In this case bulk deformation is used to create very small blobs or layers of the two fluids so that diffusion can reduce the intensity of segregation very quickly.

The qualities of a mixture that can be affected by bulk deformation we call *texture*. Texture includes anything one may say about the spatial

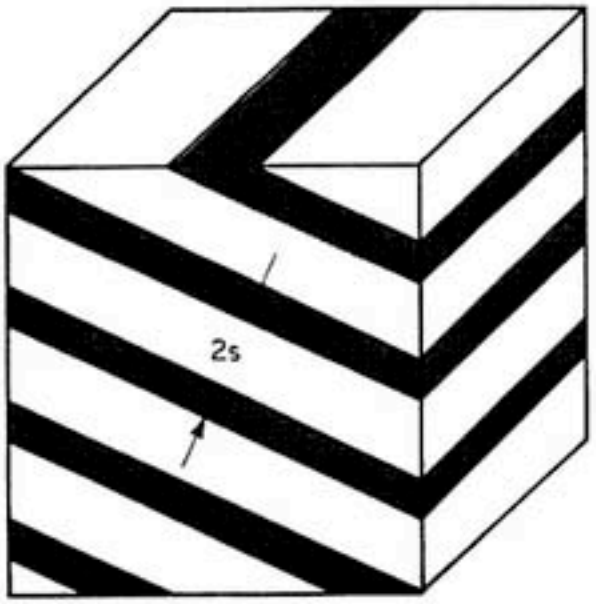

Figure 3 Definition of striation thickness s in a layered mixture.

arrangement of the components of the mixture. Is the mixture streaky, clumpy, or swirled? Are the clumps all the same size or different sizes? How big are they? Measurements of texture include interfacial area, striation thickness, and scale of segregation. We now proceed to discuss measures of texture. Intensity of segregation is the only quantity discussed in this chapter that is *not* a measure of texture.

2.3 Mixtures with No Diffusion: Interfacial Area and Striation Thickness

In mixtures with negligible diffusion one can easily identify the two components and the surfaces where they meet. Spencer and Wiley [1] were among the first to recognize that better mixing in viscous fluids meant an increase in the interfacial surface area, and this is still the quantity predicted by many theories about mixing. For measurement purposes we use A_v, the interfacial surface area per unit volume. This is one of the few measures of mixing that becomes larger as mixing becomes better: most of the other measures become smaller as mixing improves.

A special case of a mixture with no diffusion is a layered or lamellar mixture. This is an important case because laminar fluid flow tends to produce layered mixtures [2,3]. Consequently, any mixture of immiscible viscous fluids tends to have a layered structure. In such a case the striation thickness s is a measure of the texture; s is defined as one-half the thickness of the repeating unit, as shown in Figure 3. (Note that some authors do not

include the factor of one-half. Here we follow the notation of Ottino and coworkers.)

For a layered mixture the interfacial surface area and the striation thickness are simply related:

$$A_v = \frac{1}{s} \tag{5}$$

Of course, A_v can be measured for any mixture without diffusion, but s is only defined for lamellar mixtures.

Interfacial surface area and striation thickness are useful because they are easy to measure and easy to understand. However, they may be poor indicators of the quality of mixing when there is a wide range of striation thickness or particle size. For example, consider the mixtures shown in Figures 2a and b. The two mixtures have identical striation thickness and interfacial surface area. However, Figure 2a with its regular layers seems much better mixed than Figure 2b, with many small layers and a few large layers. The small layers contribute significantly to the interfacial surface area, but the large layers have more of an influence on the quality of mixing. Both Strasser and Erwin [4] and Kolodziej et al. [5] found that real mixtures have a wide distribution of striation thickness, so this is a very real problem.

One way to handle this problem is to measure the distribution function of striation thickness. One might then talk of some percentage of the volume of the mixture having striations thicker than a certain value. This type of result was presented by Kolodziej et al. [5] but has yet to be widely used. Its measurement and calculation are as complicated as the statistical measures discussed later, but it is not as general a description.

2.4 Clumpy Mixtures: Scale of Segregation

Another type of mixture that is often analyzed is the clumpy mixture. This consists of clumps of the two components that are similar in shape, at least in a statistical sense, but that have no regular arrangement or long-range order. The type of pattern one would get by spattering drops of black paint on a white wall is a good example of a clumpy mixture: the various drops are somewhat similar to one another, but their placement on the wall is random.

Clumpy textures can be characterized by the *scale of segregation*, which is a measure of the size of the clumps. The concepts of scale of segregation and intensity of segregation were originally proposed by Danckwerts [6] in his definitive paper on the definition and measurement of mixing.

The precise definition of scale of segregation is statistical in nature. To

arrive at it we must first consider the correlation function $R(\mathbf{r})$. Recall that the variance σ_a^2 is a measure of how much the composition at a point differs from the average composition [Eq. (3)]. The correlation function is closely related, but instead of considering one point at a time it considers pairs of points, choosing the points so that they are separated by a fixed distance $\mathbf{r}$. The definition is

$$R(\mathbf{r}) = \langle [a(\mathbf{x}) - \bar{a}]\,[a(\mathbf{x} + \mathbf{r}) - \bar{a}] \rangle \tag{6}$$

Here again the angle brackets denote an average over the entire mixture, that is, an average over all values of $\mathbf{x}$, with $\mathbf{r}$ remaining fixed. By repeating the calculation for each value of $\mathbf{r}$ one builds up the function $R(\mathbf{r})$. When $\mathbf{r}$ equals zero then $a(\mathbf{x})$ equals $a(\mathbf{x} + \mathbf{r})$ and a comparison between Equations (6) and (3) shows that

$$R(0) = \sigma_a^2 \tag{7}$$

This is used to normalize the correlation function, producing a frequently used quantity called the correlation coefficient $\rho(\mathbf{r})$:

$$\rho(\mathbf{r}) = \frac{R(\mathbf{r})}{\sigma_a^2} \tag{8}$$

having the property that $\rho(0)$ always equals unity. The graph of the correlation coefficient is called a correlogram. The notation used here is that $\mathbf{r}$ is a vector, but reported correlograms usually treat r as a scalar quantity. This is strictly correct only if the mixture statistics are isotropic, but it is common practice to ignore anisotropy in the mixture statistics. If this approach is taken then $\rho(r)$, where r is a scalar, should be an average of $\rho(\mathbf{r})$ over all possible directions of $\mathbf{r}$.

The correlation coefficient can be defined and measured for any mixture, regardless of whether it is clumpy or not and whether significant diffusion has occurred. To get a better idea of what the correlation coefficient means, consider a mixture of components A and B with no diffusion. Imagine we have a photograph of a section of this mixture and take a needle of length r and drop it onto the photograph. (This process is called "dipole throwing.") Each end of the needle would land on a region of A with probability $\bar{a}$ and on a region of B with probability $\bar{b}$. What about the combination of the two ends? Both ends could land in A, or both ends in B, or one end in A and one end in B. Call the probabilities of these events P_{AA}, P_{BB}, and P_{AB}, respectively. The correlation coefficient is related to these probabilities [7] by

$$\rho(\mathbf{r}) = \frac{\bar{b}}{\bar{a}} P_{AA} + \frac{\bar{a}}{\bar{b}} P_{BB} - P_{AB} \tag{9}$$

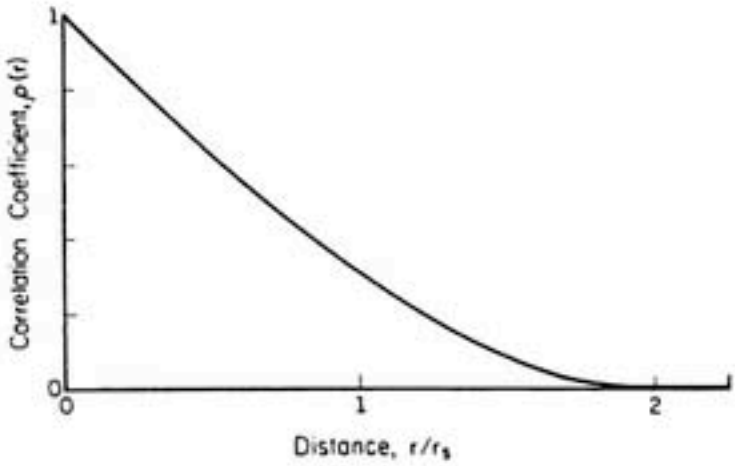

Figure 4 Correlogram for mixture with randomly arranged spherical clumps of radius r_s.

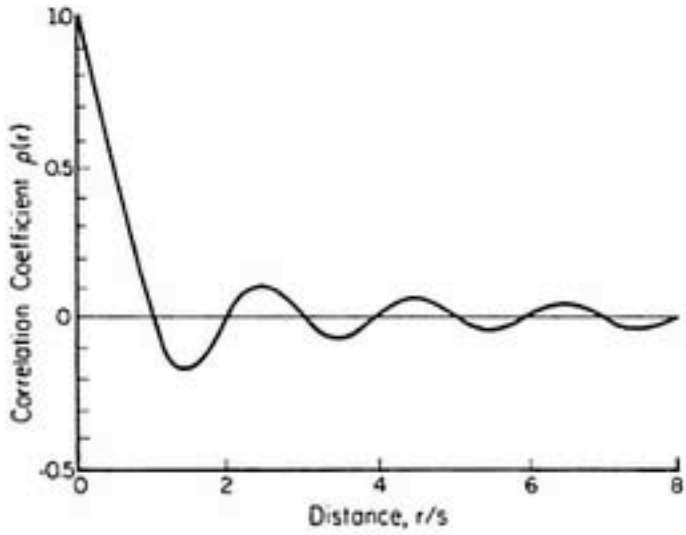

Figure 5 Correlogram (averaged over all directions) for regular layered mixture with $\bar{a} = 1/2$.

or in the case of a 50 : 50 mixture,

$$\rho(\mathbf{r}) = P(\text{both ends the same}) - P(\text{both ends different}) \tag{10}$$

If the correlation coefficient at some value of $r = 1$, then points separated by a distance r always have the same composition; if $\rho(r) = -1$ they are always different. A value of $\rho(r)$ equal to zero means that knowing the composition at one point provides no information about the composition a distance r away.

Sample correlograms are shown in Figures 4 and 5. Figure 4 is the corre-

logram for a mixture made by randomly mixing uniform spheres of the two components and then compacting the spheres until the space between them is eliminated [8]. The correlation coefficient always equals unity at zero distance. It equals zero for r greater than the diameter of the spheres, since the composition of adjacent spheres is uncorrelated. This is an example of a clumpy mixture.

Figure 5 is the correlogram of a regular layered mixture with equal proportions of A and B. A layered mixture is anisotropic, and Figure 5 is the correlogram averaged over all directions. That every layer of A is next to a layer of B shows up in the first region where the correlogram is negative. The regular alternating structure of the mixture shows as an oscillation in the correlogram.

We can now rigorously define a *clumpy mixture* as one in which the correlogram is nonnegative and equals zero for r greater than some value (as in Figure 4). For clumpy mixtures we can define the *linear scale of segregation* S_L as the area under the correlogram [6]

$$S_L = \int_0^\infty \rho(r)\, dr \tag{11}$$

This represents an average size of the clumps. Note that in a clumpy mixture there is no difficulty with the infinite upper limit on the integral, since $\rho(r)$ equals zero above some value of r. Danckwerts also defined a *volume scale of segregation* S_v as

$$S_v = 2\pi \int_0^\infty \rho(r) r^2\, dr \tag{12}$$

This represents a measure of the volume of the clumps. The volume scale of segregation is important in practice because it is easy to measure by sample variance techniques (see Section 3.2). S_v is of the order of $(S_L)^3$, but the exact relationship between S_v and S_L depends on the shape of the correlogram.

Figure 6 illustrates the relationship between scale and intensity of segregation. Note that the scale of segregation can decrease without changing the intensity (as in laminar mixing of polymer melts). The intensity can also decrease without changing the scale (molecular diffusion with no bulk deformation). The two measures, scale and intensity, are complementary.

The scale of segregation is a more general measure of texture in mixtures than interfacial surface area or striation thickness because it can be applied even when significant diffusion has occurred. Its limitation is that it is not strictly defined for mixtures with enough order to have either negative values in the correlogram or correlations at long distances. Relatively few correlograms have been measured for actual mixtures, but these invariably

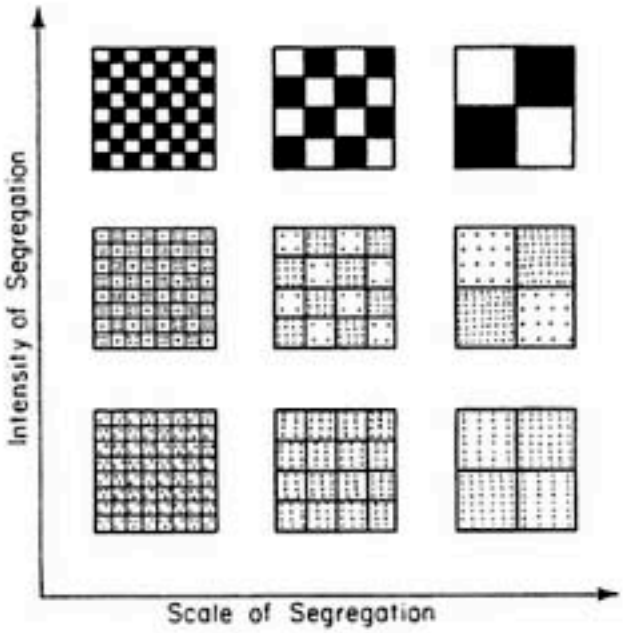

Figure 6 Examples of scale and intensity of segregation.

show some negative values and often show correlations at long distances [9,10]. Scale of segregation is a measure of the small-scale texture of a mixture—the local clump size or graininess.

2.5 Correlation Function and Spectrum: Complete Descriptions of Texture

Striation thickness, interfacial surface area, and scale of segregation are all useful measures of texture in mixtures, but each tells only part of the story. Is there some quantity that describes mixing completely and from which all other measures can be derived as special cases? This is not a question that has received a great deal of attention in the mixing literature, but it seems that the answer to the question is yes and that the quantity is the correlation function [11]. This can be expressed concisely as a hypothesis:

> The texture of a mixture is completely described by the statistics of the concentration field up to the second order.

By concentration field we mean the function $a(\mathbf{x})$. Nth order statistics are quantities computed by considering N points at a time. The variance σ_a^2 is a first-order statistic (one point at a time); the correlation function $R(\mathbf{r})$ is a second order statistic (two points at a time). There are, of course, higher order statistics: three-point correlations, four-point correlations, and so on. One may reasonably ask if these matter. The answer, at least for human

visual perception of texture, is no. This has been shown by Julez [12] in a fascinating series of experiments on visual perception. He found that humans distinguish between patterns with different second-order statistics almost without effort but could not see the differences between patterns that differed only in higher-order statistics.

Another piece of evidence in favor of the correlation function as a complete description of texture is that all the other measures of mixing we have discussed can be calculated from it (or from the correlation coefficient, which contains the same information). This is obviously the case for the linear and volume scales of segregation, which are defined in terms of the correlation coefficient [Eqs. (11) and (12)]. It has also been shown [8,13] that for mixtures with no diffusion the slope of the correlogram at zero distance is related to the interfacial surface area:

$$A_v = 4\left(\frac{dR}{dr}\right)_{r=0} \tag{13}$$

Once the interfacial area per unit volume is known, one can find the striation thickness from Equation (5). Thus, all the measures of texture we have discussed so far can be determined from the second-order statistics of a mixture.

The correlation function may be complete, but it is often hard to interpret. An alternative description of texture that contains exactly the same formation is a spectral description, which we shall call the power spectrum. This is defined as the Fourier transform of the correlation function (shown here for an isotropic mixture):

$$P(n) = \int_{-\infty}^{\infty} R(r)e^{-2\pi inr}\,dr \tag{14}$$

Here i denotes $\sqrt{-1}$. Since R(r) is real and even, Equation (14) simplifies to

$$P(n) = 2\int_{0}^{\infty} R(r)\cos 2\pi nr\,dr \tag{15}$$

The variable n is called the wave number and has units of length^{-1}. It plays the same role in space-varying problems as frequency does in time-varying problems. One may just as well calculate $R(r)$ from $P(n)$ by taking the inverse transform:

$$R(r) = \int_{-\infty}^{\infty} P(n)e^{2\pi inr}\,dn \tag{16}$$

The power spectrum has a number of interesting features. Setting r equal to zero in Equation (16) shows that

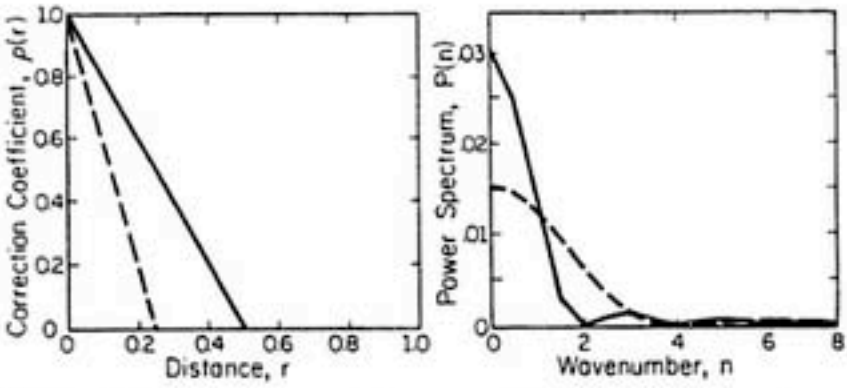

Figure 7 Two linear correlograms with different scales of segregation and the corresponding power spectra.

$$\sigma_a^2 = \int_{-\infty}^{\infty} P(n)\, dn \tag{17a}$$

That is, the area under the spectrum curve equals the total variance σ_a^2. $P(n)$ shows how this variance is divided up among different wave numbers. Setting n equal to zero in Equation (15) gives

$$P(0) = 2 \int_0^{\infty} R(\mathbf{r})\, dr = 2\sigma_a^2 S_L \tag{17b}$$

That is, the value of the power spectrum at zero wave number is proportional to the scale of segregation. This is true only for mixtures whose correlograms are always positive; negative values in the correlogram decrease the value of $P(0)$, and strictly speaking the scale of segregation is not defined in this case anyway.

The correlation function and the spectrum contain exactly the same information. However, the information is arranged in a different way. Roughly speaking, the spectrum turns the correlogram inside out. Correlations at short distances influence the spectrum at large wave numbers, and correlations at long distances influence the spectrum at small wave numbers. This is demonstrated in Figure 7, which shows two different linear correlograms and their power spectra. The mixture with correlations at longer distances (solid line) has the larger value of $P(0)$ and, hence, the larger scale of segregation. The second mixture (dashed line) has a lower scale of segregation. Its power spectrum has the same shape as the first mixture, but the peaks all occur at higher wave numbers because the correlations occur over shorter distances.

Two other mixture spectra are shown in Figure 8. The solid line has an oscillating correlation function, indicating some regularity to the structure of the mixture. This shows clearly in the spectrum as a peak at wave number

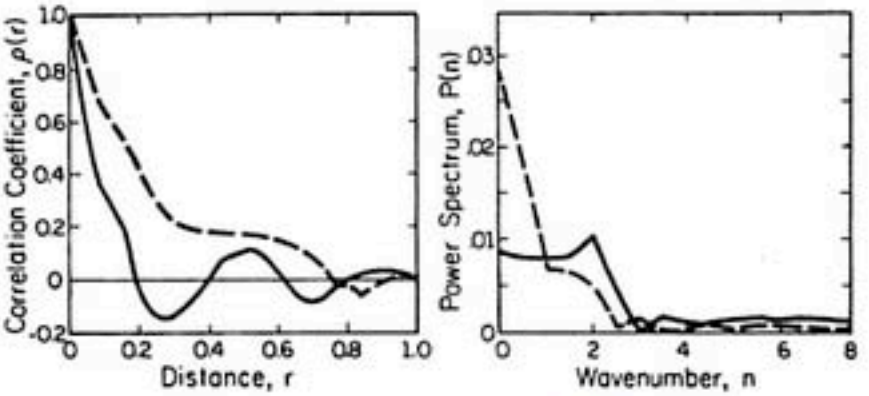

Figure 8 Correlograms and power spectra for two mixtures.

equal to 2. The spectrum indicates the strength and length scale of the repeating structure.

The dashed curves in Figure 8 illustrate a mixture with no repeating structure but a long tail in the correlation function typical of elongated clumps. This shows as a spectrum with its maximum at n equal to zero and no large peaks at other wave numbers.

The spectrum shows how concentration fluctuations are divided up among the various wave numbers, and it is not troubled by the regular repeating structures often found in mixtures. It can be interpreted more easily than a correlogram, and different mixtures are more easily compared by comparing their spectra.

Another reason the spectrum is important is that it is the fastest way to compute the correlation function. $P(n)$ is also the power spectrum of the concentration field $a(\mathbf{x})$. To compute it directly from concentrations one first defines $c(\mathbf{x})$, the local deviation of the concentration from the average:

$$c(\mathbf{x}) = a(\mathbf{x}) - \bar{a} \tag{18}$$

then takes the transform of $c(\mathbf{x})$,

$$Q(n) = \int_{-\infty}^{\infty} c(\mathbf{x}) e^{2\pi i n x} dx \tag{19}$$

$Q(n)$ is a complex function, having real and imaginary parts at each wave number. $P(n)$ is the square magnitude of these numbers:

$$P(n) = Q(n)Q^*(n) = |Q(n)|^2 \tag{20}$$

where the asterisk denotes a complex conjugate. Equations (18) through (20) and (16), together with fast Fourier transform techniques, provide the quickest way to compute $R(r)$ (see Sec. 3.3).

2.6 When Is Mixing Good Enough?

Given that we can define (and presumably measure) mixing, when is mixing good enough? For the single-valued indicators of mixing (interfacial area, striation thickness, and scale of segregation), it seems reasonable to set a critical value and say that any mixture better than the critical value is well mixed. The choice of the critical value depends entirely on the problem at hand. A complete chemical reaction in RIM is thought to require a striation thickness in the range of 15 μm [14]. If a uniform appearance is needed, then a scale of segregation or a striation thickness near the wave length of visible light (about 0.5 μm) will certainly give a texture that cannot be resolved under visible light. However, the experiments of Ng [15] suggest that a mixture with striations around 5 μm thick appears uniform to the naked eye. In other cases the physical or mechanical properties of the mixture are important, and one must correlate test results with mixing measurements to establish a sensible limit.

Even a carefully determined single-quantity limit may not always work. For instance, if the tests to establish the limits are done on mixtures with uniform striation thickness, then a mixture with a wide distribution of striation thickness may pass the mixing test but not produce the desired properties. This is an example of the limitation of striation thickness as a measure of mixing. All the single-valued measures have the same problem.

To use the complete descriptions of texture one may set a limit, for example, on the strength of the spectral components in a certain range: "no spectral components greater than P^* for wave numbers less than n^*." Any mixture passing this test would have only small concentration fluctuations for wave numbers up to n^*. This type of statement implies that segregation over distances smaller than about $1/n^*$ is not important.

3. MEASUREMENT TECHNIQUES

In discussing techniques for measurement of mixing we are concerned with two issues: acquiring the data and deciding what it means. Interpreting the data includes both relating the measurement to some fundamental description of texture and deciding how much confidence one can place in the result.

3.1 Basic Measurements on Sections

A *section* is a planar slice through a mixture, and sections are often easy to obtain in polymer mixtures. From the section one can obtain certain measurements, but the section is only a two-dimensional slice of a three-dimensional structure. The science of gaining three-dimensional informa-

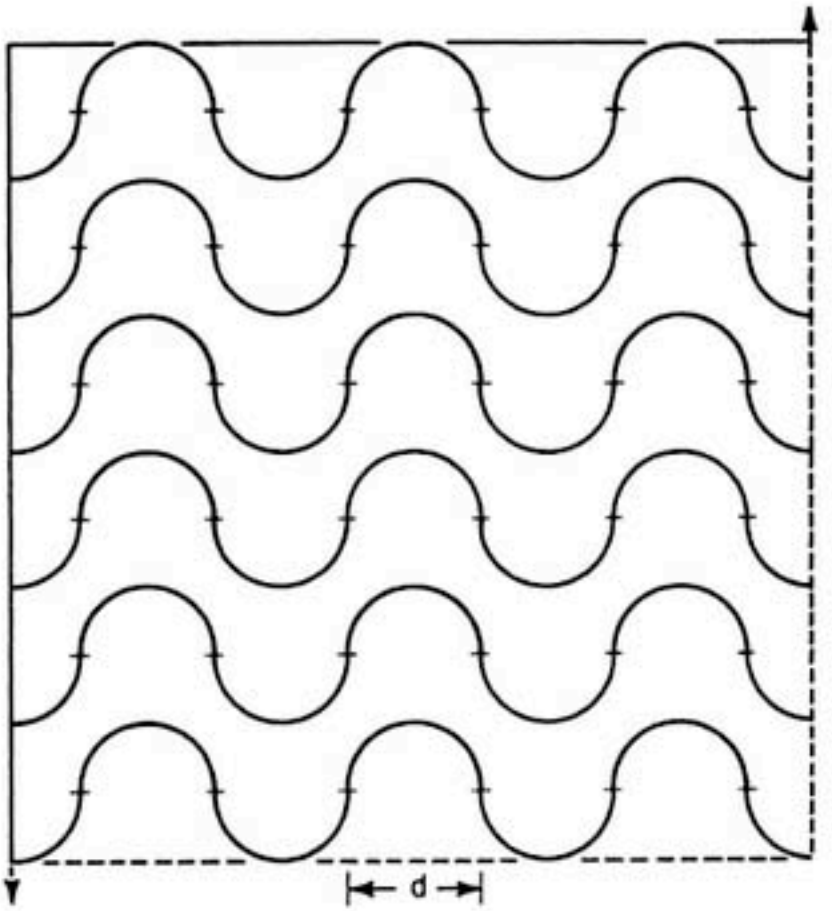

Figure 9 Test system for stereologic analysis. The points for measuring P_p are indicated by small tick marks.

tion from two-dimensional sections is called stereology. The reader is referred to Underwood [16] and Weibel [17] for comprehensive treatments of stereology. For our purposes stereology provides a simple way of determining interfacial surface area in a mixture with no diffusion.

Stereologists have determined that the most efficient way to obtain data is by a systematic counting of points and line intersections. Having first obtained several sections, for example by slicing the mixture and examining the slices in a microscope, one then chooses a test system like that shown in Figure 9. The test system is a regular geometric pattern of lines and points. One may have test systems on transparencies and simply lay them over photographs of the section. One then counts the quantities of interest, in our case the number of points of the test system falling on component A of the mixture, and the number of times the test system lines intersect an interface between components A and B. Repeating the procedure on many sections produces two stereological parameters: P_p, the fraction of points

that fall on component A, and I_L, the number of intersections per unit length of test lines.

The fraction of test points P_p is a direct measure of the overall composition of the mixture:

$$\bar{a} = P_p \tag{21}$$

Of course this equation applies only when there has been no significant diffusion.

The number of intersections per unit line length can be used to determine interfacial surface area. The exact relationship depends on the nature of the structure and on how the sampling was done. The best sampling procedure is to take isotropic sections. This means that many different sections with different spatial orientations are examined, so that all directions are equally represented. In this case the interfacial area per unit volume is

$$A_v = 2I_L \tag{22}$$

Equation (22) also applies for any type of sectioning when the mixture itself is isotropic; this case is extremely rare in practice, however.

Another possibility is that the structure of the mixture is lamellar and has all its interfaces aligned in the same direction. It has already been pointed out that this is always the case, at least over small distances, for the laminar mixing of viscous fluids. If all the sections have the same orientation relative to the layers and if ψ is the angle between the vector normal to the section plane and the vector normal to the plane of the interfaces, then the interfacial area is

$$A_v = \left(\frac{\pi}{2} \sin \psi\right) I_L \tag{23}$$

The proper choice of a test system is important if results are to be accurate. Many different test systems may be used. The test system in Figure 9 is recommended for applications in which anisotropy may be present [17], as is often the case in mixing. The size of the test system must also be chosen properly in relation to the sections being examined. The point spacing d as shown in Figure 9 should be chosen so that d^2 is greater than the area of the largest single contiguous area on the section (i.e., the largest particle). For lamellar mixtures d should be larger than the largest striation. A set of test systems of different sizes is usually needed for treating different mixtures.

Another important principle of stereology is that it is better to add together small amounts of information from a large number of sections than to collect a large amount of information from a small number of sections. This minimizes the chance of distorted results from a nonrepresen-

tative section. The number of sections that must be examined depends on the accuracy required of the measurement. If one is determining interfacial surface area, then the total length of the lines on the test system I_T required to determine A_v with a of variance $\sigma^2_{A_v}$ is [17].

$$L_T = \frac{4A_v}{\sigma^2_{A_v}} \tag{24}$$

The L_T given here is the length in real space; when examining micrographs one must account for the magnification factor.

Example

A mixture known to have A_v roughly equal to 10 mm^{-1} is sectioned and examined at $\times 60$ magnification. The test system covers an area of 120 $\times$ 120 mm on the magnified image. What point spacing should the test system have, and how many sections should be examined to measure A_v with a standard deviation of $\pm 5\%$?

Solution

The test system size d should be larger than the layers encountered on the sections. This requires d to be larger than $1/A_v = 0.1$ mm. A value of d of 20 mm on the magnified image, or 0.33 mm in real space, should be suitable. This gives the test system 36 points (as in Fig. 9) and a total line length per section of 1.131 m on the magnified image, or 18.85 mm in real space.

To get 5% accuracy we need

$$L_T = \frac{4A_v}{(0.05A_v)^2} = \frac{4}{(10\,\text{mm}^{-1})(0.05)^2} = 160\,\text{mm}$$

which is easily provided by using nine sections per measurement.

3.2 Sample Variance Measurements

A second general category of mixing measurement technique is the sample variance measurement. Here a number of small samples from the mixture are examined, and the overall composition of each sample is determined. The variance among these data is an indication of mixing.

If the compositions of the samples are denoted by C_i then the experimental average composition is

$$\bar{C} = \frac{1}{N}\sum_{i=1}^{N} C_i \tag{25}$$

and the experimental variance is

$$S^2 = \frac{1}{N-1}\sum_{i=1}^{N}(C_i - \overline{C})^2 \tag{26}$$

The average composition $\overline{C}$ is a measure of the overall composition of the mixture $\bar{a}$. The variance S^2 is a measure of the actual variance σ_c^2, which is related to the quality of mixing. This is in keeping with the general notion that mixing increases the homogeneity of the mixture. If the mixture is more homogeneous, then all the samples have a composition closer to $\overline{C}$ and the variance is small. A perfect mixture would have σ_c^2 equal to zero. σ_c^2 has a maximum possible value of σ_o^2, the variance among all points in the mixture [Eq. (3)].

There are many ways to obtain the data for sample variance measurements. Some workers have extracted the samples from the mixture with a hypodermic needle (for low-viscosity liquids) [18]; others have pumped the mixture through special cells that contain a number of sampling points [19,20]. Still others have examined sections of the solidified mixture [9,21]. For a continuous process one may also allow the mixture to flow through a measurement cell with a single sampling zone and take a series of measurements over a period of time.

Actual concentration measurements are made by any technique that is convenient for the mixture at hand. In research settings one can often dope the components of the mixture to make this as easy as possible. Techniques that have been used to measure composition include light transmittance [18,19], electrical conductivity [20], titration [22], and particle counting (in powder mixtures). A technique for mixtures of carbon black in rubber involves producing a cut surface in a reproducible way and examining the surface with dark-field microscopy [23]. The carbon black particles create roughness on the surface, which shows as a bright area in the dark-field microscope, so the intensity of light is related to the concentration of carbon black.

Any one of these techniques, or any other that measures concentration, is suitable for sample variance measurements. Sample variance techniques work best when a large number of measurements can be taken easily and when the individual concentration measurements are very accurate.

It is easy to make relative interpretations of sample variance measurements: if the sample size and shape are fixed, then a smaller variance always means better mixing. It is more difficult to compare two measurements done with differently sized or shaped samples or to relate the sample variance to a more fundamental description of mixing. This is because sample variance depends on the size and shape of the samples as well as on the texture of the mixture. The details of this dependence have been worked out [8,24], and it has been shown that the sample variance is given by

$$\frac{\sigma_c^2}{\sigma_o^2} = \frac{4\pi}{V} \int_0^\infty W(r)\,\rho(r) r^2\,dr \tag{27}$$

where V is the volume of an individual sample. The function $W(r)$ depends on the size and shape of the sample and is called the sample shape function. This is found by first defining a function $W^*(x, r)$. For a sphere of radius r centered on position $\mathbf{x}$, $W^*(\mathbf{x}, r)$ is the fraction of the surface area of the sphere that lies inside the sample. The sample shape function is the integral of this function,

$$W(r) \equiv \frac{1}{V} \int_v W^*(\mathbf{x}, r)\,dv \tag{28}$$

where the integration is carried out over the volume of the sample and each volume increment dv is located at the point defined by $\mathbf{x}$.

A few sample shape functions have simple analytic expressions. These include a spherical sample of radius r_s,

$$W(r) = \begin{cases} 1 = \dfrac{3r}{4r_s} + \dfrac{r^3}{16r_s^3} & 0 \le r \le 2r_s \\ 0 & r > 2r_s \end{cases} \tag{29}$$

and a highly elongated "line" sample with length L and cross-sectional area A_c [$(A_c)^{1/2} \ll L$],

$$W(r) = \begin{cases} \dfrac{2A_c}{4\pi r^2}\left(1 - \dfrac{r}{L}\right) & (A_c)^{1/2} \ll r \le L \\ 0 & r > L \end{cases} \tag{30}$$

Shape functions for other sample geometries can be computed numerically [8].

Equation (27) reduces to useful simple forms for samples that are very large compared to the scale of segregation. If the samples are compact in shape (spheres, cubes, and so on) then sample variance is a direct measure of the volume scale of segregation S_L [Eq. (12)] [6]:

$$\frac{\sigma_c^2}{\sigma_o^2} = \frac{2S_v}{V} \tag{31}$$

If instead the samples are highly elongated line samples, then sample variance measures the linear scale of segregation S_L [Eq. (11)]:

$$\frac{\sigma_c^2}{\sigma_o^2} = \frac{2S_L}{L} \tag{32}$$

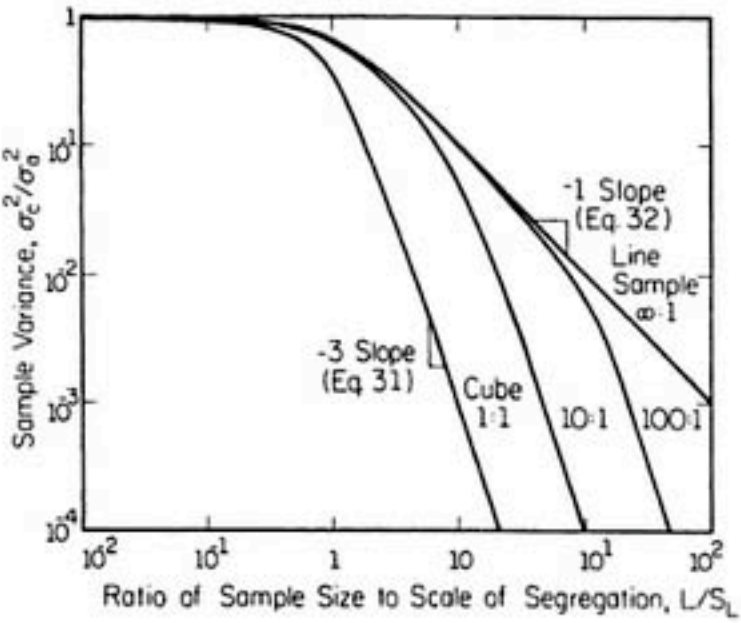

Figure 10 Effect of sample size and shape on sample variance measurements. Samples of length L and a square cross section. Numbers indicate the ratio of length to width.

Equation (31) is valid if $V \gg S_v$, and Equation (32) is valid if $L \gg S_L$. In either case one must usually assume that diffusion has been negligible, so that $\sigma_c^2 = \overline{ab}$. In practice one must have an a priori estimate of the scale of segregation to choose a sample size. This can easily be obtained from a preliminary measurement.

Another way to interpret sample variance measurements is to assume a mathematical form for the shape of the correlogram with one or more undetermined scaling factors. For example, the mixer may be known to produce mixtures with spherical clumps, in which case the correlogram shape of Figure 4 is appropriate and r_s is the only unknown parameter. Equation (27) then allows one or more measurements of sample variance to be used to set the scaling factor (in this case the radius of the clumps). The quality of results obtained this way depends heavily on the choice of a suitable correlogram shape, and the approach is not recommended unless there is strong evidence in favor of the correlogram form used.

Figure 10 demonstrates how sample size and shape affect sample variance. The curves are for samples with a square cross section and length L, with the cross section varied from L^2 (a cubic sample) to zero (a perfect line sample). Very small samples are seen to act as point samples (σ_c^2 equals σ_o^2) no matter what their shape. Large samples follow the asymptotes suggested by Equations (31) and (32).

Table 1 Confidence Limits on Sample Variance Measurements [a]

Number of Samples, N	Confidence Level							
	90%		95%		98%		99%	
	C_l	C_u	C_l	C_u	C_l	C_u	C_l	C_u
5	0.42	5.63	0.36	8.26	0.30	13.47	0.27	19.32
10	0.53	2.70	0.47	3.33	0.41	4.31	0.38	5.20
20	0.63	1.88	0.58	2.13	0.52	2.49	0.49	2.78
50	0.74	1.45	0.70	1.55	0.65	1.70	0.63	1.80
100	0.80	1.29	0.77	1.35	0.74	1.43	0.71	1.49

[a]The confidence level is the probability that the actual variance falls between C_lS^2 and C_uS^2.

The accuracy of experimental measurements of sample variance is controlled by the number of samples used. As more samples are used to compute S^2, the confidence one can have in the measured value increases. This is stated in the form of a confidence limit. That is, one names two values and the probability that the true value falls between them. The confidence limits on sample variance are given by (e.g., Ref. 25)

$$\frac{(N-1)S^2}{\chi^2_{N-1,1-\alpha/2}} < \sigma_c^2 < \frac{(N-1)S^2}{\chi^2_{N-1,\alpha/2}} \tag{33}$$

where $\chi^2_{\nu,\alpha}$ is the chi-square cumulative distribution function for ν degrees of freedom and having area α to the left of χ^2, N is the number of samples, and α is the confidence value (e.g., 0.90 for a 90% confidence limit). Table 1 gives examples of the confidence limits that may be placed on sample variance data. For a small number of samples the confidence limits can be quite far apart, and one should bear this in mind when interpreting experimental data.

The resolution of sample variance measurements is limited by the precision of the technique used to measure sample compositions. Any measurement has some inherent variation, so the measured variance S^2 never equals zero, no matter how good the mixing. Instead, some part of the measured variance is caused by the measurement technique, and any variance due to poor mixing that is smaller than this value cannot be detected. This effect is illustrated in Figure 11, which compares the sample variance predicted by Equation (27) and the actual value measured as mixing improves. This limiting value of variance can easily be determined by taking a series of measurements on very thoroughly mixed samples, and this should always be done before using a new measurement technique. Failure to do this can mean disaster if changes in mixing quality are not reflected by the measured values.

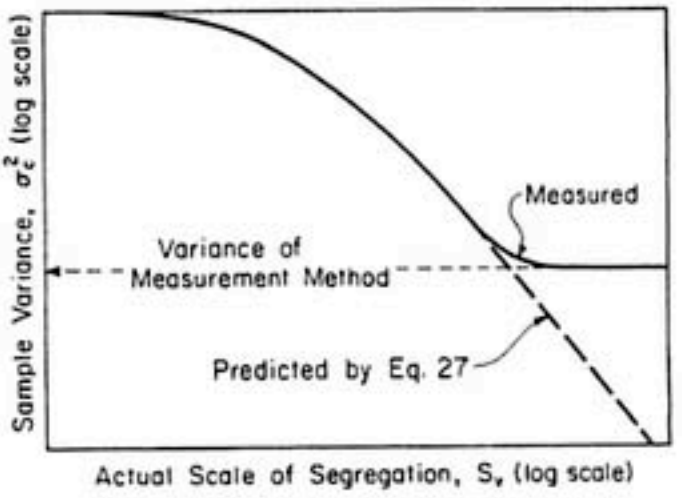

Figure 11 Effect of finite measurement accuracy on measured sample variance (solid line) versus the value predicted by Equation (27) (dashed line).

3.3 Image Analysis

Image analysis is the automated form of stereology. One still acquires sections of the mixture to analyze, but the analysis is done by computer. The steps in the procedure are: obtain a section, acquire a digital image of the section, and analyze the image. As the first step is the same as any other stereological technique, only the second and third steps are discussed here.

Acquiring Digital Images

A digital image is a way of storing pictorial information in a computer. The picture is divided up into a large number of small areas, called pixels. Normally these are arranged in a rectangular array. For each pixel the intensity of light is measured and recorded. (In color systems one may record red, green, and blue intensities.) The actual digital image is then a large array of numbers representing the light intensity at each of the pixels. Typical image analysis systems have 512 × 512 or 1024 × 1024 pixels and 256 gray levels (i.e., the light intensity is represented by an integer ranging from 0, for the lowest intensity, to 255, for the highest intensity).

The most common way to acquire a digital image is with a television camera. For a mixing analysis one may attach the camera directly to a microscope to give the necessary magnification. The camera signal is then passed to a device known as a video digitizer or a frame grabber. This electronic hardware translates the analog camera signal into digital intensity values and stores them in random-access memory. The digitizing equipment may be part of a small computer, in which case the image can be stored

directly in computer memory, or it can be a stand-alone device, in which case the image is passed to a computer over an interface.

An alternative to the video camera is laser line scanning, developed by Strasser and Erwin [4]. In this technique a low-power optical laser beam is focused on the surface of the section and the intensity of the reflected light is measured by a photodiode. By scanning the beam over the section and taking periodic intensity readings of the reflected light, one builds up a digital image of the section. The stated advantages are elimination of the need for uniform lighting and higher resolution than is available from a camera. The disadvantage is that more time is required to acquire each image—several minutes is typical. In contrast, a frame grabber acquires an image in approximately 0.03 s (although the analysis usually takes much longer).

To analyze the mixture one must relate the intensity at each pixel to the composition of the mixture at that point. This is easily done when different colors are being mixed together. If the intensity is not directly proportional to the concentration, then a calibration curve can be set up and the digital intensities transformed into compositions by a short computer program.

It is more difficult to deal with situations in which one cannot see the difference between the components of the mixture. This situation has not been reported in the literature, but one might try staining one of the components. Another possibility would be to use the x-ray microprobe capability present in some scanning electron microscopes. These instruments use x-ray fluorescence to detect the presence of a selected element and can display on the cathode-ray tube (CRT) an image showing where that element is present in the sample (e.g., see Ref. 15). Presumably one could pass the microscope's CRT signal directly to the video digitizer and eliminate the camera altogether.

Analysis of the Image

One now has a digital image stored in a computer, and the intensities are proportional to the compositions at each pixel. This may be on a continuous scale, or one may choose to ignore any diffusion that had taken place and make each pixel either all dark or all light. This latter operation is known as *thresholding*. An intermediate gray level is chosen and each pixel compared to it: those that are darker are set to black, and those that are lighter are set to white.

The most general treatment of this image for mixing analysis is to compute the spectrum $P(n)$ [Eq. (15)]. This is done using a fast Fourier transform (FFT) algorithm and the route described in Equations (18) through (20). The FFT is simply a very efficient method for computing the discrete Fourier transform (DFT). Under suitable conditions the DFT is an approxi-

mation to the continuous Fourier transform used in Equations (14), (16), and (19) (see, for example, Ref. 26). The DFT is calculated from sampling the desired function, say $c(\mathbf{x})$, at points separated by an interval X. If N points are sampled then the discrete transform is given by

$$Q\left(\frac{\ell}{NX}\right) = \sum_{k=0}^{N-1} c(kX)e^{-i2\pi k\ell/N} \quad \text{for} \quad \ell = 0, 1, 2, \ldots, N-1 \tag{34}$$

Equation (34) is a DFT for a one-dimensional function. For image analysis, intensity values in the digital image are the sampled points of the function $c(\mathbf{x})$, but the data are a two-dimensional array. A two-dimensional DFT is done by performing an FFT on each row of the array, placing the results in a new array, and performing an FFT on each column of that array. The power spectrum (again, two-dimensional) is computed by multiplying the transform at each point by its complex conjugate [Eq. (20)]. The correlation function can then be computed by taking the inverse transform of the power spectrum (again with FFT methods). For a sizable number of points this is the fastest way to compute the correlation function. For N points the use of Equation (6) requires N^2 operations and the use of the FFT requires N ($\log_2$ N + 1) operations. For example, if N equals 1024, then the FFT route is 100 times faster. If there are more points the savings are larger.

At this point one has complete information about the mixture in the image, with two limitations. First, there is no information about correlations over distances greater than the width or height of the image. Second, information about correlations over distances shorter than the spacing between pixels is either lost or, more dangerous, may be reflected as false information in the spectrum and correlogram. The latter is the well-known "aliasing" effect in which spectral components at wave numbers higher than $1/X$ appear in the spectrum at lower frequencies (e.g., see Ref. 26). Aliasing is an inherent feature of sampled data systems. Some image acquisition equipment may alleviate the problem, if each pixel is not a point sample of the image but an average over an area nearly the size of the pixel spacing. At present there is not enough experience with image analysis in mixing to say how important the aliasing problem is.

Although either the power spectrum or the correlation function contains complete information about the texture of the mixture, it may be desirable to compute other quantities, such as the scale of segregation or interfacial surface area, using the equations presented in Section 2.

Commercial image analyzers are available. These machines are packages of hardware (video camera, digitizer, and computer) and software for analyzing images. Typical capabilities include counting the volume fraction of each phase and counting the number and sizes of particles. The latter may

be very useful for dealing with the dispersion of particulates in a polymer. Commercial systems also measure other stereological parameters, including I_L, so that interfacial surface area can be computed. Some commercial image analysis packages not only include hardware and software but also allow the user to write his or her own routines for image analysis [27]. This is one way that the concepts discussed here could be realized in practice.

Image analysis gleans much more information from a single section than stereological point-counting methods. However, this does not produce more accurate results if only one or two sections are used. One must still examine a sufficient number of sections to have representative data and, in the case of measuring I_L, to cover a range of section orientations. The real advantage of image analysis is that the analysis is done automatically so that many sections can be analyzed with minimum labor.

4 SUMMARY

In any practical problem one must choose both a measure of mixing and a measurement technique. The two choices are not independent: stereological techniques measure the interfacial area or the striation thickness; sample variance techniques measure the scale of segregation; image analysis measures the concentration spectrum. Each measurement technique may be more or less difficult to apply to a given mixture; each measure of mixing may be more or less appropriate to the situation. As usual, the engineers are left to use their own good judgment. In making the choice, one should remember the limitations and pitfalls presented here.

NOMENCLATURE

a, b	Concentrations of components A and B at a point in the mixture
$\bar{a}, \bar{b}$	Averages of a and b over the entire mixture
A_c	Area of the cross section of an elongated sampling volume
A_v	Interfacial area per unit volume
c	Deviation of a from its average value
$\underline{C_i}$	Average value of c for a sample extracted from the mixture
$\overline{C}$	Average value of C_i over all the samples
d	Distance between measurement points on a test section
I	Intensity of segregation [Eq. (4)]
I_L	Number of intersections (between test lines and interfaces) per unit length of test lines in a stereological measurement
L	Length of elongated sampling volume
L_T	Total length of test lines for a set of stereological measurements
n	Wave number, the independent variable for the power spectrum

N	Number of samples
$P(n)$	Power spectrum of concentration field [Eq. (14)]
P_p	Fraction of the points (on a set of stereological test sections) that fall on component A
$Q(n)$	Fourier transform of the concentration field $c(x)$
$\mathbf{r}$	Distance between pairs of points used to evaluate the correlation function $R(\mathbf{r})$
r_s	Radius of spherical sampling volume
$R(\mathbf{r})$	Correlation function for concentration field [Eq. (6)]
s	Striation thickness (Fig. 3)
S^2	Experimentally measured variance in concentrations C_i among a number of volume samples [Eq. (26)]
S_L	Linear scale of segregation [Eq. (11)]
S_V	Volume scale of segregation [Eq. (12)]
V	Volume of sample for sample variance measurements
$W(r)$	Sample shape function [Eq. (28)]
$\mathbf{x}$	Position vector
X	Spacing between sampling points for discrete Fourier transform
$\rho(r)$	Correlation function [Eq. (8)]
σ_a^2	Variance in concentration among all points in a mixture [Eq. (3)]
σ_{Av}^2	Variance in measurement of A_v
σ_c^2	Variance in composition among volume samples extracted from a mixture

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