

1 History, Structural Formulation of the Field Through Elementary Steps, and Future Perspectives

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Polymer processing is defined as the “engineering activity concerned with operations carried out on polymeric materials or systems to increase their utility” (1). Primarily, it deals with the conversion of raw polymeric materials into finished products, involving not only shaping but also compounding and chemical reactions leading to macromolecular modifications and morphology stabilization, and thus, “value-added” structures. This chapter briefly reviews the origins of current polymer processing practices and introduces the reader to what we believe to be a rational and unifying framework for analyzing polymer processing methods and processes. The chapter closes with a commentary on the future of the field, which is currently being shaped by the demands of predicting, a priori, the final properties of processed polymers or polymer-based materials via simulation, based on first molecular principles and multiscale examination (2).

1.1 HISTORICAL NOTES

Plastics and Rubber Machinery

Modern polymer processing methods and machines are rooted in the 19th-century rubber industry and the processing of natural rubber. The earliest documented example of a rubber-processing machine is a rubber *masticator* consisting of a toothed rotor turned by a winch inside a toothed cylindrical cavity. Thomas Hancock developed it in 1820 in England, to reclaim scraps of processed natural rubber, and called it the “pickle” to confuse his competitors. A few years later, in 1836, Edwin Chaffee of Roxbury, Massachusetts, developed the *two-roll mill* for mixing additives into rubber and the *four-roll calender* for the continuous coating of cloth and leather by rubber; his inventions are still being used in the rubber and plastics industries. Henry Goodyear, brother of Charles Goodyear, is credited with developing the *steam-heated two-roll mill* (3). Henry Bewley and Richard Brooman apparently developed the first ram extruder in 1845 in England (4), which was used in wire coating. Such a ram extruder produced the first submarine cable,

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laid between Dover and Calais in 1851, as well as the first transatlantic cable, an Anglo-American venture, in 1860.

The need for continuous extrusion, particularly in the wire and cable field, brought about the single most important development in the processing field—the *single screw extruder* (SSE), which quickly replaced the noncontinuous ram extruders. Circumstantial evidence indicates that A. G. DeWolfe, in the United States, may have developed the first screw extruder in the early 1860s (5). The Phoenix Gummiwerke has published a drawing of a screw dated 1873 (6), and William Kiel and John Prior, in the United States, both claimed the development of such a machine in 1876 (7). But the birth of the extruder, which plays such a dominant role in polymer processing, is linked to the 1879 patent of Mathew Gray in England (8), which presents the first clear exposition of this type of machine. The Gray machine also included a pair of heated feeding rolls. Independent of Gray, Francis Shaw, in England, developed a screw extruder in 1879, as did John Royle in the United States in 1880.

John Wesley Hyatt invented the thermoplastics injection-molding machine in 1872 (9), which derives from metal die-casting invented and used earlier. Hyatt was a printer from Boston, who also invented Celluloid (cellulose nitrate), in response to a challenge award of \$10,000 to find a replacement material for ivory used for making billiard balls. He was a pioneering figure, who contributed many additional innovations to processing, including blow molding. His inventions also helped in the quick adoption of phenol-formaldehyde (Bakelite) thermosetting resins developed by Leo Baekeland in 1906 (10). J. F. Chabot and R. A. Malloy (11) give a detailed history of the development of injection molding up to the development and the widespread adoption of the reciprocating injection molding machine in the late 1950s.

Multiple screw extruders surfaced about the same time. Paul Pfeleiderer introduced the *nonintermeshing, counterrotating twin screw extruder* (TSE) in 1881, whereas the *intermeshing* variety of twin screw extruders came much later, with R. W Eastons co-rotating machine in 1916, and A. Olier's positive displacement counterrotating machine in 1921 (12). The former led to the ZSK-type machines invented by Rudolph Erdmenger at Bayer and developed jointly with a Werner and Pfeleiderer Co. team headed by Gustav Fahr and Herbert Ocker. This machine, like most other co-rotating, intermeshing TSEs, enjoys a growing popularity. They all have the advantage that the screws wipe one another, thus enabling the processing of a wide variety of polymeric materials. In addition, they incorporate "kneading blocks" for effective intensive and extensive mixing. They also generally have segmented barrels and screws, which enables the machine design to be matched to the processing needs. There is a broad variety of twin and multiple screw mixers and extruders; some of them are also used in the food industry. Hermann (12) and White (7) give thorough reviews of twin screw and multiple screw extruders and mixers.

The first use of gear pumps for polymeric materials dates from Willoughby Smith, who, in 1887, patented such a machine fed by a pair of rolls (4). Multistage gear pumps were patented by C. Pasquetti (13). Unlike single screw extruders and co-rotating twin screw extruders (Co-TSE), gear pumps are positive-displacement pumps, as are the counter-rotating, fully intermeshing TSEs.

The need for mixing fine carbon black particles and other additives into rubber made rubber mixing on open roll mills rather unpleasant. A number of enclosed "internal" mixers were developed in the late 19th century, but it was Fernley H. Banbury who in 1916 patented an improved design that is being used to this day. The Birmingham Iron Foundry in Derby, Connecticut, which later merged with the Farrel Foundry and Machine of Ansonia, Connecticut, built the machine. This mixer is still the workhorse of rubber

processing, and is called the Banbury mixer after its inventor (14). In 1969, at Farrel, Peter Hold et al. (15) developed a “continuous version” of the Banbury called the Farrel Continuous Mixer (FCM). A precursor of this machine was the nonintermeshing, twin-rotor mixer called the Knetwolf, invented by Ellerman in Germany in 1941 (12). The FCM never met rubber-mixing standards, but fortunately, it was developed at the time when high-density polyethylene and polypropylene, which require postreactor melting, mixing, compounding, and pelletizing, came on the market. The FCM proved to be a very effective machine for these postreactor and other compounding operations.

The Ko-Kneader developed by List in 1945 for Buss AG in Germany, is a single-rotor mixer-compounder that oscillates axially while it rotates. Moreover, the screw-type rotor has interrupted flights enabling kneading pegs to be fixed in the barrel (12).

The ram injection molding machine, which was used intensively until the late 1950s and early 1960s, was quite unsuitable to heat-sensitive polymers and a nonhomogeneous product. The introduction of the “torpedo” into the discharge end of the machine somewhat improved the situation. Later, screw plasticators were used to prepare a uniform mix fed to the ram for injection. However, the invention of the *in-line* or reciprocating-screw injection molding machine, attributed to W. H. Willert in the United States (16), which greatly improved the breadth and quality of injection molding, created the modern injection molding machine.¹

Most of the modern processing machines, with the exception of roll mills and calenders, have at their core a screw or screw-type rotor. Several proposals were published for “screwless” extruders. In 1959, Bryce Maxwell and A. J. Scalora (17) proposed the *normal stress extruder*, which consists of two closely spaced disks in relative rotational motion, with one disk having an opening at the center. The primary normal stress difference that polymeric materials exhibit generates centripetal forces pumping the material inward toward the opening. Robert Westover (18) proposed a *slider pad extruder*, also consisting of two disks in relative motion, whereby one is equipped with step-type pads generating pressure by viscous drag, as screw extruders do. Finally, in 1979, one of the authors (19) patented the *co-rotating disk processor*, which was commercialized by the Farrel Corporation under the trade name Diskpack. Table 1.1. summarizes chronologically the most important inventions and developments since Thomas Hancock’s rubber mixer of 1820. A few selected inventions of key new polymers are included, as well as two major theoretical efforts in formulating the polymer processing discipline.

A Broader Perspective: The Industrial and Scientific Revolutions

The evolution of rubber and plastics processing machinery, which began in the early 19th century, was an integral part of the great Industrial Revolution. This revolution, which transformed the world, was characterized by an abundance of innovations that, as stated by

1. William Willert filed a patent on the “in-line,” now more commonly known as the *reciprocating screw injection molding machine* in 1952. In 1953 Reed Prentice Corp. was the first to use Willert’s invention, building a 600-ton machine. The patent was issued in 1956. By the end of the decade almost all the injection molding machines being built were of the reciprocating screw type.

Albert (Aly) A. Kaufman, one of the early pioneers of extrusion, who established Prodex in New Jersey and later Kaufman S. A. in France, and introduced many innovations into extrusion practice, told one of the authors (Z.T.) that in one of the Annual Technical Conference (ANTEC) meetings long before in-line plasticating units came on board, he told the audience that the only way to get a uniform plasticized product is if the ram is replaced by a rotating and reciprocating screw. Aly never patented his innovative ideas because he believed that it is better to stay ahead of competition than to spend money and time on patents.

TABLE 1.1 The Chronological History of Processing Machines, and Some Other Key and Relevant Developments

Machine	Process	Inventor	Date	Comments
The 'Pickle'	Batch mixing	T. Hancock	1820	Reclaim rubber
Roll mill	Batch mixing	E. Chaffe	1836	Steam-heated rolls
Calender	Coating and sheet forming	E. Chaffe	1836	Coating cloth and leather
<i>Vulcanization of Rubber</i>		<i>Charles Goodyear</i>	<i>1839</i>	
Ram extruder	Extrusion	H. Bewly and R. Brooman	1845	
Screw extruder	Extrusion	A. G. DeWolfe	1860	Attributed to Archimedes for water pumping.
		PhoenixGummiwerke	1873	
		W. Kiel and J. Prior	1876	The most important machine for plastics and rubber
		M. Gray	1879	
		F. Shaw	1879	
		J. Royle	1880	
Injection molding	Injection molding	J. W. Hyatt	1872	Used first for Celluloid
Counterrotating, nonintermeshing twin screw extruder	Extrusion	P. Pfeleiderer	1881	
Gear pump	Extrusion	W. Smith	1887	Pasqueti invented the multistage gear pump.
<i>Bakelite</i>		<i>Leo Baekeland</i>		<i>First purely synthetic plastics</i>
Co-rotating, intermeshing twin screw extruder	Mixing and extrusion	R. W. Easton	1916	
The Banbury	Batch mixing	F. H. Banbury	1916	Developed for rubber mixing.
Counterrotating, intermeshing twin screws	Extrusion	A. Olier	1912	Positive displacement pump

<i>Nylon</i>									
<i>Low density polyethylene</i>									<i>At the DuPont Laboratories</i>
Knetwolf									<i>At the ICI Laboratories</i>
Ko-Kneader					Twin rotor mixing				
Triangular kneading blocks					Mixing and extrusion				
In-line reciprocating injection molding					Continuous mixing				Buss. AG
ZSK					Injection molding				Used in the ZSK extruders
									Replaced ram injection molding
					Continuous mixing and extrusion				Co-rotating intermeshing twin screw extruder with mixing elements
<i>First Systematic Formulation of Plastics Processing Theory</i>									<i>Mostly the DuPont team</i>
Transfermix					Continuous mixing				
Normal stress extruder					Extrusion				Single screw in a barrel in which screw-type channel is cut
Continuous ram extruder					Extrusion				Two disks in relative rotation
Slider-pad extruder					Extrusion				Reciprocating rams.
									Slider pads rotating on stationary disk
FCM					Continuous mixing				Continuous Banbury
Diskpack					Extrusion				Co-rotating disk processor

Landes (20) “almost defy compilation and fall under three principles: (a) the substitution of machines—rapid, regular, precise, tireless—for human skill and effort; (b) the substitution of inanimate for animate source of power, in particular, the invention of engines for converting heat into work, thereby opening an almost unlimited supply of energy; and (c) the use of new and far more abundant raw materials, in particular, the substitution of mineral, and eventually artificial materials for vegetable or animal sources.”

Central to this flurry of innovation was James Watt’s invention of the modern steam engine, in 1774. Watt was the chief instrument designer at the University of Glasgow, and he made his great invention when a broken-down Thomas Newcomen steam engine, invented in 1705 and used for research and demonstration, was brought to him. This was a rather inefficient machine, based on atmospheric pressure acting on a piston in a cylinder in which steam condensed by water injection created a vacuum, but it was the first man-made machine that was not wind or falling-water driven. Watt not only fixed the machine, but also invented the modern and vastly more efficient steam engine, with steam pressure acting on the system and the separate condenser.

The great Industrial Revolution expanded in waves with the development of steel, railroads, electricity and electric engines, the internal combustion engine, and the oil and chemical industries. It was driven by the genius of the great inventors, from James Watt (1736–1819) to Eli Whitney (1765–1825), who invented the cotton gin, Samuel Morse (1791–1872), Alexander Graham Bell (1847–1922), Thomas Alva Edison (1847–1931), Guglielmo Marchese Marconi (1874–1937), Nikola Tesla (1856–1943), and many others. These also included, of course, J. W. Hyatt, Leo Baekeland, Charles Goodyear, Thomas Hancock, Edwin Chaffe, Mathew Gray, John Royle, and Paul Pfleiderer who, among many others, through their inventive genius, created the rubber and plastics industry.

The Industrial Revolution, which was natural resource- and cheap labor-dependent, was ignited in the midst of an ongoing scientific revolution, which started over two centuries earlier with Nicolas Copernicus (1473–1543), Galileo Galilei (1564–1642), Johannes Kepler (1571–1630), René Descartes (1596–1650) and many others, all the way to Isaac Newton (1642–1727) and his great *Principia* published in 1687, and beyond—a revolution that continues unabated to these very days.

The two revolutions rolled along separate tracks, with little interaction between them. This is not surprising because technology and science have very different historical origins. Technology derives from the ordinary arts and crafts (both civilian and military). Indeed most of the great inventors were not scientists but smart artisans, technicians, and entrepreneurs. Science derives from philosophical, theological, and speculative inquiries into nature. Technology is as old as mankind and it is best defined² as our accumulated knowledge of making all we know how to make. Science, on the other hand, is defined by dictionaries as “a branch of knowledge or study derived from observation, dealing with a body of facts and truths, systematically arranged and showing the operation of general laws.” But gradually the two revolutions began reinforcing each other, with science opening new doors for technology, and technology providing increasingly sophisticated tools for scientific discovery. During the 20th century, the interaction intensified, in particular during World War II, with the Manhattan Project, the Synthetic Rubber (SBR) Project, the development of radar, and many other innovations that demonstrated the

2. Contrary to the erroneous definitions in most dictionaries as “the science of the practical or industrial arts or applied science.”

power of science when applied to technology. In the last quarter of the century, the interaction between science and technology intensified to such an extent that the two effectively merged into an almost indistinguishable entity, and in doing so ignited a new revolution, the current, ongoing scientific–technological revolution. This revolution is the alma mater of high technology, globalization, the unprecedented growth of wealth in the developed nations over the past half-century, and the modern science and technology–based economies that are driving the world.

The polymer industry and modern polymer processing, which emerged in the second half of the 20th century, are very much the product of the merging of science and technology and the new science–technology revolution, and are, therefore, by definition high-tech, as are electronics, microelectronics, laser technologies, and biotechnology.

1.2 CURRENT POLYMER PROCESSING PRACTICE

The foregoing historical review depicted the most important machines available for polymer processing at the start of the *explosive* period of development of polymers and the plastics industry, which took place after World War II, when, as previously pointed out, science and technology began to merge catalytically. Thus, the Rubber and Plastics Technology century of 1850–1950 in Table 1.2 (2a), characterized by inventive praxis yielding machines and products, which created a new class of materials and a new industry, came to a close. In the half-century that followed, “classical” polymer processing, shown again in Table 1.2, introduced and utilized engineering analysis and process simulation, as well as innovation, and created many improvements and new developments that have led to today’s diverse arsenal of sophisticated polymer processing machines and methods of processing polymers and polymer systems of ever-increasing complexity and variety. As discussed later in this chapter, we are currently in transition into a new and exciting era for polymer processing.

A snapshot of the current status of the plastics industry in the United States, from the economic and manufacturing points of view, as reported by the Society of Plastics Industries (SPI) for 2000 (21), shows that it is positioned in *fourth* place among manufacturing industries after motor vehicles and equipment, electronic components and accessories, and petroleum refining, in terms of shipments. Specifically:

1. The value of polymer-based products produced in the United States by polymer (resin) manufacturers was \$ 90 billion. This industry is characterized by a relatively small number of very large enterprises, which are either chemical companies, for which polymer production is a very sizable activity (e.g., The Dow Chemical Company), or petrochemical companies, for which, in spite of the immense volume of polymers produced, polymer production is a relatively minor activity and part of vertically integrated operations (e.g., ExxonMobil Corporation).
2. The value of finished plastics products shipped by U.S. polymer processors was \$ 330 billion. Polymer processing companies are large in number and of small-to-medium size. They are specialized, have only modest financial and research resources, but are by-and-large innovative, competitive, entrepreneurial, and seemingly in constant forward motion, which is characteristic of the first period of development of the rubber and plastics industry.

TABLE 1.2 The Historical Evolution of Polymer Processing

Time Frame	1850–1950	1950–2000	Transition	Future
	Rubber and Plastics Technology	“Classical” Polymer Processing	Polymer Processing for Structuring	Macromolecular engineering
Focus	Product	Process and machine design (product)	Process and designed products	New products and structures
Scale	Machine invention	Machine	Product microstructuring	“Pushing the Limits”
Activity	Machine Industry Entrepreneurial	Product Corporate labs Academe Industry	Product micro (structure)	Product molecular microstructure
Discipline	Inventive Praxis	Transport phenomena GNF rheology Computational fluid mechanics	Academe Corporate labs Advanced compounders Transport phenomena Full rheology Melt/solids physics Interfacial phenomena Polymer chemistry In-line characterization Thermodynamics CHE, ME, CHEM, PHYS academe/industry Customized structure/properties Value-added materials New application fields	Gov/edu/com collaboration High-tech start-ups New industry Macromolecular physics, chemistry, rheology Multiscale transport and computations Molecular-scale probes Molecular biology Macromolecular engineers/scientists Truly advanced polymer materials New generation or globally applicable polymers
Profession	Technologists Inventors New Class of Materials New Industry	CHE, ME, CHEM industry/academe Ability to process very diverse polymers Large resin and processing industries > \$10 ¹² worldwide		
Benefits				

3. The U.S. labor force employed by resin producers is a quarter of million, and by polymer processors is a million and a half.

A lay-of-the-land presentation, in *flowchart* form, of the *thermomechanical experiences* of polymer systems in *processing equipment* used for important polymer processing manufacturing activities, is presented next. The aim is not only to inform but also to illustrate the *inherent commonality* of the thermomechanical experiences of polymer systems among the various types of equipment and operations used, which will help to *unify* and *structure* the understanding and analysis of polymer processing equipment and operations.

Postreactor Polymer Processing (“Finishing”) Operations

As is depicted in flowchart form in Fig. 1.1, the product of a gas-phase polymerization reactor produced in a typical polymer (resin) manufacturer’s plant at rates up to 40 t/h, is exposed to separation and drying steps to obtain pure polymer in particulate (powder) form. It is then dry mixed with a proprietary package of very low concentration additives—thermal, ultraviolet (UV), and oxidative stabilizers, as well as processing aids. The dry-mixed powder stream is metered into very large (mega) Co-TSEs or continuous melter/mixers (CMs), where the processes of *particulate solids handling* (PSH), *melting*, *mixing/homogenizing*, and *melt conveying* and *pressurization* must take place very rapidly, due to the high production-rate requirements.

This is the *first* thermomechanical experience of the reactor polymer, and it will *not be the last*. The equipment choice of Co-TSE or CM is made on the basis of the unique ability of these devices to cause very rapid melting and laminar mixing. We refer to the four processes just discussed as the *elementary steps of polymer processing*. The melt stream exiting the Co-TSE or the CM, both of which have poor melt pumping capabilities, is fed into very large gear pumps (GPs), which are positive displacement, accurate melt conveying/pumping devices. The melt is pumped into an underwater pelletizer with a

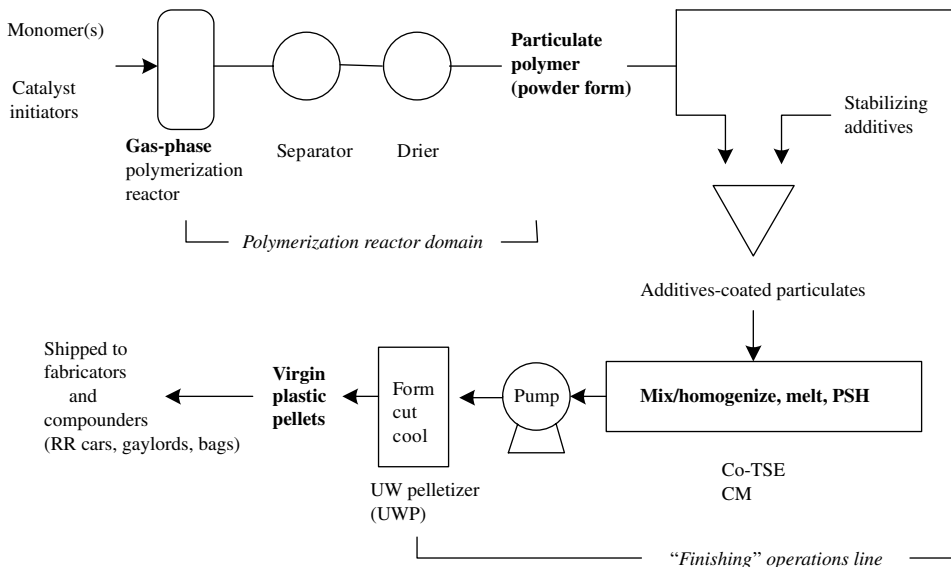


Fig. 1.1 Postreactor polymer processing (“finishing”) operations.

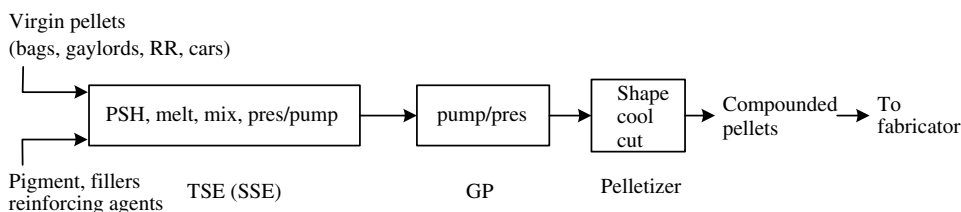


Fig. 1.2 Polymer compounding operations.

multihole die, where the exiting strands are cut into small pellets and cooled by the cold-water stream, which takes them to a water-polymer separator. The wet pellets are then dried and conveyed into silos; they are the “virgin” plastics pellets sold by polymer manufacturers to processing companies, shipped in railroad cars in 1000-lb gaylord containers or 50-lb bags.

Polymer Compounding Operations

The polymer compounding line is shown schematically in Fig. 1.2. Virgin pellets from resin manufacturers are compounded (mixed) with pigments (to form color concentrates), fillers, or reinforcing agents at moderate to high concentrations. The purpose of such operations is to improve the properties of the virgin base polymer, or to give it specialized properties, adding value in every case. The production rates are in the range of 1000–10,000 lb/h. The processing equipment’s critical task is to perform *laminar distributive* and *dispersive* mixing of the additives to the level required to obtain finished product property requirements. Furthermore, other additives, such as chopped glass fibers, are often fed after the compounding equipment has melted the pellets, in order to minimize degrading the attributes of the additives, such as fiber length. Finally, to assist the laminar mixing process, the additives may be surface-treated.

The processing equipment used by polymer compounders is mainly co-rotating and counterrotating TSEs, with occasional single-screw extruders (SSEs) in less demanding compounding lines. As is indicated in Fig. 1.2, the same elementary steps of polymer processing described previously in postreactor processing are performed by compounding equipment. The compounded stream is typically fed into a multihole strand die and the strands are first water cooled and then chopped to form pellets. The compounding operation exposes the reactor polymer to its second thermomechanical processing experience. The compounded product is shipped to fabricators of finished plastic products, commonly known as “processors.”

Reactive Polymer Processing Operations

Reactive polymer processing modifies or functionalizes the macromolecular structure of reactor polymers, via *chemical reactions*, which take place in polymer processing equipment after the polymer is brought to its molten state. The processing equipment then takes on an additional attribute, that of a “reactor,” which is natural since such equipment is uniquely able to rapidly and efficiently melt and distributively mix reactants into the very viscous molten polymers. The operation is shown schematically in Fig. 1.3.

The feed stream can be reactor polymer in powder form, which is then chemically modified (e.g., peroxide molecular weight reduction of polypropylene, known as

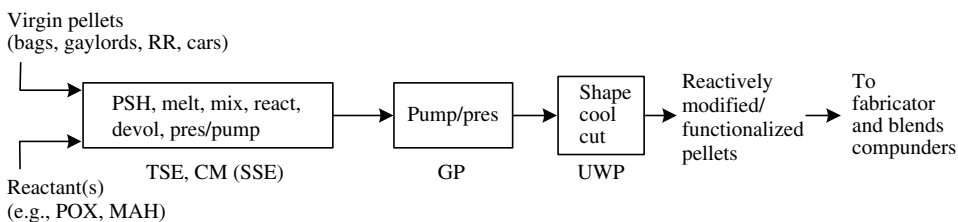


Fig. 1.3 Reactive polymer processing operations.

viscracking). Such reactive processing is usually carried out at high rates by resin manufacturers, and includes, after chemical modification and removal of volatiles, the incorporation of the proprietary additives package. Alternatively, the polymer feed stream is very often composed of virgin pellets, which undergo reactive modification such as functionalization (e.g., the creation of polar groups on polyolefin macromolecules by maleic anhydride).

As seen in Fig.1.3, here again the reactor-processing equipment used affects the same elementary steps of polymer processing as previously given, but now a *devolatilization* process to remove small reaction by-product molecules has been added. Because of the need for rapid and uniform melting and efficient distributive mixing (in order to avoid raising the molten polymer temperature), Co- and counterrotating TSEs as well as CMs are used, all of which can fulfill the reactive processing requirements for these elementary steps. Reactive processing, then, can either be the first or second thermomechanical experience of reactor polymers.

The reactively modified stream is then transformed into pellets, either by underwater or strand pelletizers. The pellets are again dried and shipped to plastic product fabricators, who need such specially modified macromolecular structures to fulfill product property requirements.

Polymer Blending (Compounding) Operations

These polymer processing (compounding) operations are employed for the purpose of creating melt-processed polymer *blends* and *alloys*. After the discovery of the major commodity and engineering polymers during the second to sixth decades of the 20th century, and as the cost of bringing a new polymer to market began to rise dramatically, both the polymer industry and academia focused on developing polymer blends with novel and valuable properties, in order to enlarge the spectrum of available polymers and to satisfy final plastic product property requirements in cost-effective ways. Thus, as is shown in Fig. 1.4, since about 1960, the increase in the number of commercially valuable polymer blends has powerfully driven the growth of the plastics industry and directly led to the rapid introduction of plastics in new and critical product application areas.

Turning to the polymer blending operations shown in Fig. 1.5, the feed stream consists of two or more polymers (virgin or reactively modified pellets) and a compatibilizer in small concentrations, which is necessary to create fine and stable polymer blend morphologies, since polymers are generally incompatible with each other. The processing equipment must quickly melt each polymer (concurrently or sequentially), and then rapidly and efficiently affect distributive and dispersive mixing of the melt components and the compatibilizer. Co- and counterrotating TSEs can satisfy these elementary steps that are important to blending operations.

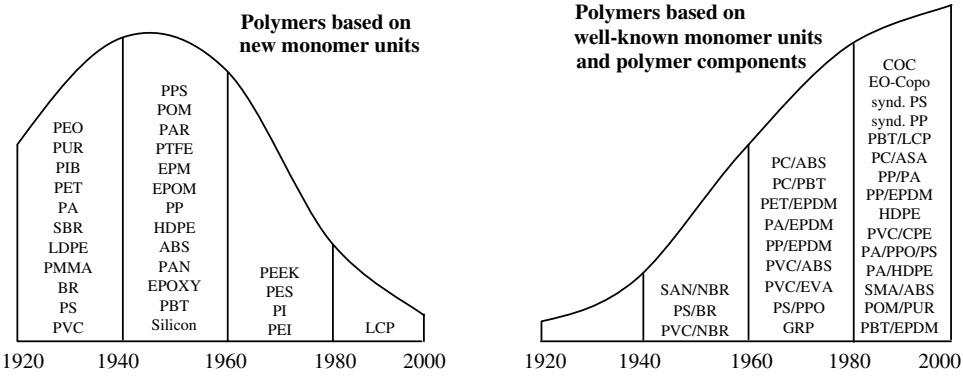


Fig. 1.4 A chronology of the discovery of polymers and their modification. [Courtesy of Prof. Hans G. Fritz of IKT Stuttgart, Stuttgart, Germany (2b).]

If the compatibilizer is reactive, the rapid and effective melting and mixing will establish the proper conditions for a uniform molten-phase reaction to take place. Thus, by employing TSEs, polymer processors (compounders or product fabricators) can create customized, “microstructured” polymer systems, which we have coined as “designer pellets” (22), to best serve the special product property needs of their customers; they are no longer solely dependent on polymer resin manufacturers.

The production rates and, thus, the equipment size, are large for resin manufacturers and moderate for compounders. We again see, that the polymer blend stream is exposed to the same elementary steps of processing and that, again, the choice of processing equipment used is based on which equipment can best perform the critical elementary steps. Finally, polymer blending operations expose the polymers to their second or perhaps third thermomechanical experience.

Plastics Product Fabricating Operations

In these operations, polymer processors fabricate finished plastics products starting from plastic pellets, which are the products of postreactor, compounding, reactive, or blending polymer processing operations. These pellets are processed alone or, in the case of producing colored products, together with a minor stream of color concentrates of the same polymer. As can be seen in Fig. 1.6, the elementary steps in the processing

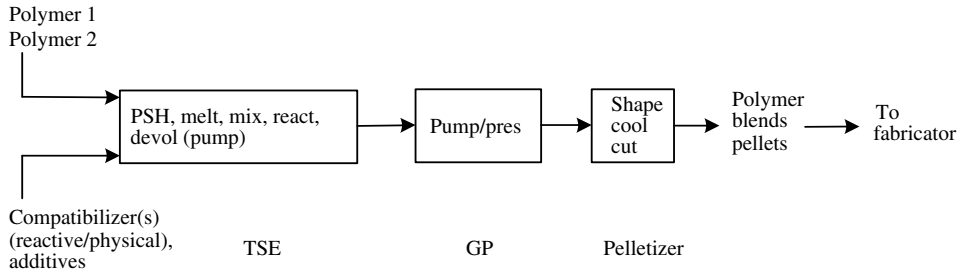


Fig. 1.5 Polymer blend formation operations.

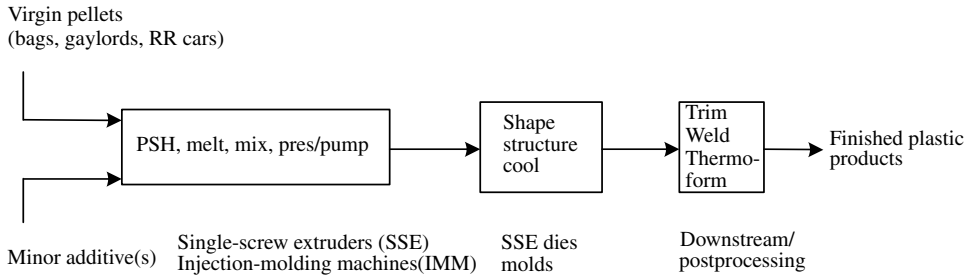


Fig. 1.6 Plastic product fabrication operations.

equipment used are again the same as given previously. In product fabrication operations, though, it is of paramount importance that the *pressurization* capabilities of the equipment be very strong, since we need a *melt pump* to form the shape of a plastic product by forcing the melt through a die or into a mold. Thus the equipment used by product fabricators are SSEs and injection molding machines, which have modest particulate solids handling, melting, and mixing capabilities, but are excellent melt pumps.

The molten stream of polymers flowing through dies or into cold molds is rapidly cooled to form the solid-product shape. As a consequence of the rapid cooling, some macromolecular orientations imparted during flow and near the product surfaces, where cooling first occurs, are retained. The retained orientations in plastic products impart specific anisotropic properties to the product and, in the case of crystalizable polymers, special property-affecting morphologies. The ability to affect the above is called *structuring* (23), which can be designed to impart extraordinarily different and beneficial properties to plastic products.

Structuring is also carried out in postshaping operations, mainly by stretching the solid formed product uni- or biaxially at temperatures appropriate to maximizing the retained orientations without affecting the mechanical integrity of the product.

In-Line Polymer Processing Operations

The polymer product fabrication operations may be either the second or third thermo-mechanical experience of the base polymer. Since polymers are subject to thermal degradation, and since there is a cost associated with each of the melting/cooling cycles, significant efforts are currently being made to develop what are called in the polymer processing industry, *in-line* processing operations. These operations and equipment sequentially conduct and functionally control any of the operations discussed earlier with plastic product fabrication at the end, thus allowing for a smaller degree of macromolecular and additive-properties degradation, and reducing the processing fabrication cost. The practice is relatively new, and has required the functional coupling and control of pieces of processing equipment that have distinctly different elementary step strengths: rapid, uniform, and efficient melting and mixing versus robust pressurization and accurate “metering” of the product stream. In-line polymer processing operations are shown schematically in Fig. 1.7.

From a plastics industry point of view, combining the various compounding, reactive processing and blending operations with the finished product fabrication operation, in a single line and under one roof, holds the potential for the product *fabricator* to become the

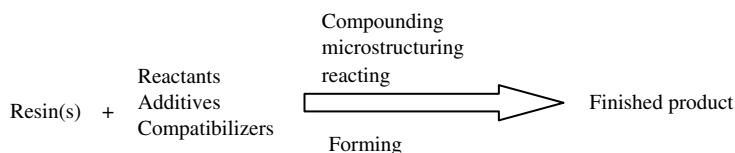


Fig. 1.7 In-line polymer processing operations (in-line compounding).

compounder as well. Furthermore, since fabricators are intimately involved with the properties needed by the finished product, they would be able to “fine-tune” the microstructuring of their polymer system to better meet the property needs of the products they are fabricating. Such capabilities will enable processors to respond to requests for customized polymer systems, that is, to satisfy “mass customization” needs of users of plastic products.

Additionally, there is clear evidence that a small number of resin manufacturers “will become more of enablers, creating new value-added businesses (of micro-structured polymer products) ever closer to the ultimate consumer” (2c). This translates into the planning by these companies for commercial expansion into compounding operations, widening the spectrum of their products, and further contributing to mass customization needs. Such developments and trends characterize the current “transition” phase of the polymer industry and of polymer processing, as depicted in Table 1.2. This period, it is hoped, will mark the gateway to a future where polymer processing will evolve into *macromolecular engineering*. We will briefly discuss this possibility in the last section of this chapter.

1.3 ANALYSIS OF POLYMER PROCESSING IN TERMS OF ELEMENTARY STEPS AND SHAPING METHODS

The field of polymer processing has been traditionally and consistently analyzed (24) in terms of the prevailing processing methods, that is, extrusion, injection molding, blow molding, calendering, mixing and dispersion, rotational molding, and so on. In analogy to chemical engineering,³ these processes have been viewed as the “unit operations” of polymer processing. At the time of the writing of the first edition of this text (24), when polymer processing was maturing into a well-defined and well-studied engineering discipline, we found it necessary to reexamine this classic way of analyzing the field, because the manner in which a field is broken down into its component elements has profound educational implications. A carefully worked out analysis should evolve into an abstract structure of the field that accomplishes the following objectives:

1. Focuses attention on underlying engineering and scientific principles, which are also the basis of the unifying elements to all processes.
2. Helps develop creative engineering thinking, leading to new, improved design.
3. Provides an overall view of the field, facilitating quick and easy assimilation of new information.

3. Systematic engineering analysis of chemical processes led to the definition of a series of “unit operations,” such as distillation, absorption, and filtration, which are common to different chemical processes (e.g., see W. L. McCabe and J. C. Smith, *Unit Operations in Chemical Engineering*, 2nd ed., McGraw-Hill, New York, 1967).

A quarter of a century later, and in retrospect, the analysis that we presented then, and that we discuss later, helped fulfill the previously defined objectives, and moved the field forward.

The Shaping Steps

The first step we take in our analysis of polymer processing is to clearly define its objective(s). In this case, the objective is undoubtedly *shaping polymer products*. The shaping operation can be preceded and followed by many manipulations of the polymer to prepare it for shaping, modify its properties, and improve its appearance. Nevertheless, the essence of polymer processing remains the shaping operation. The selection of the shaping method is dictated by product geometries and sometimes, when alternative shaping methods are available, by economic considerations. Reviewing the various shaping methods practiced in the industry, we can classify them in the following groups:

1. Calendering and coating
2. Die forming
3. Mold coating
4. Molding and casting
5. Stretch shaping

The first shaping method is a steady continuous process. It is among the oldest methods, and is used extensively in the rubber and plastics industries. It includes the classic calendering, as well as various continuous coating operations, such as knife and roll coating.

Die forming, which is perhaps the most important industrial shaping operation, includes all possible shaping operations that consist of forcing a melt through a die. Among these are fiber spinning, film and sheet forming, pipe, tube, and profile forming, and wire and cable coating. This is also a steady continuous process, in contrast to the last three shaping methods, which are cyclic.

The term “mold coating” is assigned to shaping methods such as dip coating, slush molding, powder coating, and rotational molding. All these involve the formation of a relatively thick coating on either the inner or the outer metal surfaces of the molds.

The next shaping method is molding and casting, which comprises all the different ways for stuffing molds with thermoplastics or thermosetting polymers. These include the most widely used shaping operations of injection molding, transfer molding, and compression molding, as well as the ordinary casting of monomers or low molecular weight polymers, and *in situ* polymerization.

Finally, stretch shaping, as implied by the name, involves shaping of preformed polymers by stretching. Thermoforming, blow molding, stretch blow molding, and cold forming can be classified as secondary shaping operations. The first three are very widely used.

The complex rheological properties of polymeric melts play a dominant role in the shaping operations. Thus, the introduction of one of the most striking aspects of non-Newtonian behavior, that of shear-thinning (pseudoplasticity), has been successfully incorporated into the analysis of melt flow inside polymer processing equipment. Similarly, by applying the modern sophisticated tools of numerical methods, the incorporation of the elastic nature of the polymer is being carried out with increasing success, particularly in stretch shaping.

As mentioned earlier, during shaping and postshaping operations, a good deal of structuring, that is, retained macromolecular orientation and specific morphologies, can and is being imparted to the final plastic products. Structuring has long been understood to be of very significant technological importance. The detailed understanding of structuring requires the ability to quantitatively describe the flow of rheologically complex melts, heat transfer, nucleation, and crystallization under stress. Work in this area is now underway, as we discuss in the last section of the chapter.

The Elementary Steps

The polymer is usually supplied to the processors in a particulate form. Shaping of the polymer takes place only subsequent to a series of preparatory operations. The nature of these operations determines to a large extent the shape, size, complexity, choice, and cost of the processing machinery. Hence, the significance of a thorough understanding of these operations cannot be overemphasized. One or more such operations can be found in *all* existing machinery, and we refer to them as *elementary steps* of polymer processing.

There are five clearly identifiable elementary steps:

1. Handling of particulate solids
2. Melting
3. Pressurization and pumping
4. Mixing
5. Devolatilization and stripping

Defining “handling of particulate solids” as an elementary step is justified, considering the unique properties exhibited by particulate solids systems. Subjects such as particle packing, agglomeration, consolidation, gravitational flow, arching, compaction in hoppers, and mechanically induced flow must be well understood to ensure sound engineering design of processing machines and processing plants.

Subsequent to an operation involving solids handling, the polymer must be melted or heat softened prior to shaping. Often this is the slowest, and hence the *rate-determining* step in polymer processing. Severe limitations are imposed on attainable melting rates by the thermal and physical properties of the polymers, in particular, the low thermal conductivity and thermal degradation. The former limits the rate of heat transfer, and the latter places rather low upper bounds on the temperature and time the polymer can be exposed. On the other hand, beneficial to increasing the rate of melting is the very high polymer melt viscosity, which renders dominant the role of the viscous energy dissipation (VED) heat-source term. Plastic energy dissipation (PED) (25,26) arising from the compressive and shear deformation of compacted polymer solid particulates in twin rotor equipment, such as Co-TSEs, is such a powerful heat source that it may result in nearly instant melting. All these factors emphasize the need to find the best geometrical configuration for obtaining the highest possible rates of melting, and for determining the processing equipment needed for rapid and efficient melting.

The molten polymer must be pumped and pressure must be generated to bring about shaping—for example, flow through dies or into molds. This elementary step, called *pressurization and pumping*, is completely dominated by the rheological properties of polymeric melts, and profoundly affects the physical design of processing machinery. Pressurization and melting may be simultaneous, and the two processes do interact with

each other. Moreover, at the same time, the polymer melt is also mixed by the prevailing laminar flow. Mixing the melt distributively to obtain uniform melt temperature or uniform composition (when the feed consists of a mixture rather than a single-component polymer), “working” the polymer for improving properties, and a broad range of mixing operations involving dispersive mixing of incompatible polymers, breakup of agglomerates, and fillers—all these belong to the elementary step of “mixing.”

The last elementary step of devolatilization and stripping is of particular importance to postreactor compounding, blending, and reactive processing operations, although it also occurs in commonly used processes, for example, devolatilizing in vented two-stage SSEs. This elementary step involves mass transfer phenomena, the detailed mechanisms of which have been investigated in some depth since the publication of the first edition of this book, and therefore, unlike in the first edition, here we devote a full chapter to this step. Yet, more research is needed to fully elucidate this complex process.

This theoretical analysis of processing in terms of elementary steps, which considers the basic physical principles and mechanisms involved in each elementary step, has been helpful since its introduction, in gaining better insight into the currently used processing methods, encouraging further work on their mathematical formulations, and perhaps also stimulating creative engineering thinking on improved processing methods. It has helped provide answers not only to “how” a certain product works, but to “why” a product is made a certain way and, foremost, “why” a particular machine configuration is the “best” or the appropriate one to use. The latter question is indeed the essence of engineering. For these reasons we will maintain and add to this approach in this edition.

Structural Breakdown of Polymer Processing

The elementary steps, as well as the shaping operations, are firmly based on the principles of *transport phenomena*, *fluid mechanics* and *heat and mass transfer*, *polymer melt rheology*, *solid mechanics*, and *mixing*. These principles provide the basic tools for quantitatively analyzing polymer processing. Another fundamental input necessary for understanding polymer processing is the physics and chemistry of polymers. As we noted earlier, final product properties can be immensely improved by structuring.

Figure 1.8 schematically summarizes our approach to the breakdown of the study of polymer processing. Raw material is prepared for shaping through the elementary steps. The elementary steps may precede shaping or they may be simultaneous with it. Structuring takes place throughout these processes, and subsequent to them. Finally, postshaping operations for purposes other than structuring (printing, decorating, etc.) may follow.

Clearly, to be able to fully utilize the added degree of freedom for product design provided by structuring, a full understanding and computational handling of polymer chemistry, polymer rheology at a macromolecular level, and the physics of phase changes under stress fields and nonisothermal conditions has to be carried out. With advances in those fields and the exponential growth of available computing power, significant advances are already being made toward achieving specific processed product properties, not through trial and error, but process simulation (2d).

The conceptual breakdown of polymer processing dating back to the first edition of 1979, presented earlier, *remains the same*. Yet the field and the industry, in the current transition period, have been focusing on and growing through what used to be called compounding, and is now expanded from the simple dispersion and distribution of fillers in polymer melts, to encompass microstructure development and stabilization in

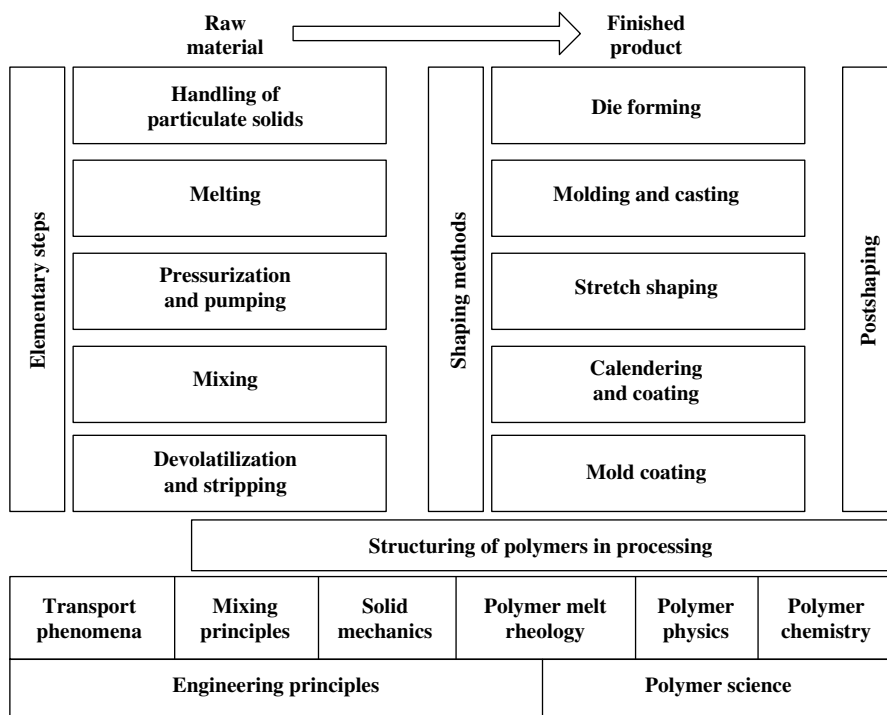


Fig. 1.8 Conceptual structural breakdown of polymer processing product fabrication operations (23).

immiscible, compatibilized, and reactive interphase multicomponent polymer systems of blends and alloys to create “designer pellets.” In this activity, the important elementary steps are rapid melting, affected mostly by PED and VED (that we referred to as dissipative mix-melting (23a, 25, 26)), rapid distributive and dispersive mixing created by extensional time-varying flows, and devolatilization, often occurring in the presence of reactions involving polymer melts. Co- and counterrotating TSEs, not shear-drag flow melting and pumping devices (e.g., SSEs), are the processing equipment used in these endeavors.

The conceptual breakdown in Fig. 1.9 (27) simply indicates the fact that in compounding, blending, and reactive processing, the base polymer(s) undergo two thermomechanical elementary-step experiences, and that the product of the first are value-added and microstructured pellets, while the second is used primarily for fabricating finished products. The important elementary steps for each experience, and the physical mechanisms that affect them, are different, because of the different objectives in each.

1.4 FUTURE PERSPECTIVES: FROM POLYMER PROCESSING TO MACROMOLECULAR ENGINEERING

In May 2002 an International Invited Workshop, attended by leading researchers in polymer processing and polymer engineering science, was convened in order to take stock of the historical evolution of the field of polymer processing, analyze current developments in research, take note of structural changes in the industry, and consider future trends. The underlying rationale, outlined in Appendix A of the final report (2), was

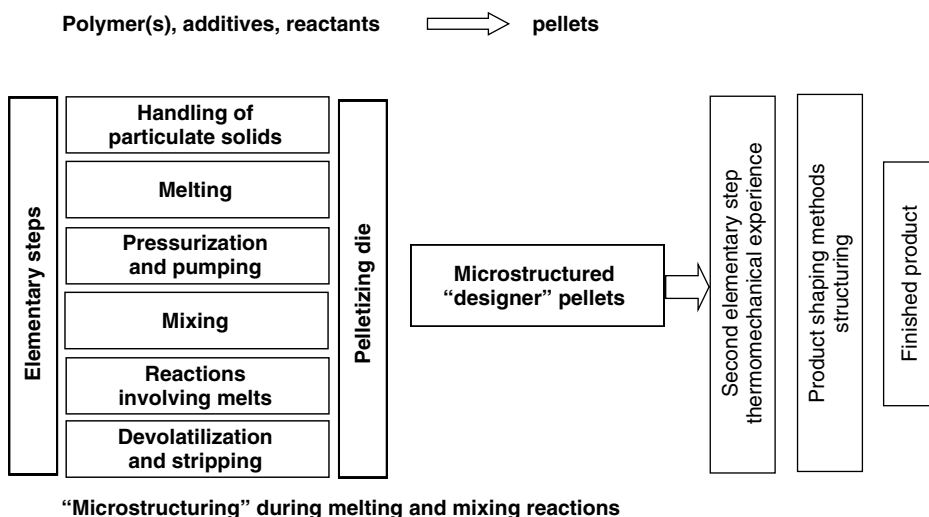


Fig. 1.9 Conceptual breakdown of polymer compounding, blending, and reactive polymer processing (27). Designer pellets are processed in extruders or injection molding machines to form products, with the possibility of further structuring or ‘destructuring’.

the proposition that this new and still evolving engineering discipline, propelled by the revolutionary developments in polymer physics, polymer chemistry, computational fluid mechanics, sophisticated novel instrumentation capabilities, modern catalysis, and developments in molecular biology, is diverging into a broad-based multidisciplinary activity, not unlike biotechnology and nanotechnology. Therefore, it is at a turning point.

Needless to say, for both authors working on this second edition, the workshop held the additional potential of providing a glimpse at the future development of the field. Thus, we present below some of the major topics of deliberation and conclusions of the workshop, drawing liberally from the text of the Final Report.

Central to the deliberations was to first outline in broad brush-strokes the knowledge so far acquired, and identify general areas where future research is needed. The guiding questions were: What do we know? What do we know that we don’t know? What do we need to know? What are the “boundaries” of the field? Which are the relevant disciplines needed for getting ahead in what increasingly appears to be a multidisciplinary field? And how can polymer processing become a strategic element in the “chain of knowledge”?

There was agreement among the participants that much has been accomplished in the past decades by classic polymer processing (Fig. 1.2). During this period, polymer processing focused on analyzing the major polymer processing equipment and processes (SSEs, TSEs, injection molding machines, blow molding machines, vacuum forming machines, calenders and roll mills, rotational molding machines, batch and continuous mixers, etc.). In doing so, the field grew and matured with the realization (as noted in Section 1.3) that there are common phenomena in the thermomechanical experiences of the material in the diverse polymer processing equipment and processes described earlier. This realization led to the elucidation and simulation of the detailed mechanisms and sequence of events that take place in these machines and in the continuous and cyclic shaping processes: flow of particulate solids; principles of melting of plastics in SSEs; principles of distributive, dispersive, and chaotic mixing;

principles and mechanisms of devolatilization; flow of non-Newtonian polymeric melts in complex conduits with moving surfaces using analytical, finite difference and finite element techniques; transient developing flows into cavities; wall stress-free one-, two- and three-dimensional flows as in fiber spinning, bubble formation, and complex blow molding operations, to name a few; degradation reactions in processing equipment, and so forth.

Not everything was elucidated to the same level and, as discussed in the following paragraphs, much remains to be done in classic polymer processing. The knowledge base developed so far was founded on, and rooted in, several disciplines, such as transport phenomena—including fluid mechanics, heat transfer and molecular diffusion of chemical species, non-Newtonian fluid mechanics, rheology (continuum and, to a lesser extent, molecular), resin thermophysical properties and state equations, classic mathematical techniques, and computational fluid mechanics, as well as polymer physics and thermodynamics. The focus of past research, as well as much of the current research, is on the *process* and the *scale of examination* of the *machine*, with the objective of developing optimized processes and improved machines.

During this period, relatively little emphasis was placed on the product and its microscopic and molecular structure, though there was rudimentary and semiquantitative treatment of what was termed *structuring* (2b, 23). Today, in some of the larger research-and-development centers, an important transition is being made, to focus on the product and its properties on the micro and molecular scale.

Areas on the process side identified as needing further research are:

- A better understanding of and advanced mathematical formulation of all the basic mechanisms under realistic machine conditions with a single polymeric feed or a mixture of them, with the goal of simulating the process as a whole;
- A fundamental and multidisciplinary understanding of melting of compacted polymer particulates under high deformation rates;
- A much deeper understanding of the details on how the process affects the structure on micro and molecular levels;
- Materials/machine interactions, three-dimensional viscoelastic behavior and stability of polymeric liquids;
- Transient flow and nonisothermal rheology;
- Nucleation and crystallization under stress;
- Molecular orientation phenomena;
- Reaction and polymerization under flow and deformation;
- Multiphase flows at high rates of strains;
- Heat, momentum, mass, entropy balances at “finite domain structure levels” of solids and liquids, during deformation, melting, and solidification;
- Thermodynamics of interfaces;
- Phase transition;
- Molecular models and modeling;
- Quantitative connection of structures and structure formation at the molecular and micro scale to final properties;
- Measurement techniques, including process in-line measurements, at the molecular and micro-scale levels to verify theories and predictions.

However, even the complete understanding of these areas will not suffice to reap the full benefits embedded in the macromolecular nature of polymeric materials, which are inherent in the naturally occurring and synthetic polymeric building blocks. For that, a priori quantitative prediction of product properties, made of yet nonexistent chains or combinations of chains of different monomeric building blocks from basic principles, requiring information of only the macromolecular structure and processing conditions, is needed.

Interesting comparisons were made to other fields, such as semiconductors, which cannot be produced without thorough knowledge at the quantum mechanics level and fine-tuned processing; multiscale computing in solids mechanics, in which microscopic behavior is being predicted from first principles on atomic scales; drug development with computer simulation screening of new molecules; modern catalysis and biocatalysts; and molecular biology with potential adaptation of self-assembly properties to other fields, such as biological microchips.

It was concluded that modern polymer processing, or rather *future* polymer processing (see Table 1.2), will focus not on the machine, but on the *product*. The long-range goal will be to predict the properties of a product made from a yet nonexistent polymer or polymer-based material, via simulation based on first molecular principles and multiple-scale examination. This approach, using increasingly available computing power and highly sophisticated simulation, might mimic nature by targeting properties via complex molecular architectural design. However, two important and key challenges have to be met successfully in order to achieve this goal: first, highly sophisticated simulations require highly sophisticated molecular models, which do not exist at present; second, a far more detailed understanding of the full and complex thermomechanical history that transpires in the polymer processing machine is needed. Then, such analysis will lead not only to new products, but will also improve existing machines or even lead to radically new machines; nevertheless, the focus will remain on the product. The goal is to engineer new and truly advanced materials with yet unknown combinations of properties, which might open up a new “golden age” for the field, reminiscent of the 1950s, 1960s, and 1970s, when most of the currently used polymers were developed.

Thus, the terms “polymer processing,” “polymer engineering,” or “plastics engineering” have become too narrow and confining, and a more accurate description of the emerging new field ought to be *macromolecular engineering*. As noted earlier, the new field is inherently *multidisciplinary* in nature, and if it is to be developed at a world-class level, requires close collaboration between many disciplines of science and engineering. Hence, the emphasis must shift from the individual researcher to large team efforts, this having profound consequences to academic research, as well as academic departmental boundaries. Real progress will only be possible by pooling substantial resources, and the allocation of these significant resources should be facilitated by vision, planning, and a comprehensive alliance between government, academia, and industry.

Macromolecular engineering is part of a broader scene. On the very fundamental level, its boundaries merge with molecular biology, on the one hand, and the growing field of complex fluids, that grows out of chemistry, physical chemistry, physics, and chemical engineering, on the other hand. The preceding, in turn, has profound educational implications, pointing to the possible creation of an entirely new and unified underlying discipline, and a basic undergraduate curriculum in *molecular, macromolecular and supramolecular engineering*, leading to specialization in *chemical molecular engineering* (currently chemical engineering), *macromolecular engineering* (currently polymer processing and engineering), and *biomacromolecular engineering* (currently

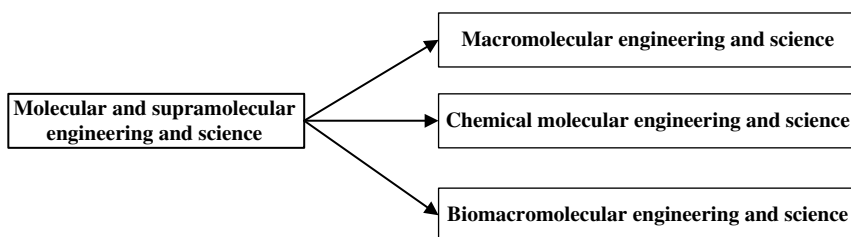


Fig. 1.10 A curricular structure discussed during the Touchstones of Modern Polymer Processing workshop, where a novel discipline called *Molecular and Supramolecular Engineering and Science*, becomes the initial, common core of macromolecular, chemical molecular, and Biomacromolecular engineering.

biochemical engineering or biotechnology). Such a curricular structure is depicted in Fig. 1.10.

Recently, Jos Put, discussed (28) the very enlightening view of J. L. Atwood et al. (29) on the nature of molecular biology and synthetic chemistry, shown in Fig. 1.11. Nature has achieved a tremendous level of complexity and control in living organisms, with a limited number of building blocks; synthetic (polymer) chemistry has used a much more diverse number of building blocks and achieved only limited, controlled structural complexity. Nature is able to do this by supreme control on the molecular level (MW, MWD, sequence, tacticity, etc.), by ordering on the nanolevel, and by perfect macroscopic design. On the other hand, macromolecular synthetic chemistry has made great strides by utilizing chemical species diversity, while achieving very modest controlled structural complexity. Biotechnology has begun to broaden the chemical diversity of bioapplicable systems, and synthetic nano chemistry is achieving remarkable controlled complexity at the nano level, utilizing and offering structurally ordered platforms to macromolecules. Thus, the merging of the boundaries of macromolecular engineering and molecular biology offers formidable potential for new materials and products. This is depicted by the 45° vector direction in Fig. 1.11.

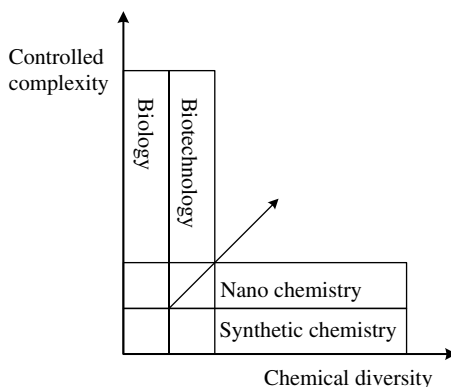


Fig. 1.11 The diagram used by J. L. Atwood et al. (29), to depict the differences between synthetic chemistry and biology in terms of the “building blocks” used and the attained structural controlled complexity.

Macromolecular engineering from the research point of view is clearly a broad-based multidisciplinary field. Consequently, the research scene and practices, in particular in academia, require restructuring. The classic “individual faculty member–graduate student(s)” model is expected to be replaced by the large, multidisciplinary team model, because, as pointed out earlier, only these larger teams can be expected to conduct groundbreaking research. Such teams should consist of several senior faculty members in the needed disciplines, co-advising several graduate students as well as trained professionals who deal with advanced instrumentation, computing, data analysis, and literature searches.

It is perhaps worth adding that such large multidisciplinary groups already exist at leading centers of macromolecular engineering research. In fact, we are witnessing the first promising examples of a priori quantitative predictions of the solid product properties requiring information of only the macromolecular structure and processing conditions from such large multidisciplinary groups. For example, Han E. H. Meijer et al. at the Materials Technology, Dutch Polymer Institute, Eindhoven University of Technology (30,31) proposed such an a priori prediction for the yield stress of polycarbonate (PC) specimens obtained under different molding conditions. Their work is based on defining a novel state parameter that uniquely determines the current state of amorphous solids and utilizes the classic constitutive model representation of such solids as presented by Haward and Thackray (32), who identified two contributions to the total stress: one that accounts for the rate-dependent plastic flow response attributed to intermolecular interactions on a segmental scale (33,34) and represented by a nonlinear Maxwell element (35), and the other that accounts for the strain-hardening contribution that is due to the macromolecular orientation of the entangled network using a neo-Hookean elastic model (36).

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