1

Polymer Blend Compounding and Processing

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1.1

Introduction and Early Studies of Blending

Humankind has been mixing together different materials since the dawn of written history to produce products with improved engineering properties. The term "Bronze Age" (which began around 3000 BC) indicated the blending of tin into copper to improve its mechanical performance. Concrete was also introduced by the ancients with similar purposes in mind.

The polymer industry as we know it dates only from the first part of the nineteenth century, where the major industrial polymers aside from wood were natural rubber (*cis*-1,4-polyisoprene) from Brazil, gutta-percha (*trans*-1,4-polyisoprene) from Singapore and Malaya from the 1840s, and natural fibers, including cellulose (cotton, linen) and protein (wool) fibers and leather. Many of the earliest patents involved coating fabrics and leather with natural rubber [1–6]. There was a gradual realization in this period of the usefulness, in terms of improving the properties or rubber, of introducing solid particulates [7–10] or chemicals such as sulfur and its compounds [10–13], which caused vulcanization/crosslinking.

It was only with the commercial appearance of gutta-percha in about 1845 [14–17] that there were investigations of polymer blends (gutta-percha with natural rubber). These were reported in patents of C. Hancock [17, 18], A. Parkes [13] and W. Brockedon and T. Hancock [19] in 1846. All of these inventors knew each other, Two were brothers (C. Hancock and T. Hancock) and two others (Brockedon and Parkes) were at the time business colleagues of the above T. Hancock. The patents cited above generally cite one or more of the others. This all took place in or near London, England.

The mixing processes are usually not critically discussed in these early patents. Brockedon and Hancock [19] indicate they used the single rotor masticating machine discussed in T. Hancock's earlier patents [6, 7]. One can conclude by reading their patents that C. Hancock and Parkes used the same or similar machines. Parkes [13] mentioned using rollers, perhaps similar to the machine of Chaffee's patent [5]. In addition, significant amounts of solvents derived from coal tar were used.

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Blending technology developed slowly. The third processable polymer of the nineteenth century was cellulose nitrate, developed by Schonbein [20] as an explosive. An 1855 patent by Parkes [21] describes the blending of natural rubber and gutta-percha with a solution of cellulose nitrate, and fabricating the resultant sheets for various applications.

Cellulose nitrate was a particularly difficult material to work with because it could only be shaped when in solution. We find Parkes [22, 23] a decade later dissolving cellulose nitrate into organic oils, introducing his sulfur dichloride invention into the mix for crosslinking. He also used vegetable oils [22] and blended in camphor [23]. Further efforts to produce cellulose nitrate–camphor compounds were made in 1869–1872 patents of Spill [24, 25] and the Hyatt Brothers [26, 27]. Camphor was useful because it was not volatile and did not evaporate like vegetable oils, leading to residual stresses in products.

Blends involving synthetic polymers were not developed until the twentieth century. The first synthetic high molecular weight polymers were developed by Farbenfabriken Bayer in the first two decades of the twentieth century. These were the first synthetic elastomers. Poly(dimethyl butadiene), widely used in Germany, was used in World War I (Section 1.3.1).

1.2
Methods of Compounding

1.2.1
Batch Mixers

1.2.1.1 Introductory

The earliest blends developed that we discussed in Section 1.1 were prepared in batch mixers, notably T. Hancock's (1820–1838) masticator (or "Pickle" [6, 28]) or Chaffee's (1836) two roll mill [5]. The two roll mill was widely manufactured by machinery companies in the USA and Europe. It became the primary method of preparing compounds in the (natural) rubber industry well into the second decade of the twentieth century [29, 30].

Single-screw extruders seem to have been introduced in the 1870s, but were primarily used for wire coating and profiles.

These were not the only mixing machines developed in the nineteenth century. The food industry, especially the baking industry, had needs for such machines. This led Paul Pfleiderer and Hermann Werner to undertake the manufacture of batch mixers for this purpose in Stuttgart in Germany about 1880 [31–33]. Werner & Pfleiderer GmbH was organized and developed and manufactured a batch mixer based upon a twin rotor design due to Paul Pfleiderer [34]. This was marketed as a "Universal Misch und Knet Maschine." This is shown in Figure 1.1 and is essentially a double rotor mixer open to the environment. Werner & Pfleiderer subsequently became an international company. They set up Werner & Pfleiderer, Ltd. in London and merged in 1893 with A. M. Perkins and Son of London (whose principal had

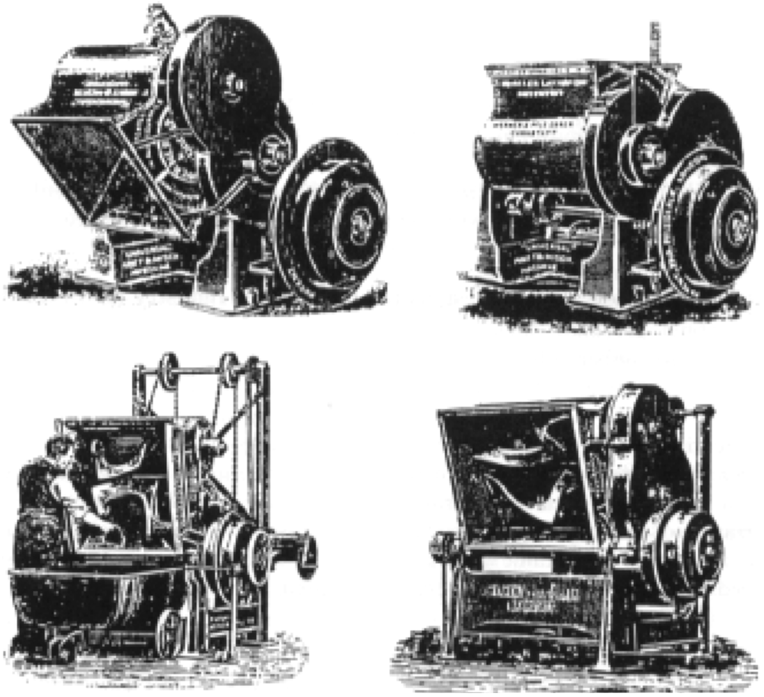


Figure 1.1 Werner & Pfleiderer 1895 Universal Misch und Knet Maschine.

recently died) to form Werner, Pfleiderer and Perkins [31, 33]. They then had manufacturing facilities in England and could trade within the British Empire.

This seems to have been masterminded by Paul Pfleiderer, who had already moved to England and would manage the company. Hermann Werner remained in Stuttgart. The Perkins family largely withdrew from this company.

In 1897, Werner & Pfleiderer GmbH, presumably together with Werner, Pfleiderer and Perkins, established a manufacturing facility in the United States in Saginaw, Michigan. They, however, lost both their English and American facilities in World War I.

1.2.1.2 **Non-intermeshing Rotor Mixers**

Werner & Pfleiderer sought to broaden their mixing activities beyond baking dough to industrial materials in general. The internal combustion engine based automobile had its origins in Stuttgart with Gottfried Daimler. The automobile would need tires, which would be largely made out of vulcanized rubber–small particulate compounds. Soon, rubber product manufacturers around the world were trying to produce tires for automobile manufacturers. Most of the mixing at first used large two roll mills [29, 30]. Werner & Pfleiderer GmbH then sought to develop an internal mixer for rubber compounding. It required sturdier rotors than those of Figure 1.1. Such an internal mixer was developed by Kempter [35, 36]. Figure 1.2 shows a 1910 Werner & Pfleiderer Universal Gummi Kneter [32].

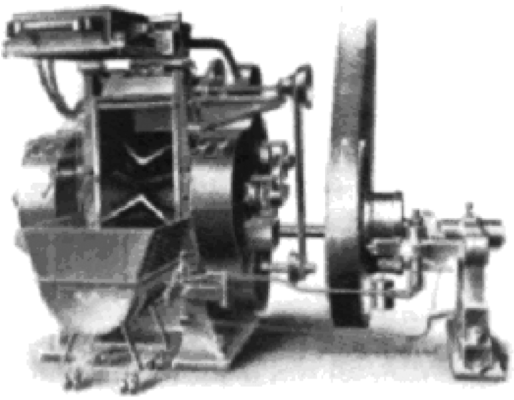


Figure 1.2 Werner & Pfleiderer 1910 Universal Gummi Kneter.

As Paul Pfleiderer had become ill in the late 1890s, he along with Hermann Werner decided that he would be replaced at Werner, Pfleiderer and Perkins by F. C. Ihlee. Pfleiderer's son Kurt also worked at the firm. Paul Pfleiderer died in 1903.

Werner, Pfleiderer and Perkins was also concerned with the new tire industry and its needs for mixing machines. D.H. Killheffer [30] describes Banbury's various meetings with Kurt Pfleiderer and of being convinced by him to join Werner & Pfleiderer in Saginaw, Michigan. Banbury was sent to Werner, Pfleiderer and Perkins' facility in Peterborugh, England, where he met with F.C. Ihlee and the chief engineer, J. H. Pointon. This was in late 1913. Banbury later stated that he designed a new set of rotors and these gave improved mixing performance [30]. The rotors were then patented by Pointon in his own name [37], to Banbury's dismay [30].

Banbury now returned to the USA and was soon visiting Werner & Pfleiderer customers. He found there were various problems, including the mixer being open to the atmosphere and the design of the rotors. The mixer's large opening not only lowered the ability of the rotors to mix the compound but allowed various chemicals in the compound, notably amine accelerators, to escape into the atmosphere and poison workers. Banbury saw that the introduction of a ram into the mixer's opening to push the rubber into the rotors would substantially improve the mixing and improve the safety of the workers. In the fall of 1915, he wrote a patent application on an internal mixer with a ram. However, the management of the Saginaw based Werner & Pfleiderer refused to file the application. Banbury then resigned from the firm.

Banbury filed his patent [38] in January 1916 in the United States and sought a new machinery manufacturer to support his efforts [30]. He found this support from the Wanning family and their Birmingham Iron Foundry of Ansonia, CT, to whom he assigned his patent. Banbury was able to negotiate that his name would be associated with the mixer as a trademark. The Banbury® Mixer was born. Banbury's patent drawing showing a mixing chamber with a ram is given in Figure 1.3 [38].

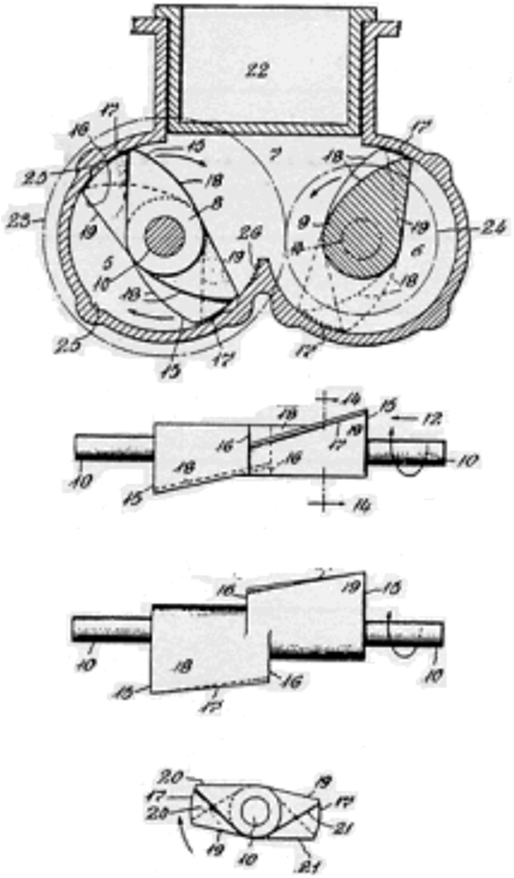


Figure 1.3 Banbury's 1915 US patent drawing showing a ram and mixing chamber. From Reference [38].

Banbury now worked out a more detailed design of his internal mixer, including the ram system, a mixing chamber with a bottom door and cooling channels, a feeding system, and take-off equipment for compounding rubber. These are described in several patent applications that were filed beginning in late 1916 [39–42]. Figures 1.4 and 1.5 show more comprehensive descriptions of Banbury's internal mixer design.

The Banbury mixer prospered through the 1920s, but not the Wanning family that owned the Birmingham Iron Foundry. In 1927, it was merged with Farrel Foundry and Machine to form Farrel Birmingham (later Farrel Inc.). They continued to manufacture the Banbury mixer [30].

1.2.1.3 Intermeshing Rotor Mixers

In the 1930s, there was a major innovation in the rubber industry with the invention of intermeshing rotor internal mixers. A June 1934 British patent

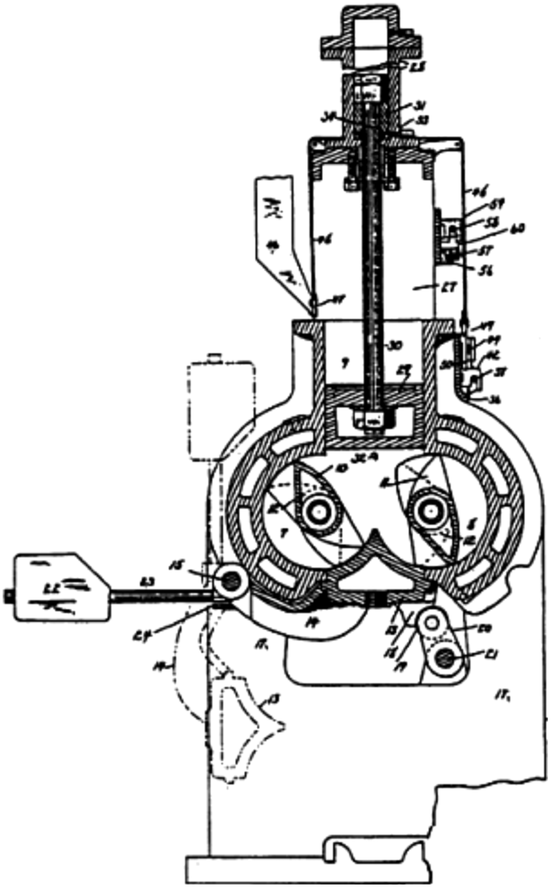


Figure 1.4 Banbury's November 18, 1916 US patent application drawing showing internal mixer ram system and mixing chamber with door. From Reference [39].

application by R.T. Cooke [43] described such a machine (Figure 1.6). High shear stresses were applied to the compounds between the rotors as well as between the rotor and the mixing chamber wall. The design of the remainder of the machine, which also has a ram, followed the ideas contained in Banbury's earlier patents [39–42]. An October 1934 German patent application of A. Lasch and E. Stromer [44] of Werner & Pfleiderer GmbH also has intermeshing rotors. The design of this machine has no ram. Cooke's intermeshing internal mixer was soon commercialized by Francis Shaw and Company as Shaw Intermix. In the years that followed, the Shaw Intermix and a similar intermeshing machine developed by Werner & Pfleiderer GmbH [45] obtained a major position in the rubber mechanical goods industry, especially in Europe, for products such seals, gaskets, and timing belts. The machines were not successful in the tire industry, where the lower mixing chamber volumes compared to Banbury's design were viewed unfavorably.

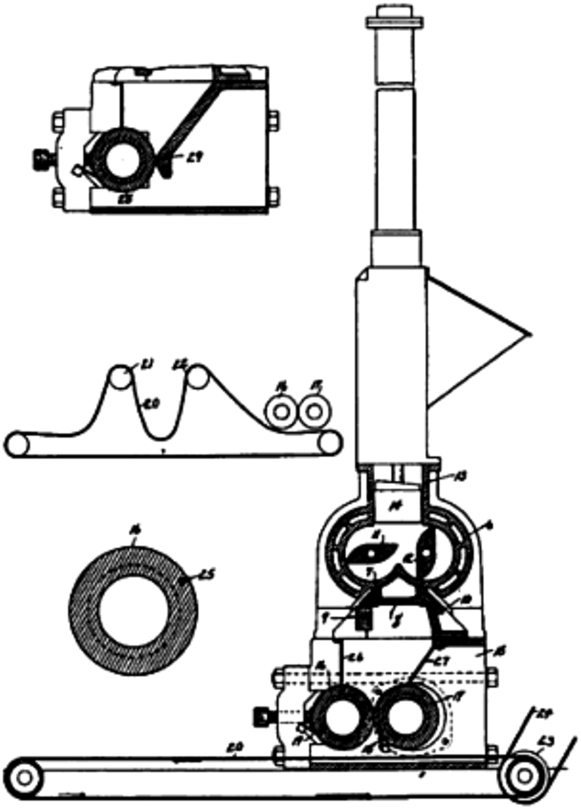


Figure 1.5 Banbury's January 31, 1921 US patent application drawing showing internal mixer with keep section, sheeting rolls, and continuous apron following discharge. From Reference [42].

1.2.1.4 **Post-World War II Development**

A new direction in the design of the separated rotor internal mixers came with the doubling of the number of flights on the rotors from two to four. This was first done by Lasch and Frei of Werner & Pfleiderer in an October 1939 patent application [46] (Figure 1.7a). A second four-flighted rotor design was contained in a January 1964 patent application of Tyson and Comper [47] of Goodyear (Figure 1.7b). This patent seems to have been licensed to Farrel-Birmingham/Farrel Inc. who then manufactured machines of this design. In the post-war period, Farrel Inc. set up new licensees in Asia and Europe. Kobe Steel of Kobe, Japan became a licensee in Asia and Pomini of Castellanza, Italy became a licensee in Europe. Both began manufacturing internal mixers of Farrel design. Kobe Steel and its largest customer, the Bridgestone Tire Company of Tokyo, concluded that the two-flighted and four-flighted Banbury mixer rotors were not of optimal design. In the 1970s, they carried out a joint research program that included flow visualization of a polymer solution with polystyrene beads in a transparent glassy poly(methyl methacrylate) internal mixer. The flight lengths and angles of the rotors were varied. This was described in a patent

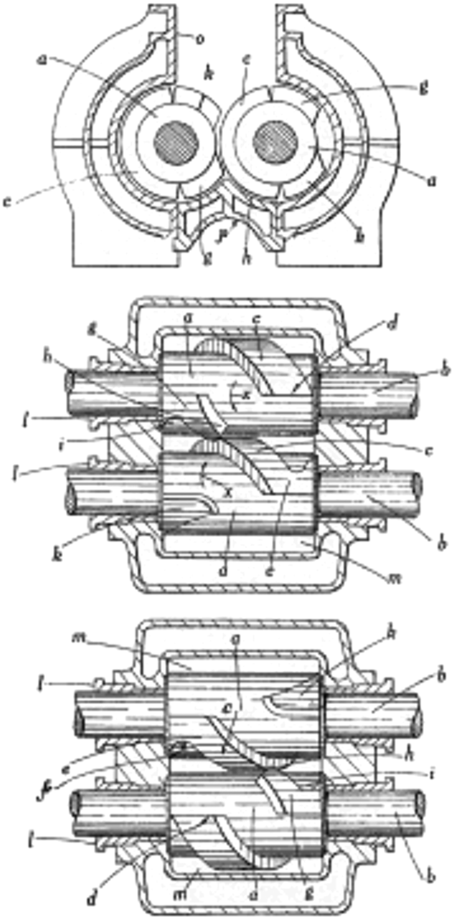


Figure 1.6 Cook's June 14 1934 British patent application drawing for an internal mixer with intermeshing rotor. From Reference [43].

application by N. Sato *et al.*, representing both Bridgestone and Kobe Steel, in a June 1979 US patent application [48] and by Kobe Steel's, Asai *et al.* in a subsequent presentation [49] at the International Rubber Conference in Paris in 1983 (Figure 1.7c). They concluded that the best results are obtained when the ratio of the lengths of the short to long flight are 0.15–0.3. However, ratios of greater than 0.4 are not recommended because longer flights are too dominant. Too much thrust load is created on the rotors in the chamber and this also leads to overheating. A second Sato *et al.* US patent application [50] is similar to the first one.

Other Kobe Steel patents followed. In a February 1981 US patent application, Inoue *et al.* [51] described a pair of juxtaposed double flighted rotors. In an August 1986, patent application Asai and Hagiwara [52] described a new double flighted rotor design. The intention was to increase the rotor tip flight clearance to values greater

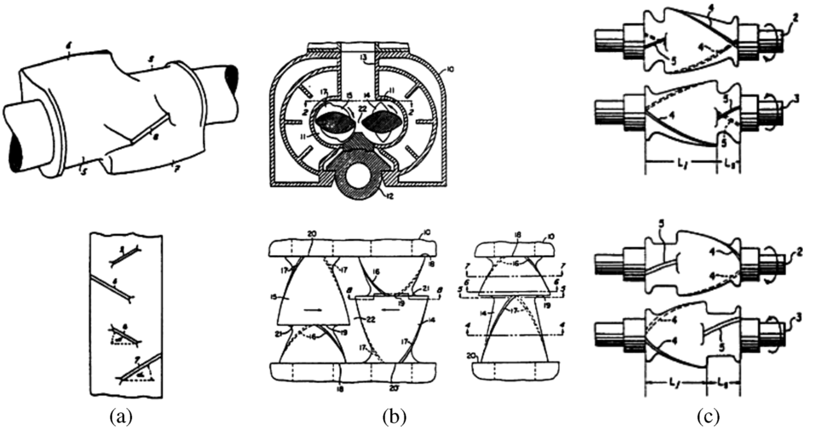


Figure 1.7 Four flighted non-intermeshing rotors: (a) Lasch and Frei 1938 design; (b) Tyson and Comper 1964 design; (c) Sato *et al.* 1979 design.

than those used for conventional mixing. They sought to increase rotor speed and machine productivity. In 1988, Kobe Steel acquired the Stewart Bolling Company (based in Cleveland, Ohio), a small manufacturer of internal mixers. They established a new manufacturing site in Hudson, Ohio (near Akron, Ohio) near Goodyear plus Bridgestone-Firestone, the American subsidiary of Bridgestone. The licensing relationship with Farrel had ended in 1985.

There have also been new designs of internal mixer rotors, notably by Millauer [53] of Werner & Pfleiderer (Figure 1.8a) and Johnson *et al.* [54] of Francis Shaw (Figure 1.8b). Passoni [55] of Pomini has described a completely new design of intermeshing rotor internal mixer in which the rotor inter-axial distances may be

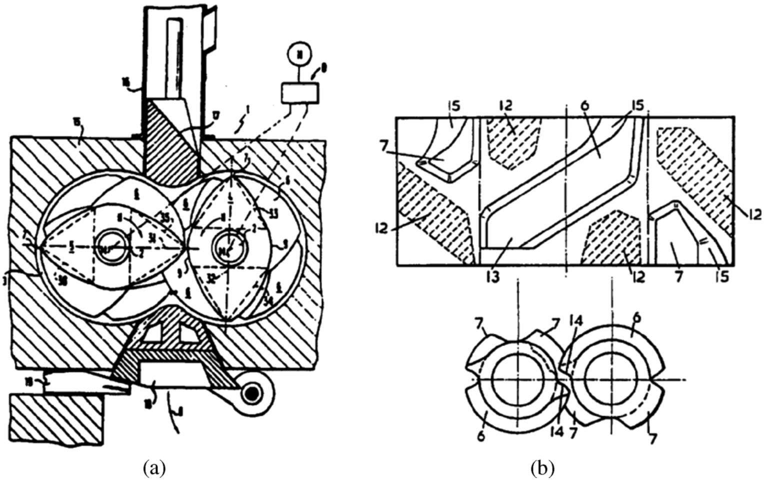


Figure 1.8 Post-Cooke intermeshing internal mixer rotors: (a) Millauer [53]; (b) Johnson *et al.* [54].

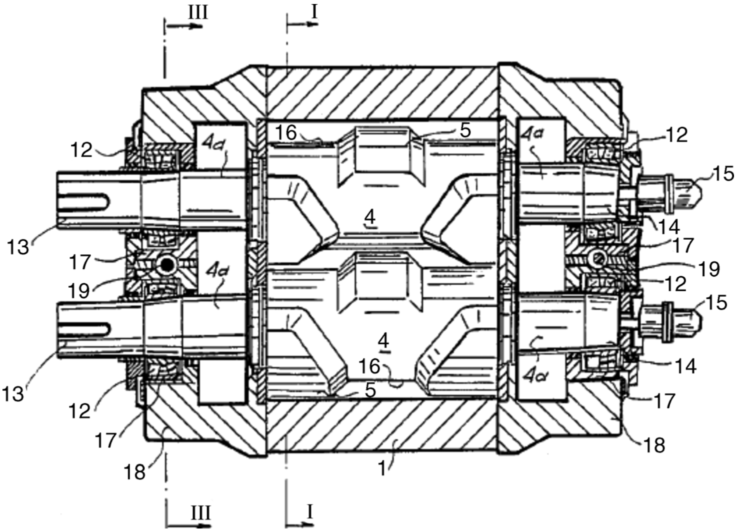


Figure 1.9 Passoni's [55] variable clearance intermeshing internal mixer.

varied for the preparation of different compounds or during the mixing cycle itself for different compounds (Figure 1.9). Again the licensing relationship with Farrel had ended in 1985.

1.2.2
Continuous Mixers

1.2.2.1 Early Activities

The earliest description of a continuous mixer appeared in an 1882 patent of Paul Pfleiderer (Figure 1.10) [56]. It was certainly intended for dough in a large bakery. It contains two non-intermeshing counter-rotating shafts with sigma blade and screw sections.

Single-screw extruders dominated continuous blending and compounding in the first part of the twentieth century and, indeed, through the 1960s. More sophisticated

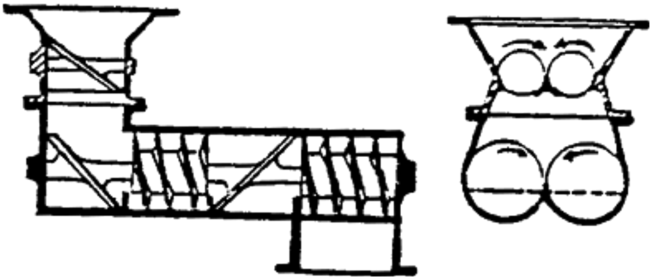


Figure 1.10 Pfleiderer's [56] continuous mixer.

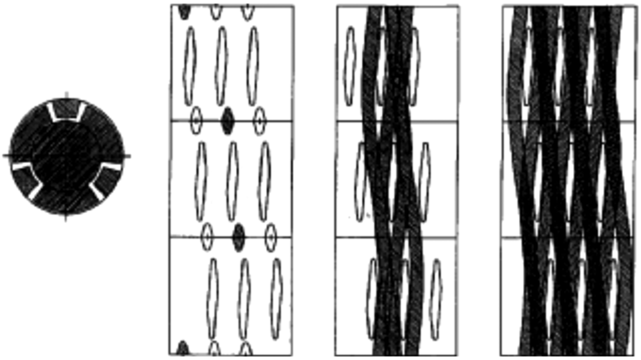


Figure 1.11 Buss Kokneter.

machine devices for mastication, compounding, and blending occur in the patent literature in the 1930s and 1940s [57–71]. Some are single screw devices such as List's Buss Kokneter. These include the intermeshing counter-rotating kneading pumps of the IG Farbenindustrie [58–62] and Maschinenfabrik Paul Leistritz [63–65], the "Knetwolf" of Krupp [66–68], and the modular tangential counter-rotating twin-screw extruder of Welding Engineers [71]. These machines have been reviewed in the books of Herrmann [67] and White [68]. Of these early machines only the Buss Kokneter (Figure 1.11) [69, 70] and the Welding Engineers modular tangential counter-rotating screw extruder (Figure 1.12) [71] survived and were successful.

1.2.2.2 **Single-Screw Extrusion**

Many modified screw designs for improved mixing have appeared in the patent literature [72–76]. Some of these designs are shown in Figure 1.13. In the last 30 years of the twentieth century it was realized that twin screw machines were better continuous mixers.

1.2.2.3 **Co-rotating Twin-Screw Extrusion**

The concept of a self-wiping co-rotating twin-screw extruder dates to the beginning of the twentieth century (Figure 1.14) [77, 78]. However, an intermeshing co-rotating twin-screw extruder was not commercialized until 1939. This was initiated by Roberto Colombo [79] and Lavorazione Materie Plastische (LMP) in Turin, Italy.

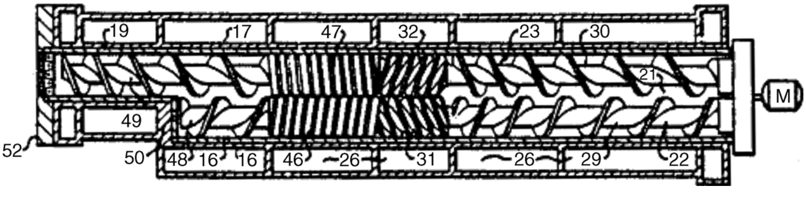


Figure 1.12 Fuller Welding Engineering modular tangential counter-rotating twin-screw extruder [71].

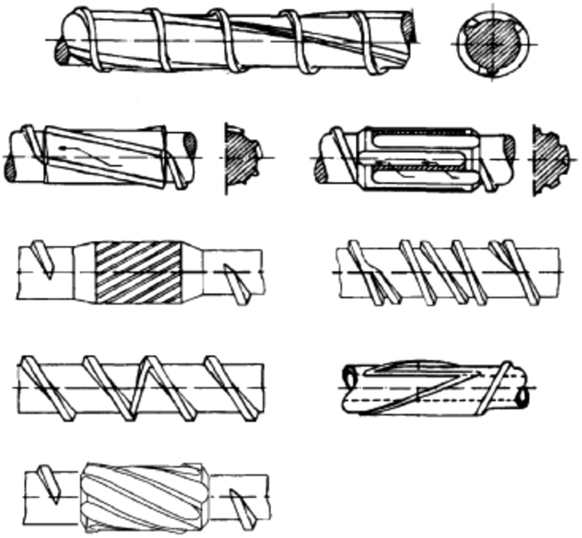


Figure 1.13 Mixing screw sections for single-screw extruders [77].

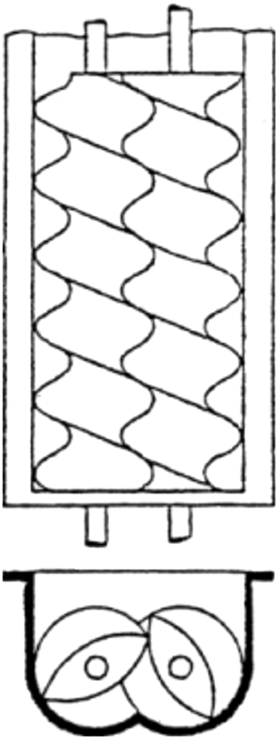


Figure 1.14 Wunsche 1901 self-wiping co-rotating twin-screw extruder.

Several of these machines were purchased by the IG Farbenindustrie and applied to reactive extrusion [80], dewatering [81], and kneading [82]. The most enthusiastic supporters of this machine in IG Farbenindustrie were Walter Meskat, Rudolf Erdmenger, and A. Geberg at the Wolfen Works on the Elbe River [81, 82]. They believed it would be much better if the screws were self-wiping and Geberg devised mathematical formulae for the necessary screw cross-section, a problem previously developed by Wunsche [77].

Following World War II, Meskat and Erdmenger were able to escape to the British zone and obtain positions in the re-invented Farbenfabriken Bayer, working for their former Wolfen Works manager, Kurt Riess. Meskat based in Dormagen and Erdmenger in Leverkusen set out with their new coworkers to develop a new generation of intermeshing co-rotating machines. As soon as the German patent office was back in operation in July 1949, Meskat and Erdmenger began submitting patent applications [83–86]. The second of these patents by Erdmenger was for a continuous twin rotor kneading disc block mixing machine [84] and the third for a twin screw devolatilizer [85]. Meskat and Pawlowski [86] on December 10, 1950 filed a patent for a modular co-rotating twin-screw extruder (Figure 1.15). In August 1958 Erdmenger filed for a German patent on a machine with screw and kneading disc blocks and in August 1959 for an American patent. The German patent application was rejected and the US patent application accepted [87]. Figure 1.16 shows the Erdmenger machine.

Notably, these were not the only co-rotating twin screw extrusion patents. Colombo and LMP filed for patents in France, Switzerland [88], and Germany [89] in the early 1940s and after the WWII in England [90], USA [91], and Canada [92]. These expanded on his 1939 Italian patent [79]. They had various screw designs and machine designs including six- and eight-screw machines. The machines seemed to be intended by the inventor to be profile extruders. W. Ellermann [93, 94] now based in Dusseldorf, who had invented the Krupp "Knetwolf" [66–68], filed patent applications on intermeshing counter-rotating and co-rotating machined shaft continuous mixers.

The Bayer co-rotating twin screw technology was licensed in the mid-1950s to Werner & Pfleiderer GmbH (now Coperion) of Stuttgart (Figure 1.17) [95].

At about the same the time, the Ellermann machine was licensed to Krauss-Maffei of Munich (Figure 1.18) [96] and later to the Japan Steel Works. When the Bayer AGs patent system expired in the early 1970s, other machinery manufacturers began to

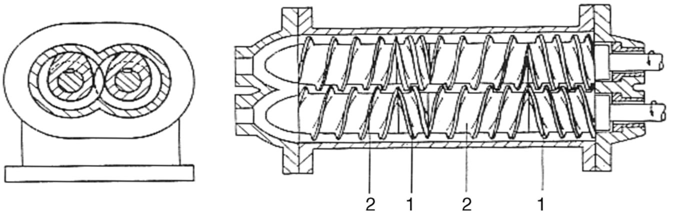


Figure 1.15 Meskat–Pawlowski modular co-rotating twin-screw extruder [86].

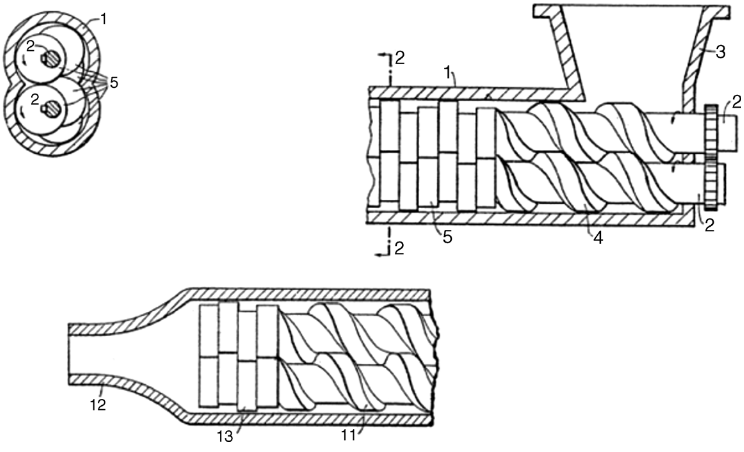


Figure 1.16 Erdmenger 1958 modular co-rotating twin-screw extruder [87].

produce modular co-rotating twin-screw extruders. These included Berstorff of Hannover, Germany; Leistritz AG of Nuremberg, Germany; Farrel Inc. of Ansonia; CT, USA; Japan Steel Works, Kobe Steel, and Toshiba Machine of Japan; in total more than 50 concerns around the world.

New mixing elements have been devised more recently, including (i) "Banbury Mixer" similar rotors by Kobe Steel and Farrel Inc. [97, 98] to be used in place of kneading disc blocks and (ii) special milder mixing in elements by Berstorff and Werner & Pfleiderer [99–101] to be used in place of kneading disc blocks for specific applications such as brittle glass fibers. Baker Perkins was in this period a major stockholder in Werner & Pfleiderer. They began to manufacture these machines on their own in the 1960s [102].

There have been many efforts directed towards modeling flow, both in individual modules [103–105] and in composite modular machines [103, 106–109]. The latter models can predict fill factor and pressure and temperature profiles along the screws.

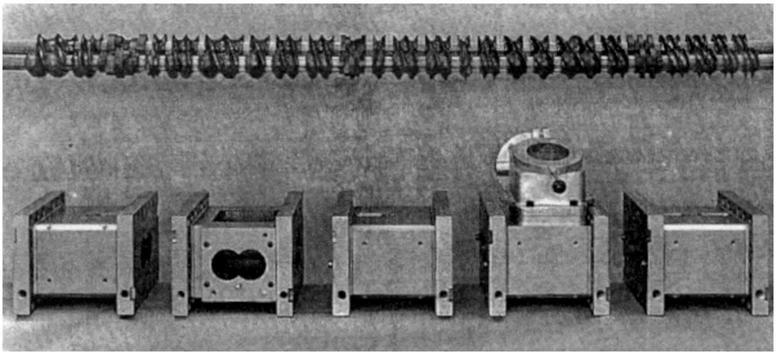


Figure 1.17 Werner & Pfleiderer ZSK modular co-rotating twin-screw extruder.

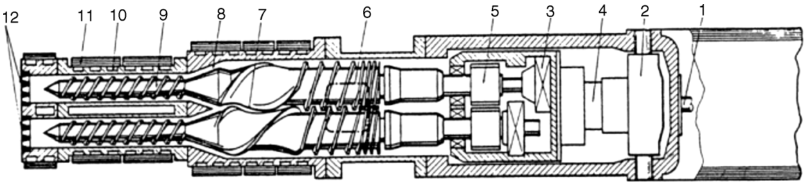


Figure 1.18 Ellermann machine licensed to Krauss-Maffei.

1.2.2.4 Tangential Counter-Rotating Twin-Screw Extrusion

Tangential counter-rotating twin-screw extruders begin with the patents of Fuller [71] and later Street [110] in the 1940s and 1950s. This machine is shown in Figure 1.18. The tangential counter-rotating twin-screw extruder was widely discussed and used from about 1950. From the 1960s it has received more attention from the chemical processing industry [111, 112] as opposed to it being used for polymer blending. Many efforts have been made to simulate the flow in individual modules of the machine [113–115] as well as composite models of the mixing and metering section near the machine exit [115].

A second non-intermeshing counter-rotating twin-screw extruder is the Farrel Continuous Mixer™ (Figure 1.19) [116, 117]. It has rotors consisting of screws leading to Banbury-like rotors. It was originally intended to be a continuous Banbury Mixer for the tire industry but met with greater success in the compounding and polymerization industries.

These machines were also produced by Kobe Steel and Pomini. Various calculations have been made to analyze the flow in their mixing, including fill factors and pressure profiles [118, 119].

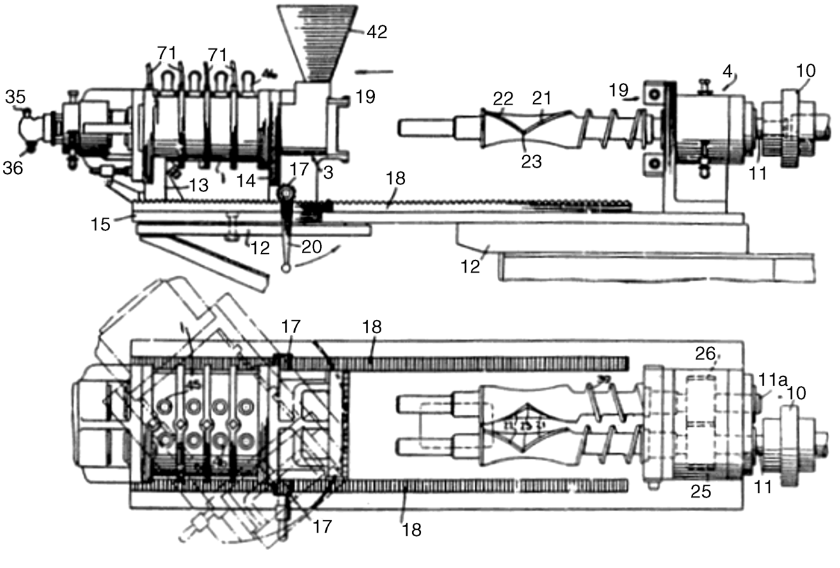


Figure 1.19 Farrel Continuous Mixer [116].

1.2.2.5 **Modular Intermeshing Counter-Rotating Twin-Screw Mixer**

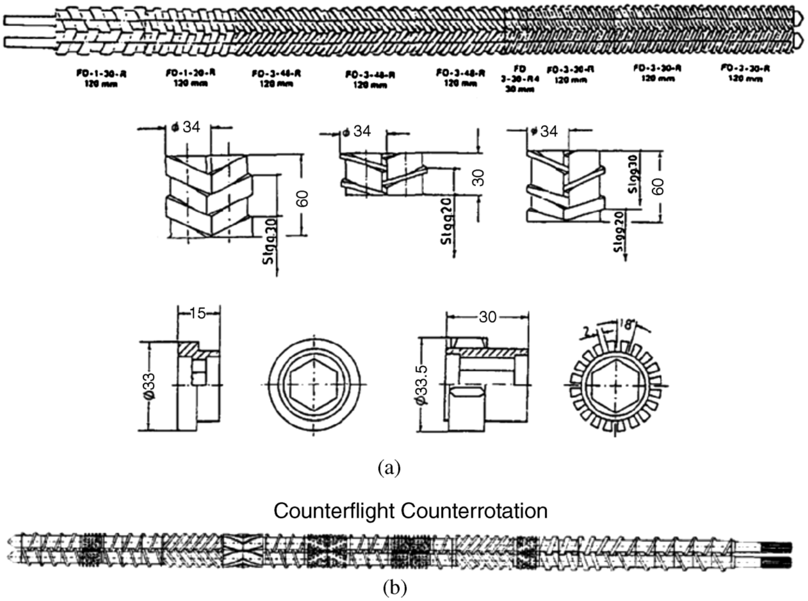
Early intermeshing counter-rotating twin-screw mixers including the Krupp Knetwolf [66, 68] and Ellermann's post-World War II 1951 Eck Mixtruder [88], did not prove successful. The Leistritz modular intermeshing counter rotating twin-screw extruder (Figure 1.20) of Tenner [120] and Thiele [121–123] (GG and Counterflight models) have proven more successful [124]. These machines were developed from the 1960s through to the 1990s.

1.2.2.6 **Modular Buss Kokneter**

The modular Buss Kokneter [125–128] is an excellent distributive mixer that is widely used in the food and polymer industries (Figure 1.21). It consists of a single screw with slices in its flights in a barrel containing pins or clogs. The screw both rotates and reciprocates in such a manner as to be self-wiping. The individual modules are designed for melt pumping, mixing, and melting. This machine has been analyzed for flow both in individual elements and global behavior [129, 130].

1.2.3
Comparisons

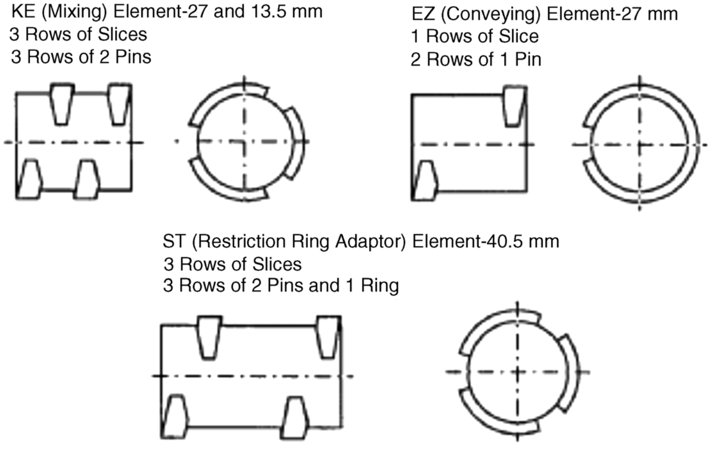
There are very few comparisons of different types of mixers. It is worth summarizing what we do know. We begin with batch mixers. Obviously, the Banbury design internal mixers were found to be superior to the Werner & Pfleiderer Gummikneter. In comparing two-flight and four-flight rotors in Banbury design internal mixers,



(a)

(b)

Figure 1.20 Leistritz modular intermeshing counter-rotating twin-screw extruders [120–124]: (a) Tenner GG machine; (b) Thiele counter flight machine.


KE (Mixing) Element-27 and 13.5 mm
3 Rows of Slices
3 Rows of 2 Pins

EZ (Conveying) Element-27 mm
1 Rows of Slice
2 Rows of 1 Pin

ST (Restriction Ring Adaptor) Element-40.5 mm
3 Rows of Slices
3 Rows of 2 Pins and 1 Ring

Figure 1.21 Modular Buss Kokneter Elements.

various patents describe four-flighted rotors as providing both better mixing and greater heat buildup. A clear comparison of two- and four-flighted rotors was given by Cho *et al.* [131] in a 1997 paper showing the superior mixing ability of the four-flighted rotors.

Turning now to intermeshing rotor machines versus Banbury-type separate rotor machines, we find the various manufacturers defending their designs. P. S. Kim and J. L. White [132] have published experimental studies showing that intermeshing rotor internal mixers are much superior to separated rotor machines in dispersive mixing. Machine manufacturers (e.g., Techint Pomini) claim they have better heat transfer because of the lower operating temperatures than FH Banbury design machine because they have much more machine surface area. Mixing of rubber mechanical goods in Europe and East Asia is carried out in intermeshing rotor machines and tire compounds in separated rotor machines. The separated rotor machines are preferred by the tire industry because of their larger mixing chamber volumes.

We now turn to continuous mixers. Again, we must be concerned about the claims of machinery manufacturers. In recent years, Shon *et al.* have made comparative studies of the mixing of glass fibers [133] and small particulates [134] into polymer melt matrices as well as dispersive mixing of blends [135]. They seek to compare machine characteristics with regard to dispersive mixing and glass fiber breakage. They found the severity (breakage of glass fibers, fineness of dispersion) of the mixing machines to order as Leistritz GG Intermeshing counter-rotating > Intermeshing co-rotating > Buss Kokneter.

However, the results depend on the arrangement of the modular elements. The modular co-rotating machine is much milder in the absence of kneading disc blocks.

Generally, continuous mixers are superior to batch mixers. The compounds are more uniform have superior mechanical properties and much shorter residence times [135, 136]. The major continuous mixers used commercially in 2009 for compounding and blending are modular co-rotating self-wiping twin-screw extruders.

1.3
Processing Polymer Blends

1.3.1
Early Synthetic Polymer Blends

As described in Section 1.1, the first commercial polymers, which were naturally occurring, were polyisoprenes (natural rubber and gutta-percha) and subsequently cellulose derivatives. From the early twentieth century, various totally synthetic polymers were introduced. Farbenfabriken Bayer introduced bulk polymerized totally synthetic elastomers in 1910. Poly(dimethyl butadiene) synthetic rubber was produced commercially by Bayer in Leverkusen during World War I. The 1920s saw the commercial development of polystyrene (PS) and poly(vinyl chloride) (PVC). In 1934, the IG Farbenindustrie (a combine of Bayer, BASF, Hoechst, and other firms) began to commercially manufacture butadiene–acrylonitrile copolymer (NBR) as an oil resistant rubber and in 1937 butadiene–styrene copolymer (SBR) intended for pneumatic tires.

Blends of the natural rubber and the new synthetic elastomers must have been studied by the I.G. Farbenindustrie and various German rubber fabricators such as Continental Gummi-Werke in the 1930s. Perhaps the first widely used synthetic polymer blend was the NBR–poly(vinyl chloride) system. NBR was widely used in under the hood applications in automobiles. It aged badly because of ozone attack in these applications. Introducing PVC into NBR improved its aging at some expense in stiffening. The IG Farbenindustrie would seem to have marketed NBR grades that were blends [137]. NBR is miscible with PVC so it would seem that this was a feasible solution at the time. In the 1940s, the United States went into large-scale production of butadiene styrene and acrylonitrile elastomers (SBR and NBR). Polystyrene (PS) and styrene–acrylonitrile copolymer (SAN) also became major commercial polymers. Both were brittle and tougher rubber modified blends were developed. Notably, high-impact polystyrene (HIPS) and ABS resins were devised by introducing polybutadiene or its copolymers (SBR and NBR). These new blends were in time optimized by producing them by polymerizing monomer solutions of the elastomers. Research activities on improving the properties of polymers by blending have continued since that time.

From the 1960s onwards there have been extensive investigations of polymers blends in both industrial and academic laboratories around the world.

1.3.2
General Ideas and Stability of Blend Phase Morphology

Polymer melt blends may be miscible or immiscible. Miscible blends form solutions and there is no phase morphology to be of concern. Immiscible blends are characterized by two or more phases that are separated by interfaces. Most polymer blend systems are immiscible because of the low entropies of mixing associated with mixing chain-like molecules to produce homogeneous solution.

The interface between two phases in a liquid system is characterized by an interfacial tension (κ), which seeks to control the interface shape and coalesce with other dispersed phase. The interfacial tension is generally resisted by the melt viscosity, which slows the changes the interfacial tension seeks to achieve.

Notably, interfacial tension in two-phase low viscosity systems has been recognized and studied since the nineteenth century. Indeed Clerk Maxwell [138] discussed it in an 1879 *Encyclopedia Britannica* review. Various researchers developed methods and made measurements of the interfacial tension in the nineteenth century and early twentieth century. Measurements for combinations of polymer melts, however, date back only to the 1960s [139–142] and generally accepted values were available by the 1990s [143–146]. We summarize data for various binary systems in Table 1.1.

When the interfacial tension goes to zero, the blend becomes miscible. Large interfacial tensions lead to unstable interfaces, especially when the viscosity is low. This leads to coalescence phenomena, which are best known in "salad dressing" but also occur in polymer melt blends.

It is possible to modify the interfaces between liquids with specific additives. This was discovered by ancient and medieval investigators and applied in the form of soaps, and later in food technology and in the application of dyes. The mechanisms of these additives only came to be realized in about 1900. Such additives are generally molecules with hydrophobic and hydrophilic sections that align along interfaces between the two liquid phases. They reduce interfacial tension and stabilize phase morphology to smaller dispersed phase sites. This phenomenon was realized by IG Farbenindustrie chemists who applied it in the late 1920s in emulsion polymerization that they used to produce synthetic rubber.

As described in Section 1.3.1, many polymer blends were developed in the years following World War I. By the 1960s, there was interest in understanding the interfaces between the individual polymers in the blends. It came to be realized that in some of the successful blend systems such as HIPS and ABS resins there were substantial amounts of graft copolymer products at the interface between the polymer phases.

Table 1.1 Interfacial tension (κ) between polymer melts based upon the breaking thread method (Yoon and White [146]).

Polymer 1	Polymer 2	Temperature (°C)	κ (dyne cm^{-1})
Polyethylene	Polystyrene	290	5.0
Polyethylene	Polysulfone	290	6.5
Polyethylene	Poly(*p*-phenylene sulfide)	290	7.2
Polyethylene	Poly(ethylene terephthalate)	290	9.2
Polyethylene	Poly(bisphenol A carbonate)	290	13.0
Polyethylene	Polyamide 6	290	13.2
Poly(*p*-phenylene sulfide)	Polysulfone	290	1.6
Poly(*p*-phenylene sulfide)	Polycarbonate	290	3.5
Poly(*p*-phenylene sulfide)	Polyamide 6	290	9.9

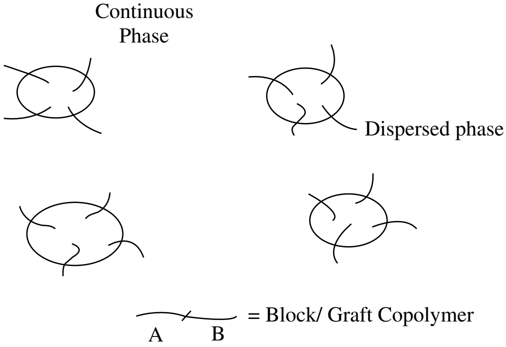


Figure 1.22 Compatibilized dispersed polymer blend phase showing compatibilizing agents.

This led to extensive investigations of polymeric interfacial agents, increasingly known as "compatibilizing agents," in polymer blends [145, 147–152]. These produced a reduction in dispersed phase size, enhanced phase stability, and increased mechanical properties (Figure 1.22). These were invariably block and graft copolymers. The property enhancement is due to their occupying the blend interface and having long chains in each phase. Subsequently, various investigators [145, 153] measured the interfacial tensions in these compatibilized blends and found that they were significantly reduced when appropriate compatibilizing agent were introduced. Typical results are shown in Table 1.2, where great reductions interfacial tension of polyethylene/poly(ethylene terephthalate) (PET) produced by the introduction of compatibilizing agents can be seen. Note the effectiveness of the maleated polymers, which react with the PET chain ends to produce block copolymers.

Generally, phase morphologies produced in blending involve disperse phases sizes that vary with interfacial tension, κ, or with the dimensionless group $\kappa/\eta v$ or $\kappa/\sigma_{12}d$, where η is viscosity, v is velocity, and σ_{12} a shear stress [154, 155]. This dimensionless group represents a ratio of interfacial to viscous forces.

Table 1.2 Interfacial tension (κ) between polymer melts in compatibilized blend systems [153].

Polymer 1	Polymer 2	Additive (5pt)	Temperature (°C)	κ (dyne cm^{-1})
Polyethylene	Poly(ethylene terephthalate) (PET)	—	270	9.7
Polyethylene	PET	PBT-*b*-PE copolymer	270	1.7
Polyethylene	PET	Maleated HDPE (high density polyethylene)	270	1.9
Polyethylene	PET	SEBS (styrene–ethylene/ butylene–styrene)	270	7.5
Polyethylene	PET	Maleated SEBS	270	1.8

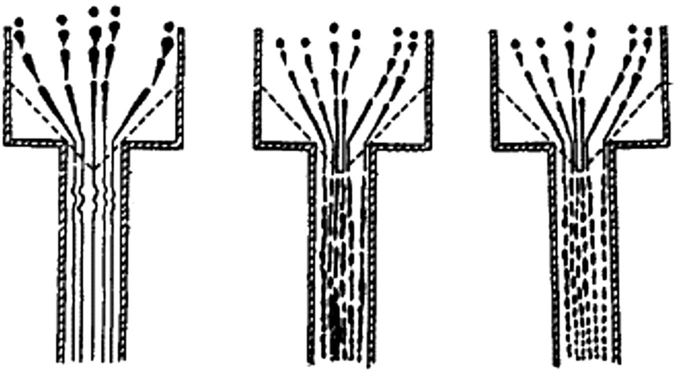


Figure 1.23 Formation of mini-fibers in melt spinning.

1.3.3
Phase Morphology Variations in Processing Operations

1.3.3.1 Melt Spinning

The phase morphology of polymer blends shows significant variations in polymer melt processing. One of the most striking observations is the formation of mini-fibers in melt spun blends (Figure 1.23), where the blend experiences uniaxial elongational flow. If the major phase can be dissolved away, these mini-fibers can be isolated [156, 157]. Experiments of this type have notably been carried out by Japanese fiber companies since 1970 in trying to produces small diameter fibers for luxury clothing. One published study of this type involves the formation of polyethylene mini-fibers (0.2 μm) from polyethylene/polystyrene blends by Min *et al.* (Figure 1.24) [158].

Mini-fibers have also been observed by Liang *et al.* [159] on melt spinning polypropylene/polyamide blends. The diameters of the dispersed polyamide 6 phase mini-fibers are tens of microns and more. This is clearly due to the large interfacial tension in this system (polypropylene/polyamide 6) as compared to polyethylene/polystyrene blends of Min *et al.* (Table 1.1).

1.3.3.2 Die Extrusion

Another geometry that has received some study is extrusion through dies. In flow through a die, there is Poiseuille flow with high shear stress near the die wall and low shear stresses at the center-line or center-plane. The situation here is more complex than in melt spinning because of the distributions across the die radius. Generally, dispersed phase droplets at high radii in a cylindrical die where shear stresses and shear rates are large are stretched out into long filaments. However, at the center-line, where deformation rates and shear stresses are small and near zero, the dispersed phase is not stretched out and remains as nearly isotropic droplets [160].

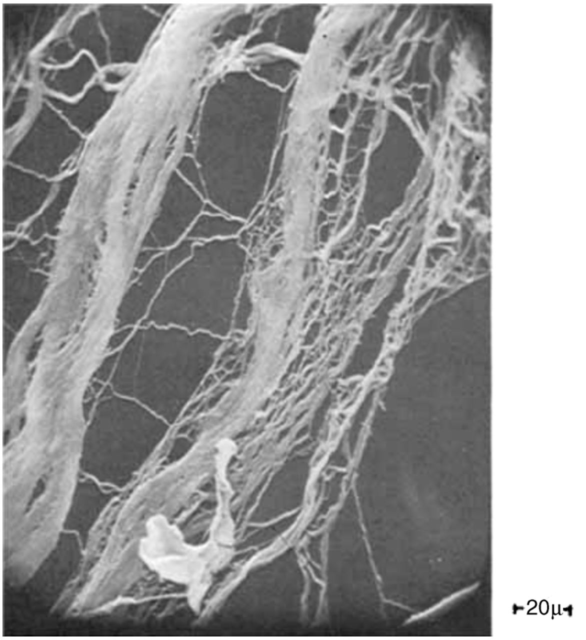


Figure 1.24 Polyethylene mini-fibers produced from polyethylene/polystyrene blends.

1.3.3.3 Injection Molding

Injection molded parts also exhibit blend morphology variations associated with melt processing. These tend to be more complex than those described earlier. As a hot blend melt moves through a cold mold, the dispersed phase in regions near the mold

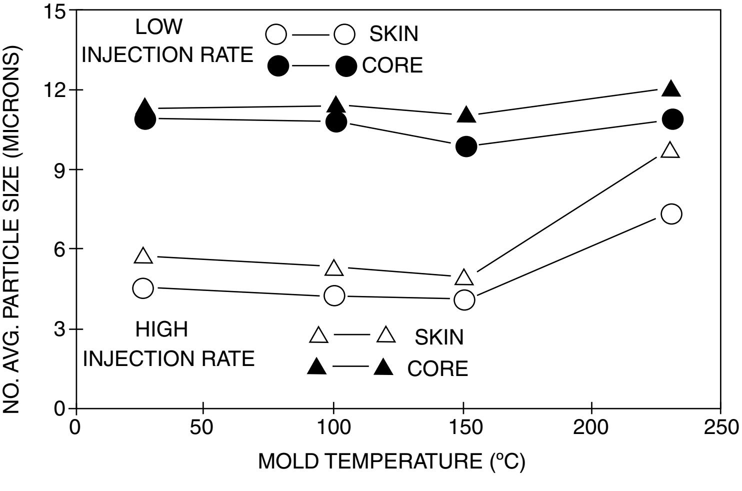


Figure 1.25 Dispersed number average phase size as a function of injection rate and mold temperature for an 80/20 polyamide 6/HDPE injection molded blend.

wall tends to be drawn out more than in the low deformation rate core region. However, the moving melt front has a fountain like flow that deposits isotropic core melt blend on the mold walls. The result is that the greatest blend anisotropy is not in the skin layer but at intermediate positions between the core and the mold wall.

Ghiam and White [161] have studied this behavior in the injection molding of blends of polyethylene and polyamide 6, which as we have already seen has a high interfacial tension. Figure 1.25 shows that the smallest dispersed phase is in the high stress region near the mold wall and a much coarser morphology exists in the core [161]. If the mold temperature is maintained above the melting temperatures, coalescence proceeds. It has been observed that the greatest coalescence occurs not in the layer near the wall rather than in the core.

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