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Introduction

All polymer processes share one straightforward objective—to convert raw materials to finished products. However, this branch of technology is not as simple as it seems.

Tadmor and Gogos [1] pointed out that polymer processing is a multi-discipline. It involves different science and engineering principles. A successful conversion from raw materials to finished products will depend on our understanding of these principles. They suggested a comprehensive conceptual structural breakdown of this technology (Figure 1.1) to illustrate the inter- and intra-relationship of all the major subjects involved in this discipline.

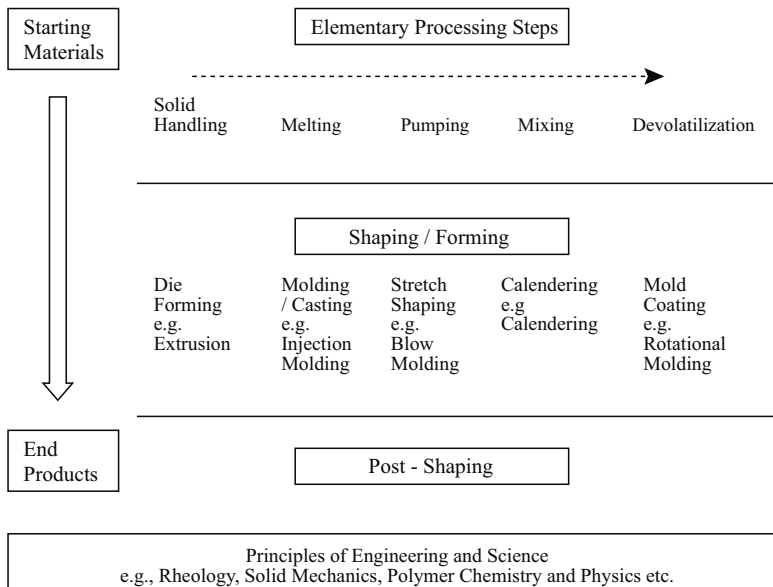


Figure 1.1 Conceptual structural breakdown of polymer processing suggested by Tadmor and Gogos [1]

It can be seen from Figure 1.1 that the conversion process was sequentially categorized into processes of:

elementary processing steps

shaping/forming methods

post-shaping

Common components within the category of elementary steps are *handling of particulate solids, melting, pressurization and pumping, mixing, and devolatilization and stripping*, regardless of the subsequent chosen shaping methods. Placing *handling of particulate solids* as the first required task in the elementary steps is well-justified, since almost all polymer processes start with raw materials in solid forms.

The comprehensiveness of the structural breakdown concept suggested by Tadmor and Gogos [1] is evident when tracking the “experience” that the solid raw materials have as soon as they are discharged into the hopper. Take blown film extrusion as an example. The homogenized solid raw materials will drop into the metal barrel as soon as they pass through the hopper throat. The solid materials will then be pushed (in the form of a solid plug) to the downstream by the combined effect of the rotation of the screw and the designed friction characteristics of the inner metal surfaces of the extruder. As the materials move forward, they will be compacted due to the decreasing clearance of the screw channels, causing the pressure to build up. This is a purposeful design to ensure that the compacted materials will be ready to melt at the compression/melting zone of the screw.

Melting of polymers is a slow process because polymers have low thermal conductivity and low thermal degradation. Thus, it is often a rate-determining processing step. Once molten polymer has accumulated inside the barrel, it will be continuously “pumped” by the rotating screw to travel further down. This transportation mechanism is different from the one that governs the transportation of the solid materials in the feeding zone of the screw. High pressure is generated instantaneously, which is needed for enhancing homogenization and effective subsequent shaping.

The processes of melting and pressurization may not necessarily be two distinct steps. There can be interactions between them. Therefore, as pointed out by Tadmor and Gogos [1], the two steps may occur simultaneously.

After pumping and pressurization, the next step is mixing. This is an important processing step because this is the last step in preparing the material for shaping. If the required mixing quality is not achieved at this mixing region, the quality of the finished products will inevitably be affected. It is worth mentioning that the purpose of this mixing step is not simply to obtain a physically well-homogenized mixture. It also serves the purpose of getting a mixture to have homogenized thermodynamic properties such as temperature.

If a polymeric system contains low molecular weight substances or substances of volatile properties, they must be expelled from the system prior to shaping once they have performed their expected functions. This practice forms the last component (i.e., *devolatilization and stripping*) in the suggested elementary steps.

Tadmor and Gogos [1] classified the different shaping methods adopted in the industry into *calendering and coating, die forming, mold coating, molding and casting, and stretch shaping*. These classifications were made based on the common required hardware and operation practice among the shaping methods. For example, the shaping devices in sheet extrusion, profile extrusion, pipe extrusion, etc., are all die-related. Therefore, they are grouped under the same classification of *die forming*.

Post-shaping essentially involves simple processes such as trimming, printing, punching, etc., which, in many cases, are relatively simpler and less complicated than the processes described above.

Figure 1.1 shows that elementary steps, shaping methods, and post-shaping processes are all firmly rooted in a number of science and engineering subjects. The principles of these subjects govern the conversion of raw materials to finished products. During the course of any conversion process, raw materials go through a series of phase changes, changing from solid to molten and back to solid again. These phase changes require a tremendous amount of work to be done on the system. For example, in the case of a single screw extruder running at a steady state, one rotation of the screw will need to perform all the elementary steps instantaneously. The efficiency of the screw in performing these designed functions greatly depends on our understanding of the principles of transport phenomena, rheological behavior, mixing characteristics, etc., and how these principles could be effectively applied in the hardware and process design considerations.

In the aviation industry, it is often said that a successful and smooth landing of a plane closely depends on how well the landing process is prepared beforehand. Similarly, a successful polymer manufacturing process is closely related to our understanding of the fundamental characteristics of the starting solid raw materials. The subsequent chapters of this book will systematically discuss these characteristics.

References

- [1] Tadmor, Z. and Gogos, C.G., *Principles of Polymer Processing*, 2nd Ed. (2006), Wiley, New Jersey

■ 3.2 Particle Size and Size Distribution

A bulk of particles is never of mono-size. It consists of particles of different sizes. In other words, it has a size distribution.

Table 3.1 shows a set of size data for 1,000 particles obtained by Seville et al. [2]. They noted that the data were determined by an unspecified measuring method. They used the data as an example to illustrate the basic way of presenting particle size. Columns A and B of Table 3.1 refer to the lower and upper limits of the chosen size range, whereas the data in column C are the number of particle counts corresponding to the chosen size range. The table is a typical presentation example of a “number distribution”. As pointed out by Seville et al. [2], although the simplest way to present the data in Table 3.1 is using a frequency histogram (Figure 3.2), such a presentation cannot provide a direct data comparison because column heights in a histogram depend on the width of the interval chosen. Therefore, it is more common to calculate the fractional count (f_i) (i.e., frequency, also known as frequency distribution function) in each chosen size range and then divided them by the interval width (x_i) to obtain the fraction per unit length, i.e.:

$$f_i = \frac{n_i}{N} \quad (3.1)$$

$$\text{Fraction per unit diameter length} = \frac{f_i}{x_i} \quad (= \text{column “D”}) \quad (3.2)$$

where

f_i = fractional count (i.e., frequency, also known as frequency distribution function)

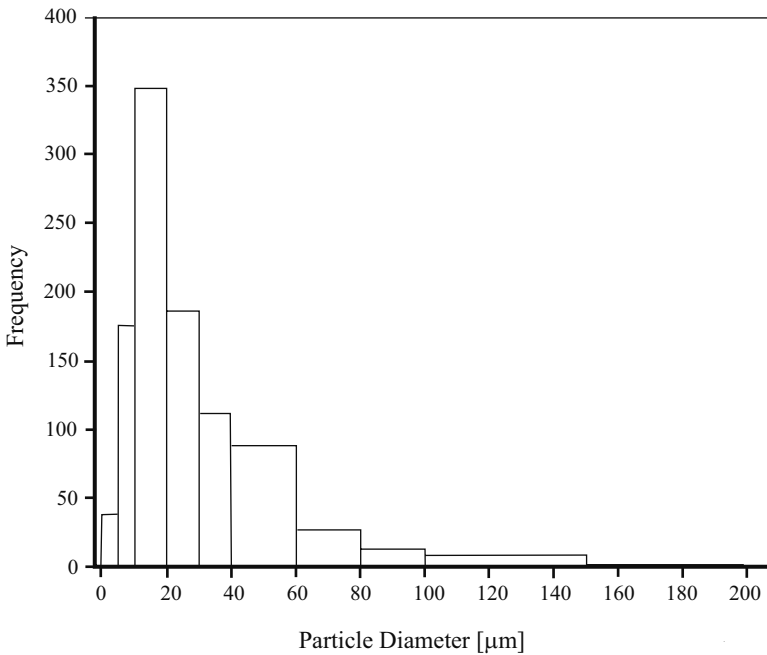
n_i = interval count

N = total number of counts

x_i = interval width

Table 3.1 Example of Particle Size Distribution (Seville et al. [2])

A	B	C	D	E	F
Diameter range (μm)		Count frequency	Fraction per μm	Percent	Cumulative percentage
Lower	Upper				
0	5	39	0.00780	3.9	3.9
5	10	175	0.03500	17.5	21.4
10	20	348	0.03480	34.8	56.2
20	30	187	0.01870	18.7	74.9
30	40	112	0.01120	11.2	86.1
40	60	89	0.00445	8.9	95.0
60	80	27	0.00135	2.7	97.7
80	100	13	0.00065	1.3	99.0
100	150	8	0.00016	0.8	99.8
150	200	2	0.00004	0.2	100.0
		Total: 1,000		Total: 100.0	

**Figure 3.2** Number frequency distribution (Seville et al. [2])

Referring to the 7th size class from the top of Table 3.1:

Lower size limit, $d_l = 60 \mu\text{m}$

Upper size limit, $d_u = 80 \mu\text{m}$

Therefore,

Interval width, $x_i = d_u - d_l = 80 - 60 = 20 \mu\text{m}$

Interval count, $n_i = 27$

Total number of counts, $N = 1,000$

From Equation 3.1:

$$\text{Fractional count, } f_i, (\text{i.e., frequency}) = \frac{27}{1000} = 0.027 \quad (3.3)$$

From Equation 3.2:

$$\text{Fraction per unit diameter length} = \frac{0.027}{20} = 0.00135 \mu\text{m}^{-1} \quad (3.4)$$

Following this simple calculation procedure, we can obtain the data shown in column D of Table 3.1 for each size class.

A more meaningful graphical presentation of the data is shown in Figure 3.3, wherein “frequency” is replaced with Fraction per unit length (i.e., column D). In this way, the area under each column of the histogram represents the fraction of the particle counts within their respective size intervals, and the summation of all the areas under each column must equal to 1.

That is,

$$f_i = \frac{n_i}{N} = h_i \cdot \Delta d_i \quad (3.5)$$

$$\sum f_i = \sum_i (h_i \cdot \Delta d_i) = 1 \quad (3.6)$$

where

h_i = height of the i th interval

Δd_i = interval width

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Solid-Solid Mixing

■ 4.1 Overview

Solid-solid mixing is not only a common industrial process, but it is also an important practice across many industrial sectors. Plastics processing is an industry that relies heavily on the application of mixing technology.

Solid plastic resins are rarely used alone in any shaping processes because they generally cannot satisfy all the designed requirements by themselves. Over the years, adding regrinds, fillers, and additives, etc., into the virgin plastic resins has become an effective and simple method to meet the required product and process objectives, including cost reduction. The degree of mixing quality of the solid components involved in a polymeric system has proven to be an essential factor closely related to the quality of finished products.

Despite being one of the oldest industrial technologies, solid-solid mixing is still one of the least understood of these technologies. Its development has been slow and complicated due to the intricacies of the multifarious physical characteristics (e.g., particle size and shape that were discussed in the previous chapter) of the involved solid particles. Research efforts in this branch of science have not been able to generate breakthroughs that are transferrable into many daily industrial practices. Thus, many of the complexities of solid mixing are still not understood.

Using techniques for mixing liquids on solid mixing systems has been a general industrial habit for years. However, techniques that are successfully applied to liquid mixing are often found to be almost entirely unsuitable for solid mixing. For example, whereas stirring or shaking are both commonly used methods for effective liquid mixing, applying these processes to solid particles fails to yield a well-mixed solid system. In many situations, they may even cause solid segregation to occur. The main cause for the different mixing behavior between liquids and solids lies in the difference in the mobility of the substance involved. Solids' mobility is poorer than that of liquids, resulting in poor mixing rate and, thus, poor mixing performance.

A variety of mixing device designs are available that meet different mixing requirements. However, this does not mean that mixing mechanisms are well understood. There are still fundamental misconceptions about mixing mechanisms that are prevalent in industries. Some misconceptions include:

1. the longer the mixing time, the better the mixing quality, and
2. mixing quality is independent of the types of mixers chosen.

Quantification of the degree of mixing (or mixing quality) of particulate systems can be comprehensively achieved by the use of statistics concepts. This chapter will therefore discuss basic statistic treatments on mixing quality, mixing mechanisms and selection of a mixer for a specific mixing job.

■ 4.2 The Statistical Assessment of Degrees of Mixing

When solids are mixed, the mixture obtained at the end of a mixing process belongs to one of the three possible types of mixtures: perfect mixture, random mixture, or segregating mixture. Figure 4.1 illustrates these three types of mixtures in a binary system.

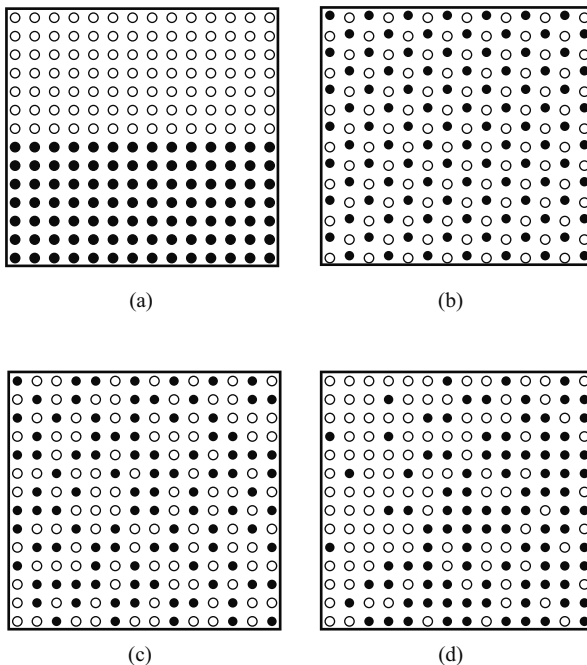


Figure 4.1

Graphical presentation of different types of mixture: (a) unmixed state; (b) perfect mixture; (c) random mixture; (d) segregating mixture

A perfect mixture is a mixture in which the proportions of its components drawn from any locations in the mixture are exactly same as their proportions in the bulk before it is mixed. A random mixture is a mixture in which the probability of finding the proportion of a component at any locations in the mixture is the same, and is also equal to the proportion of that particle component in the bulk as a whole before it is mixed. Perfect mixtures are the ideal mixtures but they can never be achieved in reality. In fact, random mixtures have the best mixing quality that one could possibly obtain. If the probability of a particle component of a bulk is found to be greater at a certain place in the mixture, then the mixture is classified as a segregating mixture.

For a binary system, if the true proportions of the two particle components are unknown, their estimated values can be determined by measuring the proportions of the particle components from a number of samples taken at various locations in the mixture.

Assuming the total number of samples extracted from the mixture at different places is N , and the proportions of one particle component (i.e., y) is $y_1, y_2, y_3, \dots, y_n$, then the estimated mean proportion of the particle component of interest (\bar{y}) can be calculated using Equation 4.1, i.e.,

$$\bar{y} = \frac{1}{n} \sum_{i=1}^n y_i \quad (4.1)$$

This simple estimate is not expected to give an answer close to the true mean proportion, μ , unless numerous samples are taken from the mixture for examination (i.e., $n \rightarrow \infty$). In this situation, \bar{y} is more representative, but the examination procedure may not be at all practical.

The true mean proportion of one particle component in a binary mixture, μ , can be estimated if (a) mixture samples can be taken from a random mixture at any positions, and (b) the proportions of the particle component of interest in the mixture sample exhibit a normal distribution. It follows:

$$\mu \in \bar{y} \pm t_{n-1} \frac{s}{\sqrt{n}} \quad (4.2)$$

where

t_{n-1} = critical value of Student's t at degrees of freedom $n - 1$, which can be found from standard statistical tables

s = standard deviation of the sample proportion

This equation gives the possible values of μ with a specific level of certainty.

The standard deviation of the proportions of the sample mixture, s , may be used as an indication of the mixing quality. Williams [1] pointed out that the lower the standard deviation, the narrower spread in the compositions of samples and, thus, the better the mixing.