Handbook for the Chemical Analysis of Plastic and Polymer Additives

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Overview of Polymers, Additives, and Processing

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CHAPTER 1

Overview of Polymers, Additives, and Processing

Introduction

Polymers are available in a wide range of formulations and properties achieved through selection of the base polymer and additives. Two types of chemical reactions produce polymers:

1) Condensation between polyfunctional molecules (monomers) that react with each other. This reaction is heat driven, sometimes with the aid of a catalyst. The longer the exposure to heat, the longer the polymer chain becomes. A common example of this is nylon, a reaction of a diamine with a dicarboxylic acid producing a polyamide.

2) Reaction of a molecule that is activated with an initiator to form a free radical. This free radical, when reacting with a “normal” molecule creates a new free radical, causing a full fledged chain reaction. This process creates, from a monomer, a long chain polymer instantaneously. No intermediate chain length polymers are present. This process is also called vinyl polymerization.

Most polymers are identified on the basis of their common name. Examples include polyethylene, polyvinyl chloride, butyl rubber, acrylonitrile-butadiene, and styrene (co-polymer ABS). However, few polymers are used in pure form since they often require chemical modification to achieve optimum properties and promote non-inherent performance. Some of these property enhancements include improved resistance to oxidation, high temperatures, flammability, impact loads, surfactants, ultraviolet radiation, as well as modification of a wide range of other properties. The process of adding essential ingredients to polymers to achieve these results is termed compounding. However, it is generally not practical to precisely match the inherent properties of a base polymer to a specific application. While some polymers such as polyethylene are available with a wide range of properties based on a range of molecular weights, molecular weight distributions, and tacticity (stereostructure), other polymers have a finite range of properties for which compounding provides a practical method for adjustment of general or specific properties. For example, polyvinyl chloride is the most commonly used thermoplastic. In the raw form, this is a rigid, transparent polymer; however, in the most familiar applications, this “vinyl” polymer is flexible and colored as in black electrical tape or a yellow rain coat.

As stated above, the modification to achieve these results is usually achieved by mixing a polymer with other polymers, both organic and inorganic materials including additives, metal powders, glass fibers, and other materials to match the end-use application.

This chapter addresses three basic classes of polymers and the approaches for processing them into practical compounds. These classes include thermoplastic polymers, and two types of elastomers — crosslinked elastomers and thermoplastic elastomers. Compounds prepared from each class have a range of achievable properties, and each category of compounds may have overlapping properties. Each category is prepared by different technical approaches with varying controls, energy requirements, and limitations. A brief definition of each class follows. Also included, later in the chapter, is a detailed description of how additives influence the production process. The overview of polymer compounding is presented next to provide the analyst an introduction into the many processing steps where polymer composition changes occur, deliberately and otherwise.
Classes of Polymeric Compounds

In the form of raw materials, polymers exhibit a wide range of compositions and properties. These properties can be enhanced or tuned to specific applications through the preparation of compounds. This section addresses three basic classes of polymers and the approaches for the preparation of compounds.

Thermoplastic Polymers

Thermoplastics are polymers that can be melted, prepared into a desired form, and then re-melted. Thermoplastics can be processed into a desired shape through many processes, the most common of which are injection molding and extrusion. Blow molding, transfer molding, calendaring, casting, and other forming operations are all possible with thermoplastics.

Crosslinked Elastomers

Crosslinked elastomers are polymers that are first prepared by compounding a base elastomeric polymer with property-modifying additives and a reactive crosslinking agent. Polymers of this type can be formed into a desired shape through many different operations; however, the final operation requires that the shaped article be heated to a temperature at which the crosslinking agent decomposes to produce free radicals. These radicals react with the base polymer to form chemical crosslinks transforming the linear “two-dimensional chain” into a “three-dimensional object”. This class of material cannot be melted and reformed. Alternate crosslinking methods are used for special applications including the use of ionizing (gamma) radiation, ultraviolet radiation, and water-initiated (silanol) cure systems.

Thermoplastic elastomers

Thermoplastic elastomers (TPEs) are a more recently developed class of polymer in which the neat polymer has inherently elastomeric properties, yet it behaves thermoplastically. With some limitations, these materials can be formed by essentially the same operations as thermoplastics, but the final object exhibits elastomeric behavior. Objects molded with thermoplastic elastomers can be melted and re-shaped. Since these are not crosslinked, their creep resistance and extended high temperature use are limited.

Thermosets

This family of polymeric materials includes liquid polymers and thermoplastics that have been crosslinked. Preparation of thermosets follows the same compounding route used for thermoplastics; however, a crosslinking agent or ionizing radiation are used to form chemical crosslinks.

Liquid polymers can be chemically crosslinked to form thermosets. Materials in this category include epoxies, embedding compounds, coating materials, urethanes, silicone polymers, and others. Due to the inherently low viscosity of liquid polymers, they are compounded using a variety of mixing systems, including high shear devices.

Compounding Objectives

Polymeric compounds must behave as a system, consisting of the base polymer and additives, selected to achieve a set of final properties. During compounding, mixing must occur at two fundamental levels — dispersive mixing and distributive mixing. Dispersive mixing relies on shear action to blend the additives into the polymer. Dispersive mixing must overcome differences in viscosity, surface energy, chemical compatibility, melting temperature, and others to achieve
Overview of Polymers, Additives, and Processing

Overall homogeneity of the formulation. Improperly dispersed polymer compounds will typically contain domains where ingredients have not been blended properly, as shown in Figure 1-1. Dispersive mixing focuses on short-range blending of the compound, while distributive mixing addresses the overall homogeneity of a batch. Distributive mixing places different requirements on the mixing process, depending on the type of equipment that is being used. This will be further addressed in the Compounding Overview section in this chapter.

During the compounding process, it is essential that all ingredients added to a polymer are retained within the compound in a stable manner that assures functionality. Thermal degradation and excessive shear action may selectively degrade different additives. It is imperative that processes are developed and validated by functional testing of the final compound. Mixing processes must be very carefully controlled to assure consistent quality. Variations in compound quality can have an adverse and varying impact on components prepared from the compound.

Thermoplastic Compounding

Thermoplastic compounds are typically prepared by mixing organic or inorganic compounds with a single base polymer, copolymers, or blends. The base polymer may consist of a chemically bonded blend such as the block copolymer acrylonitrile-butadiene styrene (ABS) or a second base polymer may be used to enhance the overall end properties of the compound.

A base polymer, such as an ethylene-propylene (EP) copolymer, can be acquired in a range of compositions, molecular weights, various ethylene-to-propylene ratios, various molecular weight distributions, and a range of densities. Each of these variations results in a base polymer that has specific practical properties such as flexibility, elastic recovery, tensile strength, and thermal limit to name a few. As a base polymer, ethylene-propylene polymers and most other non-crosslinked elastomers have no significant commercial application, since they are essentially a liquid with very high viscosity.

Organic Additives

Antioxidants

Thermoplastics may contain a wide range of organic additives that are incorporated into the polymers to improve selected properties. In virtually all cases, an antioxidant must be added to allow the compound to be blended with other ingredients, to be pelletized or chopped into...
intermediate form, and to survive thermal stresses associated with the final forming process. In some cases, the base polymer is blended with an antioxidant at the time of preparation of the base resin. This type of antioxidant is intended to add thermal stability for processing considerations. External antioxidants can also be added to improve shelf life of the product or to improve its high temperature stability, while adding a stability margin during thermal processing.

Internal Lubricants
These may be added to the polymer to reduce the shear rate during processing, especially when an inorganic material is being added. If the shear level gets too high, thermal damage and polymer chain scission can result. The lubricant must be selected properly to avoid having it decompose or affect the polymer compound in some adverse manner. Common lubricants include fatty alcohols (C14-C18), fatty acid esters (C14-C18), dicarboxylic acid esters (C14-C18), fatty acid amides (C16-C18), and esters (C26-C32).

Release Agents
They are often blended into compounds that are developed for injection molding applications. Where such an additive is absent, molded components tend to stick to mold surfaces. To prevent this, mold surfaces must be treated between every cycle, or they can be coated with a range of semi-permanent mold release treatments. Inclusion of an internal release agent prevents mold surface build-up, surface charring, and simplifies production. Internal mold release agents may include hydrocarbons, alcohols, carboxylic acids, halogenated compounds, ketones, carboxylic acid esters, amides, metal salts, and silicone compounds.

Plasticizers
Plasticizers are added to thermoplastic compounds to improve flexibility, increase the acceptance level for inorganic additives, and to aid in processing, such as melt flow reduction. Synergistic effects can also be obtained such as reduction of shear during mixing and improved impact resistance. Plasticizer compounds typically include phthalates, adipates, esters, and fatty acid esters (oleates, palmitates, stearates).

Impact Modifiers
These are often added to otherwise brittle thermoplastics to improve impact resistance. In some cases, the addition of inorganic materials renders plastics hard and brittle, thus requiring the addition of an impact modifier. Impact resistance can be improved through addition of polymers with increased flexibility or elastomeric characteristics. Acrylics and butadiene are common impact modifiers. Styrene is commonly impact-modified through graft polymerization with acrylonitrile or polybutadiene (hence ABS [acrylonitrile-butadiene-styrene]), or it can be grafted to an ethylene propylene diene elastomer. Polypropylene can be made impact resistant through various blending methods to incorporate ethylene-propylene monomer.

Electrostatic Control Agents
They are required for thermoplastics applications where surface electric charge must be controlled or prevented. There are a number of compounds available for this function and these can be divided into two general categories: bulk and surface-modifying. Bulk additives may be simple, such as carbon black, which, when added in sufficient concentration, provides a semiconducting matrix, thus controlling the accumulation of localized charge. Metal salts can also be used for this purpose in some polymers. Cationic compounds can impart bulk conductive properties and these include compounds with a bulky cation such as quaternary ammonium, sulphonium salts, or imidazoline compounds. Anionic compounds are also used and these include, for example,
Overview of Polymers, Additives, and Processing

alkylsulphonates. Nonionic compounds can also be used for controlling charge distribution through interfacial activity. Compounds in this category include ethoxylated fatty amines, ethanolamides, polyethylene glycol esters, and others. Some organic compounds are also useful for controlling surface charge. These function by having limited solubility in the host polymer. Compounds of this type migrate to the surface of the polymer where their nominally low concentration increases locally at the surface, and thus provide a conductive surface bridge.

Dyes and Organic Pigments
Dyes are chemical compounds that impart color to plastic compounds. These dissolve in the host polymer and are therefore not present as discrete particles. Dyes are typically azo or anthraquinone compounds.

Pigments are discrete particulate materials of very small particle size, which are blended into a thermoplastic compound to impart color. Organic pigments are typically of an azo or cyanine structure. Most organic pigments also have good thermal stability across the thermoplastic processing range; however, they are less well-suited for crosslinking and elevated temperature applications. Due to their insolubility in the polymer, these serve as nucleating agents during recrystallization. Thus, pigments may play a significant role in controlling the final properties of a compound.

Polymer Blending
For some applications, polymers are blended to provide a balance of properties. Some polymers blend well due to mutual solubility, but if the solubility parameter of the candidate polymers is different by more than about 3 SI units, the polymers must be blended with an intermediate material to improve compatibility. Typically, this involves an intermediate polymer with a low molecular weight. In the melt, this serves to reduce the surface tension between two incompatible polymers, thus improving dispersion. Low molecular weight polyethylene is an example of a polymer blending aid. In other cases, metal stearates or salts can be used to aid dispersion. Examples include zinc stearate and calcium stearate.

Inorganic Additives
Fillers and Reinforcers
Thermoplastics often have physical properties that are inherently well suited to a particular application. In such a case, there is little need for addition of inorganic materials. Inorganic additives are very useful for improving the physical strength and deformation resistance of thermoplastics. They function by forming a network of pinning points in the polymer wherein the slippage of polymer chains under mechanical stress is impeded. Inorganic reinforcements are of many types, ranging from natural minerals to synthetic minerals to specialized materials with directional physical properties. Clays in common use for higher quality plastics include kaolin, other natural silicates, and others. Synthetic and high purity reinforcements include titanium dioxide, calcium carbonate, silica, and many others.

Inorganic additives are also useful for controlling the onset temperature, extent, and dimensions of the crystalline phase in semi-crystalline polymers. The inorganic component acts as a site for heterogeneous nucleation of polymer crystallites. By initiating nucleation at many closely spaced sites, the polymer solidifies with a network of small uniformly distributed crystalline domains. By balancing the comparative strengths, flexibility, and creep resistance of crystalline and amorphous phases of a polymer, a balance can be achieved for engineering applications. Heterogeneous nucleation is also helpful for controlling the structure of polymers with a slow rate of
recrystallization. During injection molding, for example, as the molded part cools, heat transfer to the chilled mold causes the polymer in the outer surface of the part to nucleate first, followed by the core of the component. Heterogeneous nucleation occurs at the mold interface, but homogeneous nucleation may occur in the core of the sample. This would proceed slowly due to the ratio of heat capacity of the polymer to poor thermal conductivity. Addition of a matrix of fine inorganic particles increases molding throughput and improves the bulk properties of the polymer. Titanium dioxide and silica are typical additives in this category. Titanium dioxide has a dual purpose in many cases in that it is a very efficient whitener. Nucleating agents can also have the form of dispersed polymers with a higher melting point.

Inorganic Pigments
Wide ranges of compositions are used to impart color to thermoplastic compounds. Pigments are discrete particulate materials, of very small particle size, that are blended into a thermoplastic compound to impart color. Inorganic pigments are commonly found in the form of metallic compounds. Oxides of iron, chromium, molybdenum, cadmium, nickel, antimony, and titanium produce a wide range of vivid colors. Variations in oxygen stoichiometry have a pronounced effect on the color of many of these metal oxides. Carbon black is also a very effective colorant. Inorganic pigments are very stable in a polymer and generally exhibit high color retention. These often have a synergistic effect on the recrystallization performance of polymers during thermal processing, due to their role as heterogeneous nucleation sites.

Crosslinked Elastomer Compounding

Organic Additives

Antioxidants
Raw elastomeric polymers typically contain an antioxidant that is added at the time of manufacture to provide thermal stability for compounding, milling, and subsequent operations to produce beads, bales, or other forms where the polymer is first heated, then cooled into an intermediate form for storage, transport, and metering. The as-provided antioxidant does not generally provide sufficient stability to protect an elastomeric compound through final forming and curing due to the high shear energy required for mixing. External antioxidants are often added to provide additional protection. Antioxidants are available in many forms and they vary in functionality, according to their composition and structure. Typical antioxidants for elastomers include a range of phenolics, amines, and bisphenol derivatives.

Crosslinking Agents
Elastomers must be crosslinked to hold their final form. The crosslinking reaction takes place through generation of free radicals that promote bonding at sites of unsaturation. The most common crosslinking agents for this include reactive peroxides, such as dicumyl peroxide, diacetyl peroxide, di-tert butyl peroxide, and others. Since each has a different temperature at which thermal decomposition initiates, curing conditions vary with the peroxide type.

For some products, elemental sulfur or sulfur-containing benzothiazole compounds are added to the compound as a curing agent. Sulfur reacts to form C-S-C bonds. This is an inexpensive reaction scheme and it is useful for production of rubber compounds across a very wide hardness range. Residual sulfur compounds lead to odors and acid products that are not well suited to applications where clean materials are desired. Thiazole compounds provide better handling and more controllable crosslinking processes, with low residual odor and extractables.
Cure Rate Modifiers

The crosslinking reaction rate may be too slow for some commercial processes and the reaction may exceed the oxidation resistance time for the elastomer compound. In such cases, curing accelerators are used with the sulfur-curing process. Zinc oxide is a commonly used accelerator; however, thioureas, hexamethylenetetramine, and others are effective. For organic peroxides, the cure rate can be greatly increased with an increase in applied temperature, though oxides of zinc, magnesium, or calcium can be used to limited effect. The rate of crosslinking reaction can be slowed for those cases when the rate exceeds the formation process for some components. Cure retarders include compounds such as nitrosodiphenylamine, benzoic acid, and phthalic anhydride. Use of a cure retarder increases the burden on an antioxidant to protect the polymer against thermal degradation.

Lubricants and Related Compounds

During the compounding operation, shear stresses in an elastomer compound are very high. To reduce shear and to promote more efficient wetting of inorganic ingredients, processing aids can be used. Zinc and calcium soap compounds are very efficient for reducing shear viscosity during mixing. Fatty acid compounds and fatty acid esters are also useful and examples include stearic acid and palmitic acid. Various hydrocarbon oils are often used for shear viscosity reduction. These may include high purity white mineral oils.

Coupling Agents

Elastomer compounds are typically blended with an inorganic reinforcement to provide enhanced physical properties. Bonding between these is typically mechanical rather than chemical in nature. Due to the high flexibility of elastomers in normal applications, shear stresses at the interface between the inorganic and polymer can cause a failure of the mechanical bond. For high performance compounds, a coupling agent is used to form a chemical bond between the host polymer and an inorganic, such as kaolin clay. Typically, siloxane compounds are used as coupling agents.

Carbon Black

Carbon black is a very effective strength modifier for a wide range of elastomeric compounds. Since carbon black contains reactive surface groups, it bonds and interacts efficiently with the base polymer. Carbon black can be blended from a concentration of a few phr (parts per hundred resin by weight) to as much as 40 phr to achieve a wide range of physical properties. Due to the chemical bonding between carbon black and rubber, it is very effective at increasing hardness without a corresponding major reduction in tensile strength, tear resistance, or elongation limit. Carbon black addition reduces the free volume in rubber compounds, thus improving solvent tolerance, oil tolerance, and gas impermeability. Carbon black improves oxidative stability and protects the polymer against UV damage. Carbon blacks are available from a range of sources and all are produced from an incomplete combustion process. Sources include oils, tars, and reclaimed hydrocarbon materials. In other cases, carbon blacks of high purity can be derived from acetylene gas, low molecular weight polymers, and other clean sources.

Release Agents

Organic release agents and anti-blocking agents are occasionally used for elastomer compounds. Generally, these compounds have limited solubility in the elastomer compound, so they migrate and concentrate at the surface, where they can be effective to prevent cohesion and/or adhesion. Waxes and high molecular weight adipic acid esters are examples of compounds in this category.
Liquid polymers are occasionally used for softer grades of rubber compounds, where a base polymer will not provide the required balance between strength and flexibility. Liquid rubbers are of low molecular weight and would be fairly useless unless blended with other materials. In some cases, an external diene is added through a liquid base polymer. Liquid rubber is typically added during the milling operation.

**Plasticizers**

Elastomer compounds can be plasticized by addition of organic compounds. Elastomer compounds are inherently flexible and selection of a base polymer on the basis of molecular weight characteristics, chemical composition, and degree of crystallinity serves as the basis for the properties of the compound from which an elastomer is made. Oils are the most common plasticizer for elastomers. Oils of paraffinic structure or aromatic structure can be used with elastomers in which they are compatible. Paraffin wax would also be included in this category. Other plasticizers include phthalic acid esters and adipic acid esters. Fatty acids can be used as plasticizers but these contribute to an increase in surface tack of elastomer compounds. Examples include stearic and palmitic acid. Plasticizer addition has the added benefit of aiding with incorporation of inorganic materials.

**Pigments and Dyes**

Color-tinting of crosslinked rubbers follows the same description presented for thermoplastic compounds. A major problem with the use of organic pigments and dyes is that many decompose when high temperature curing agents are used. For these compounds, inorganic pigments are typically the only option.

**Inorganic Additives**

**Fillers and Reinforcement Agents**

Many commercial elastomer compounds are mechanically reinforced through the addition of inorganic compounds. These physically and/or chemically bond to the polymer to provide a more rigid matrix. Reinforcement agents include talc, various clays, silica, titanium dioxide, and many others. In some cases, fillers with high aspect ratios are used to impart directional reinforcement. A balance between particle size, surface structure, and dispersion efficiency is necessary for obtaining the best and most uniform performance of an elastomer compound. Many inorganic additives are first dried at high temperature (calcining) to split off water of hydration. This prevents moisture release during compounding and crosslinking. Moisture produces voids and often inhibits proper curing of crosslinked elastomers.

Inorganic additives for rubber compounds also include materials that enhance performance under various accelerated stress conditions. Zinc oxide is an effective heat stabilizer for some types of elastomers. Iron oxide, lead compounds, barium salts, and specially treated clays, such as kaolinite, add performance margin in wet service conditions.

**Thermoplastic Elastomer Compounding**

Compounded polymers prepared with thermoplastic elastomers (TPE) are prepared in much the same manner as thermoplastics, with some exceptions. Thermoplastic elastomers generally combine the flexibility and frictional behavior of rubber compounds with the practical forming considerations of thermoplastic materials. These are commonly encountered in automotive and appliance applications where non-slip surfaces are desirable. Since compounds in this class have elastomeric physical characteristics, this often requires that a twin-screw mixer makes use of
screws with a profile that is different than for thermoplastic compounding. Differences include the use of tapered screws, an increased frequency of barriers along the screw length to increase localized shear, separate zones of high and low shear action, and others. TPE compounds use mixers with high length-to-diameter (L/D) ratios (see Compounding Overview at the end of the chapter).

Thermoplastic elastomers are most commonly formulated from elastomeric polyurethane or block copolymers of polystyrene-elastomer, polyamide-elastomer, or polyether-elastomer bases. Thermoplastic elastomers are provided as a raw material in pelletized form for subsequent compounding. The internal domain structure that is required for thermoplastic-elastomeric performance has been established by specific considerations of blending and structural-chemical interactions. In compounding operations, specific temperature ranges are required to assure that phase separation does not occur in the TPE base polymer.

Organic and inorganic compounds for modification of thermoplastic elastomers follow the previous descriptions for thermoplastics. Addition of inorganic materials requires a screw type mixer with sufficient cooling to remove the heat developed due to high shear viscosity. The mixer must also include some areas with very high shear to assure proper dispersive mixing. Antioxidants for thermoplastic elastomer protection during compounding must have good longevity at elevated temperature and they must have good solubility in the compound to prevent separation.

**COMPOUNDING OVERVIEW**

**Introduction**

This overview of polymer compounding was prepared to provide the reader with an overview of compounding methods and equipment. Since possible contamination and subsequent failure of an end product can be associated with a compounding process, the authors believe that a brief introduction into the engineering and practical aspects of compounding is relevant.

**Methods of Compounding: Thermoplastic Polymers**

Thermoplastic polymer compounds are typically prepared by use of a single- or twin-screw mixer. This consists of parallel, threaded cylinders (screws) that are enclosed within a heated barrel. Heating is applied and separately controlled in zones along the barrel. The screws are caused to rotate with a gear reduction electric drive at one end. The barrel is a high strength enclosure, designed to sustain very high pressure, temperature, and shear conditions. The screws counter-rotate and the rate is variable. At the driven end of the mixer, polymer is added through a hopper into the throat of the mixer. Pre-weighed and mixed additives are also incorporated or metering hoppers may add proportioned quantities of polymer and additives that will form the compound. Due to the threaded nature of the screws and their proximity in an enclosed heated barrel, the ingredients are subjected to high shear as they melt. The thread pitch causes the compound to travel down the barrel, where mixing time increases and viscosity drops as the compound heats. Mixers for thermoplastics typically have long barrels and a length-to-diameter ratio of at least 20. At the end of the mixer is a screen pack, followed by a die for extruding the compound into tapes, strands, or other forms. A rotary cutter may be mounted over a strand dye to produce the “pellet” form in which the bulk of thermoplastics are supplied. The screen pack is used to remove any non-dispersed materials and to capture large particles or contaminants that would otherwise be detrimental to the finished compound. The screen pack also contributes to effective mixing by providing back pressure.
Figure 1-2 presents an illustration of several types of mixing screws. These show variations in thread pitch as different profiles or offsets in the diameter of the screws between the threaded lands. Screw profiles vary for the type of compound being mixed. In some cases, very high shear is required to assure proper dispersion of ingredients. For other compounds, aggressive shear will damage the base polymer, so reduced shear and longer mixing times are targeted. Screw profiles vary in thread land, length, and distribution of thread pitch along the screw length. Some screws contain radial pins, staggered knives, or other features for specialized applications. Some mixers include three or more nested screws.

Figure 1-2 Several Types of Thermoplastic Mixing Screws

Some thermoplastic compounds require multi-step mixing. This is required where a high degree of homogeneity is essential and ingredients may require sequential addition to avoid segregation or chemical interactions. For compounds of this type, the intermediate compound is typically extruded into pellets or chopped strips for re-introduction into the mixer and further addition of compounding ingredients.
Overview of Polymers, Additives, and Processing

A Buss mixer is a variation of the screw mixer design in which a long barrel can be configured to allow high shear mixing of ingredients at one end, with separate feed ports for sensitive additives into a less aggressive mixing zone. This design also allows liquid additives to be directly added during compounding. With a traditional screw type mixer, liquids are often added in the form of a mixture with inorganic materials. Figure 1-3 shows a view of a Buss mixer and Figure 1-4 illustrates the internal and external configuration. Polymer compounding with a Buss mixer is a continuous process. Batches are typically defined in context of a campaign wherein a batch of raw materials is used to completion or a particular production target compound weight is met. Precise metering of the raw materials is a key consideration for assuring consistent quality of the thermoplastic compound.

Figure 1-3 Buss Mixer
It is rare to use a Buss mixer for multi-stage compounding operations. In Figure 1-4, the output of the Buss mixer is directly fed into a feed screw machine where high pressure forces the compound through a die or into a pelletizer head.

**Multistage Mixing**

In some cases, polymers may be compounded from simpler starting compounds formed with two or more of the raw materials. These are identified as master batches and are often prepared when bulk addition to a single stage process would cause them to separate or to alter the bulk polymer properties during mixing to the point where mixing would be inefficient.

Proper dispersive mixing, which focuses on short-range blending of the compound, is achieved through careful selection of the proper mixing screw, mixing temperature, screw rotational speed, back-pressure, sequence of addition, and proper preparation of the raw materials to avoid caking. Distributive mixing, which addresses the overall homogeneity of the batch, is controlled in a single compounding operation by careful and absolutely consistent metering of raw materials. Without a second mixing step, distributive mixing is limited to the volume of compound contained within the mixer barrel. Improved distributive mixing can be achieved where the compound is prepared in two stages.

**Mixer Cleaning**

Cleaning of the mixer is required between runs and when changing to a different compound. In some cases, the extruder is torn down and the barrel and screws are mechanically cleaned. An alternate method is to run a high-shear cleaning compound through the mixer, followed by a purge period with the new compound before production of the new compound begins. Some types of
compounds with sensitive end-use considerations are isolated to particular machines to protect against carryover risk.

**Final Form**

Thermoplastic compounds are most commonly supplied in the form of pellets. These are formed by extrusion of the polymer through a strand-forming die plate with a pattern of round holes. This is run under water, in a water-spray environment, or in a chilled airstream. As the hot polymer is extruded, a continuously rotating blade cuts the polymer strands into short segments, thus forming the pellet geometry. With water-cooled pelletizing, the quality of the quench water must be controlled to prevent contamination.

**Methods of Compounding: Crosslinked Elastomers**

Elastomeric compounds are typically prepared in a two-stage process. The base polymer enjoys a certain level of fluidity, so it typically does not require much heat addition for processing. Since the viscosity is very high and does not lower significantly with temperature, mixing requires very high shear of the ingredients. Mixers contain two intermeshing counter-driven rotors (Figure 1-5) each of which has a complementary lobed or convoluted profile. These profiles serve to shear the compound in the gaps, while also circulating the ingredients. The profiles vary and are recognized typically by the mixer manufacturer, such as Farrell (Figure 1-6), Banbury, Francis Shaw, Werner & Pfleiderer, and others. The rotors are enclosed in a heavy casing since the internal pressure and shear energy are very high. Mixers are water-jacketed so that the frictional heat developed during mixing can be removed through a heat exchanger. With the completely enclosed internal mixer, compounds are prepared in one batch. In other words, all ingredients get introduced and co-mixed in a closed mixing cycle. A variation of this technology will be described later in this chapter.
Batch Mixing

Mixing occurs in stages, beginning with the base polymer. This is pressure-fed into the mixer by injection of a bale, strips, or pellets, using a hydraulic or pneumatic ram. The polymer heats and its viscosity reduces, then the inorganic ingredients are added. Processing aids such as carboxylic acids may be added to help reduce shear and to improve wetting of the inorganic compound. If an external antioxidant is needed, this would be added with or before introduction of the reinforcement to protect the polymer against oxidation. Liquid processing aids and coupling agents may be added first to the inorganic so that they are not lost during processing. Due to the extremely fine particle size and low density of carbon black, this is normally added in the form of a high concentration of carbon black in the base polymer or other polymer, separately prepared into a master batch by twin-screw mixing.

In other stages of mixing, additional polymers, waxes, extender oils, and internal lubricants might be added. Addition sequence is driven by melting temperature, viscosity, and thermal stability of the ingredient. Internal mixers are sealed against leaks of high viscosity, cohesive elastomer compounds; however, ingredients in liquid form will not be retained in the mix unless added in master batch form or blended with inorganic ingredients.

In a final mixing step, the crosslinking agent is added. Internal heat generation in the mix must be low enough to prevent the peroxide from decomposing and initiating a crosslinking reaction within the mixer.

Internal mixers must be run in a full or nearly full condition, so a batch recipe is calculated to provide an appropriate volume. If not filled, the ingredients will not be properly sheared and heat transfer will be compromised. Typical commercial mixers have a batch size of at least 100 pounds.
Overview of Polymers, Additives, and Processing

of compound. A mixer of this size will have a drive motor of no less than 75 horsepower. Proper dispersive mixing is a balance between proper shear, sequence of addition of ingredients, and thermal stability. Mixers have extensive monitoring instrumentation that provides continuous feedback about thermal conditions, rotor torque, and rotor speed. Once a mixing process has been developed, a standard protocol is followed for preparation of the compound.

An internal mixer provides the shear necessary to mix a raw elastomer with its compounding ingredients. It is imperative that the compound is homogeneous throughout the batch so that its properties are uniform. For distributive mixing, a second stage of mixing is used. In many cases, an internal mixer is mounted above a two-roll mill (Figure 1-7) and when mixing is completed a bottom hatch is opened, allowing the compound to fall onto the two-roll mill. In other cases, the compound will be transported to the mill.

Processing

A two-roll mill consists of two large-diameter counter-rotating cylinders, with a variable gap between them. The rolls are maintained at a fixed temperature through internal fluid heating and an external heat exchanger. The elastomer compound forms a sheet on the roll surface. This is continuously cut into wide strips by the operator, folded over, and placed back on the rolls. This process is repeated for perhaps 15 minutes to assure that the compound is fully homogenized.

In some cases, the curing agent is added during the milling operation, generally in the form of a master batch. This practice is used for peroxides that decompose at a lower temperature, to reduce the risk of accidental curing in the internal mixer, when localized temperature can be very high.

Figure 1-7 Laboratory Scale Two-Roll Mill
With a closed mixer, control of distributive mixing is inherently good, since all materials are added in a single batch and mixing occurs in two stages. Failure to add an ingredient or to improperly treat raw materials may lead to dispersion and homogeneity problems.

**Continuous Mixing**

A second type of elastomer compounding makes use of a continuous mixer. This type of machine is most often used where a high volume of rubber compound is required to feed large production lines for applications that include tires, sheet rubber products, cable insulation, hoses, belts, and others. Figure 1-8 is an illustration that shows the internal configuration of a continuous mixer. This is a hybrid design that features a feed screw, similar to a screw type mixer that feeds raw materials into a heated high shear rotor type mixer. As shown in this figure, raw materials are fed continuously and mixed compound is continuously discharged. Control of dispersive mixing is achieved by designing a process that optimizes residence time in the mixer, rotor speed, temperature, and rotor profile. Continuously blended rubber compound is typically transferred directly to a two-roll or calendaring mill for distributive mixing.

Since internal mixers can be opened for material feed and compound removal, these are generally simpler to clean when compared to screw-type mixers. It is a common practice to run natural rubber or special high-tack, cohesive compounds through a mixer as a final stage of cleaning. Further, the first batch of compound is typically sacrificed or saved for experimental work following clean-out.

![Figure 1-8 Continuous Mixer for Elastomer Compounding](image)

**Mixer Cleaning**

Cleaning of the two-roll mill is a simple operation since the compound only contacts the exposed external surface of the rolls. Typically a natural rubber compound may be used for surface cleaning and/or the first batch of polymer compound might be used for this purpose.
Overview of Polymers, Additives, and Processing

Intermediate Forms of Compounds

Strips of elastomer compound can be manually or automatically cut directly from the milling operation and placed into release packaging. In other cases, the warm compound might be placed directly into an extruder where it is pressed through a cylindrical or rectangular die and cut into short sections or coiled for subsequent use. In all cases, non-crosslinked rubber compounds cohere strongly; therefore, a release agent (anti-blocking compound) or physical method is required to maintain a manageable form of the compound. Surface treatment options are significant. These may include water baths with talc, direct application of talc, treatment with the same inorganic in the compound, surface wetting with silicones, and others. Physical treatments include release films, physical separation of pre-forms onto release layers, or packaging into trays that prevent contact between pre-forms.

The more amorphous grades of elastomer compounds tend to have high surface tack before crosslinking, so the elastomer in the form of pellets tends to form an inseparable bond between pellets. Blocking can be reduced by the addition of an inorganic anti-blocking ingredient, such as talc. This is generally added in a water slurry, so that the talc coats the exterior surface of the compound with a very thin layer. Surfactants are often used to enhance talc coating of the surface. In some cases, organic anti-blocking agents are used.

Prior to crosslinking, softer grades of elastomer compounds flow slowly, so these cannot be produced in a form that is unconstrained. A common intermediate form of such compounds is long, continuous ribbons that are dusted with a release agent and coiled. Sheets or other forms can also be hot-pressed, dusted, and shipped with release packaging that helps to separate the layers for subsequent processing. In still other cases, the elastomer compound is wrapped into a polyethylene sheet to hold its shape and to protect against contamination. In this approach, the elastomer bonds to the packaging material and both are blended in the final extrusion operation.

Final Form

Crystalline forms of elastomer compounds can be produced into pellet form in some cases. These are typically pressed in a compression molding operation or in a continuous molding press, resulting in pellets that are about 0.5 inch diameter. If a compound has a high density, it may retain its shape sufficiently to allow it to be packaged into gaylords in pellet form. Contracted forms are often supplied from compounders to molders. The latter might specify compounds in the form of molded disks, which can then be fed directly into molding machines where the final forms are produced and crosslinked.