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Mixing of Rubbers

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ACKNOWLEDGEMENTS

First and foremost I wish to thank Dr. John Jepson and his colleagues in the Research & Development Division of Acushnet Company whose generous support and faith in the application of analysis to industrial processes has made this work feasible. As with all books such as this, the success of the project hinges on the tireless support of a good, competent secretary and typist. Susan Hartman has performed a yeoman task with rare skill and good humour. Finally, Professor J.R.A. Pearson has served me well as a sounding board for the development of arguments. As a colleague he has been a delight and as a teacher he has been an inspiration.

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INTRODUCTION

Since the discovery of vulcanization in the nineteenth century, rubber has been a major industrial product. From its inception, the use of vulcanizing agents, reinforcing fillers and other additives has been a major feature of the rubber industry. Innumerable articles and texts attest to the chemist's skill in balancing the chemical and physical properties of the manufactured products.

In most cases, experimenters have been concerned with how recipe changes affect the product properties while the physical processes which formed the test specimen are not considered. For the rubber processor, however, it is these mechanical operations which form the heart of his business. The equipment needed for plant-scale production requires millions of dollars of capital investment. In the highly competitive rubber industry, the ability to save two or three cents per pound of product through better design or more efficient operation of mixing equipment can make a tremendous difference in the profitability of a company. Despite the commercial importance of the process, no comprehensive analysis of rubber mixing, considered as a unit operation, is currently available. This monograph is designed to fill that gap in the arsenal available for problem solving by the production engineer or the machine designer.

Mixing as a general operation may be considered as three basic processes occurring simultaneously. Simple mixing ensures that the mixture has a uniform composition throughout its bulk, at least when viewed on a scale large compared to the size of the individual particles. In the case of solids blending (Chapter II), the particle size need not change, but the distribution of particles throughout the mixture approaches a random distribution.

If the shear forces are sufficiently large, particles may fracture, as in dispersive mixing, and the polymer may flow, as in laminar mixing (Chapter III). In both of these processes, the size of the original particles or fluid elements changes because of the mixing process. Then the properties of the mixture depend upon the size of the basic structures reached during mixing. In the case of laminar mixing, the size may be the striation thickness of a hypothetical fluid element, which is inversely related to the total shear strain. If relatively strong particles, or aggregates of particles, are present, these must be reduced in size by the action of forces generated by flow in the mixer. Then the size is the actual additive particle size.

The relative balance between the importance of these three processes in determining the efficiency of mixing and the product quality depends upon the attraction between additive particles, the rubber flow properties, the geometry of the mixer and the operating conditions such as temperature, mixing time and rotor speed.

The interaction of operating conditions, raw material properties and the quality of mixing can be a formidable phenomenon to analyze. However, in many cases a number of simplifying assumptions about the operation can be made. The first of these is that in any piece of mixing equipment, there is one vital section where the flow conditions in that region determine the rate and quality of mixing; the essential physical processes can be described if flow in that region can be analyzed. For two roll-mills (Chapter IV) this is the nip region; it is the region between the rotor tip and chamber wall for internal mixers (Chapter V) and the channel and flight gap in an extruder (Chapter VI). In every case, the geometry of the mixer is treated locally as if it were flow between parallel planes and the actual mixer geometry is incorporated by allowing the space between these hypothetical planes to vary with position in the mixer; this is the basis of the lubrication approximation.

For most mixing operations, the primary driving force for fluid motion is drag flow caused by the relative motions of metal boundaries in the equipment. Pressure flow is relatively unimportant for mixing. In many cases, the rubber can be treated as Newtonian or a power-law fluid, which greatly simplifies the analysis. However, the viscoelastic nature of rubber compounds imposes a severe limitation on the stability of the mixing operation (Chapter IV).

One major limitation to the speed of operation of a mixing process, besides the mechanical ruggedness of the equipment, is the temperature rise in the rubber stock because of viscous dissipation. The heat transfer in mixing equipment may be a problem, especially in larger mixers. The efficiency of heat transfer depends upon the geometry of the mixer and the operation conditions, as treated in the analyses.

Following a basic description of the three fundamental processes it is necessary to see how these occur in actual mixers. The primary difference between types of mixers is the geometry of the metal boundaries. In two-roll mills (Chapter IV) the geometry is the simple symmetry of parallel cylinders. With internal mixers (Chapter V) and continuous mixers (Chapter VI) the geometry is more complex. Yet the same kind of fluid mechanical analysis can be used for all types of mixers.

One of the most common problems facing a process engineer is how to transfer a product from a small laboratory mixer to a plant scale machine. Simple rules for scale-up can be extracted from the analyses of each mixer type based upon an understanding of the fundamental processes. These are treated in some detail for each mixer because of their importance in handling processing problems. Although the terminology used is that for scale-up, the same rules can easily be used for process control to reduce batch-to-batch variability. Essentially the rules tell how to set the operating variables for a mixer when the required conditions for good mixing of a material on the same or a different mixer are known.

The basic flow equations can also be used in their complete form for the model calculations on a computer to study basic mixer performance.

In the chapters that follow, a description of the basic flow processes is first developed. Then these are applied to commercially important mixers to obtain a quantitative description of their operation. These analyses form the basis of a rational, coherent description of rubber mixing which can be used for maching design, process control and process scale-up.

CHAPTER II

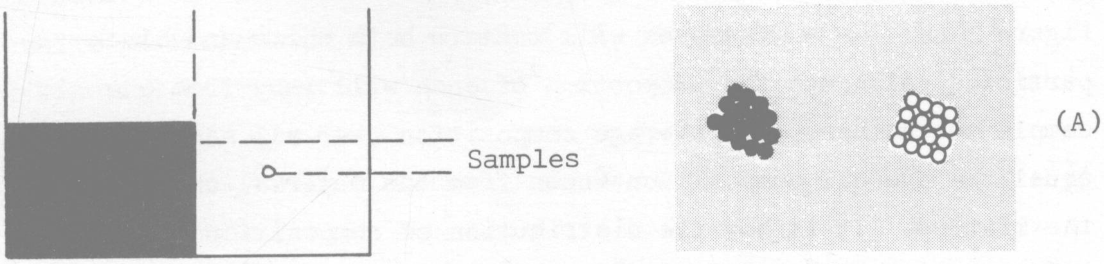
BLENDING OF PARTICLES

The blending of particulate solids without a phase change involves the spatial rearrangement of the particles without a change in particle size. A random distribution of the particles is usually sought and expected so that the concepts of probability and statistics can be used to describe the process. In this chapter quantitative methods for calculating the state of the mixture will be described followed by a discussion of the kinetics of mixing and the efficiency of mixer designs.

A. The Statistical Description of Mixing

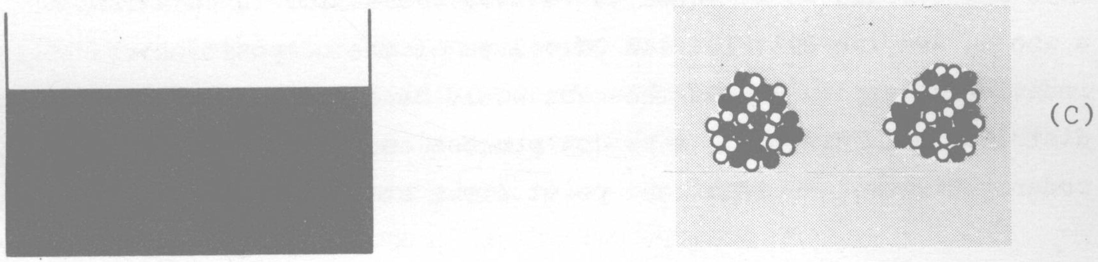
The quantitative evaluation of the state of a mixture, its degree of mixing and the kinetics of mixing is given by the statistical theory of mixing. Simple mixing, the process achieved by blending, can be understood by considering Figure 2.1. Initially the entire contents of the mixer or blender is partitioned into two sections, one of which contains only white particles and the other contains only black particles. Each particle is very small compared to the size of the apparatus and there is a large but finite number of each kind of particle. Consider then that a number of small samples are extracted from the apparatus from randomly selected positions in the mixture. Each sample thus selected will be large enough to contain a sufficient number of particles to treat using statistical methods but will be small enough to leave the mixture essentially unchanged. These requirements on sample selection can pose experimental problems for a practical application, but for the idealized mixture considered here, the conditions can be considered to be met. Several representative samples taken from the mixture, as suggested in Figure 2.1A, are shown enlarged in Figure 2.1B. The scale of mixing is the average distance separating one type of particle from a different type of particle {1}. Before the process commences, the scale of mixing in this example is larger than a sample size, Figure 2.1B, and is of the same order as the dimensions of the equipment. Except for a few samples which might be selected from the interface separating the two mixer regions, a sample from the starting material will contain either all white particles or all black particles.

At a later time after the mixing process has begun, some black particles have moved into the region initially occupied by white particles and some white particles have moved into the black zone, as in Figure 2.1C. The average distance between white and black particles, the scale of mixing, has been reduced. Again a random

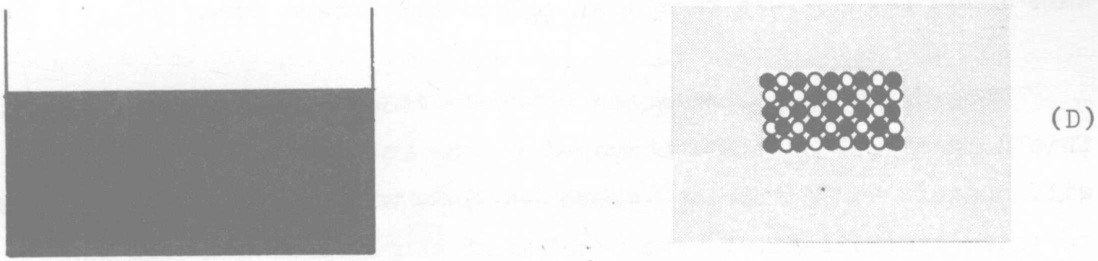


Segregated

Partially mixed



Randomly mixed



Not mixed

Figure 2.1: Simple mixing

selection of samples is extracted from the mixture as shown in Figure 2.1D. Now most samples will contain both white and black particles, although the proportion of each will vary from one sample to another. The average composition over all samples will equal the overall composition known from the material charged to the mixture. It is how the distribution of compositions of samples around the average value changes which is important for the description of mixing.

With further mixing, the black and white particles intermingle to a greater extent. In a good blender (as described later) a state of random mixing is ultimately reached. Now the probability of finding a particle of a given type at any particular point in the mixer is a constant which equals the proportion of that type of particle in the mix. If the composition of a number of random samples extracted from the mixture were measured, the mean value over all samples would equal the average value for the mixture as a whole, and the distribution of values of the composition of individual samples around the mean would be a binomial or equivalent distribution. Mixing is a random process and does not yield an orderly mixture, an important point first stated by Lacey {2}.

Although a number of workers were introducing the concepts of statistical analysis for the description of simple mixing at the same time, Beaudry was the first to quantify these ideas {3}.

Consider a sample selected randomly from the entire mixture. This sample will be small compared to the total mixer volume but will contain n particles, where n is a sufficiently large number to treat statistically. The problem of sample size and sampling errors is a standard problem in experimental design {4} and need not be discussed here. If the mixture contains two components, say black and white particles, then let p equal the fraction of white particles in the entire mixture. If the quantities of materials charged to the blender are known, then p is known. Then the probability P that a randomly selected sample has exactly x white particles out of a total of n particles is given by the binomial distribution [4-7]:

$$P\left(\frac{x}{n}\right) = \left(n!/x!(n-x)!\right) p^x (1-p)^{n-x} \qquad \ldots(2.1)$$

The average value of the concentration for a sufficiently large number of samples of sufficient and equal size is the mean of the population and equals p . If there are r samples, where r is a very large number, then the variance of the mixture is given by:

$$\sigma^2 = p(1-p)/r \qquad \ldots(2.2)$$

which is a measure of how the concentration can be expected to differ from the mean value.

Because only whole particles are in the sample, the measured values of concentration can only assume discrete values. The binomial distribution is a discrete-valued function and can therefore properly describe the sample composition. However, with the large number of sample particles, calculations using a discrete function can become tedious. If the conditions:

$$p < 0.5 \qquad \ldots(2.3)$$

and

$$rp > 5 \qquad \ldots(2.4)$$

are met, which define what is meant by a sufficiently large number of samples, then the distribution can be treated as continuous to a good approximation and the Gaussian distribution results:

$$f\left(\frac{x}{n}\right) = \frac{1}{\sigma(2\pi)^{\frac{1}{2}}} \exp\left(-\tfrac{1}{2}\left(\frac{x}{n} - p\right)^2/\sigma^2\right) \qquad \ldots(2.5)$$

where f is the probability that a sample has composition x/n . If the fraction of the component of interest p is small, then a better approximation to the binomial distribution is given by the Poisson distribution [4,5]:

$$f\left(\frac{x}{n}\right) = e^{-m} m^x / x! \qquad \ldots(2.6)$$

where $m = n\,p$.

In practice, a limited number of samples, each with a different number of particles, is counted. Then if r is the number of samples measured, the mean value of the sample concentration can be calculated:

$$\overline{\left(\frac{x}{n}\right)} = \sum_{i=1}^{r} \left(\frac{x}{n}\right)_i / r \qquad \ldots(2.7)$$

where $(x/n)_i$ is the measured particle fraction of the component of interest in sample i . The variance of the sample can be calculated:

$$s^2 = \sum_{i=1}^{r} \left[\left(\frac{x}{n}\right)_i - \overline{\left(\frac{x}{n}\right)}\right]^2 / (r-1) \qquad \ldots(2.8)$$

or equivalently:

$$s^2 = \left[r \sum_{i=1}^{r} \left(\frac{x}{n}\right)^2 - \left(\sum_{i=1}^{r} \left(\frac{x}{n}\right)_i\right)^2 \right] / r(r-1) \qquad \ldots(2.9)$$

The calculated values of the sample mean and variance can be used in two ways. As will be discussed in §B, the variance can be used to characterize the state of mixing for kinetic calculations. But first, this information can be used to answer the important question of how closely do the samples represent the mixture as a whole. The concentrations in individual samples would be expected to vary because of the random nature of the mixture, because of random sampling errors and because of random errors in measurement. The actual mean and variance of the population as a whole, that is the entire mixture, are unknown so some estimate must be made as to whether or not the measured values are those expected from samples taken from a random mixture. Statistical tests using confidence limits are used for this purpose. A related problem is to decide whether or not two mixtures with different measured values of the mean and variance can be considered to the the same or different, for which purpose significance tests may be used.

1. Confidence limits

Confidence limits express quantitatively the percentage of times the true but unknown values of the population mean or variance, that is the values of the complete mixture, will lie within a range of values based upon estimates made from a limited number of sample measurements. For example, using the Student's t-Test described below, the measured value of the average sample composition can be used to make a statement such as "nineteen times out of twenty, the true mean composition of the batch will be between 26% and 32% carbon black". Information of this type is used for calculations in processes downstream from the blending operation where there may be a limit on the maximum, minimum or range of compositions which will yield a satisfactory product.

a. *Confidence limits for the mean.* From the mean and variance calculated for r samples from equations (2.7), (2.8) and (2.9), the confidence limits of the population mean are calculated:

$$p = \overline{\left(\frac{x}{n}\right)} \pm t\,s/r^{\frac{1}{2}} \qquad \text{---(2.10)}$$

where p is the population mean. Values of t are tabulated in standard references[4,8]. For the desired confidence limits, usually 95% certainty, the value of t for the $r-1$ degrees of freedom are found in the appropriate table and substituted into equation (2.10), as shown in Example 1.

b. Confidence limits for the variance. Chi-squared (χ^2) tables[4,8] are used to calculate the confidence limits for the population variance in a similar manner. For r-1 degrees of freedom, two values are found in the table. First the value χ_1^2 is found which is so small that anything less than that would occur less than 2.5% of the time. Secondly, the value χ_2^2 is found which is so large that any value greater than that will occur less than 2.5% of the time. These correspond to probabilities $P = 0.025$ and 0.975 respectively. Then the chi-squared values will be within these limits 95% of the time and the population variance can be estimated:

$$\frac{rs^2}{\chi_2^2} < \sigma^2 < \frac{rs^2}{\chi_1^2} \qquad \text{...(2.11)}$$

as shown in Example 2. In addition to placing limits on the values of the mean and variance of the mixture as a whole, confidence limits test can be used to describe blender efficiency as presented in a later section.

2. Significance tests

Significance tests express quantitatively whether or not the set of samples has the same characteristics as some reference material. This reference material may be the composition required for processing downstream for quality control purposes in preparing new batches. The reference material may be a hypothetical perfectly random mixture having the same overall composition as the sample, or the reference material may be a laboratory-mixed sample when scaling large-size equipment.

Each of the significance tests is a "null hypothesis" test. First it is postulated that the reference and the sample material have exactly the same composition. Then a parameter is calculated based on the values of the mean and variance of the sample and on the known values of the reference. The calculated parameter is compared to