

# Elastomer Macrocomposites

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**Abstract** This chapter summarizes many of the recent technical research accomplishments in the area of elastomer macrocomposites. Firstly, it explains the compounds that exist in elastomeric matrices as well as the types of filler used in order to reinforce them. Then, the various recent attempts reported on advances of elastomer based macrocomposites are discussed. In addition, an analytical description in their manufacturing techniques and processes is comprehensively reported. Moreover, the techniques used to structurally and mechanically characterize the elastomeric macrocomposites are covered. Their usage in commercial applications is described as a final point.

## 1 Introduction

Materials with synergistic properties are chosen to create composites with tailored properties; for example, brittle carbon fibers of high-modulus, are added to low-modulus polymers, to create stiff, lightweight composites with a reasonable degree of toughness. The properties achieved by conventional macrocomposites, however, usually involve compromises [1–10]. In conventional macrocomposites the dispersed phase has dimensions in the order of tens of microns to tens of

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millimeters. The mechanism of mechanical property reinforcement in these materials is well understood and the properties can be predicted using sum of properties of each component weighted by the volume fraction of that component. Because the size of individual component phases, in macrocomposite elastomers, cannot be reduced beyond a limit, the composite properties are linearly dependent on the component properties; non-linear or exponential improvement in composite properties therefore requires looking beyond conventional macrocomposites [11–14]. Macrocomposite is making a part from two or more different materials. In ancient times *swords* were made by combining tough, ductile steel with hard, brittle steel. The result was a combination of stiffness and toughness far superior than could be obtained from any material available at that time. It is this ability to produce combinations of stiffness and toughness not obtainable in a single material which gives the macrocomposite concept great potential as a means of using engineering plastics to replace steel and other metals. To make such a macrocomposite, one resin would be molded into a part which would then be used as an insert when a second resin was molded in a second molding operation. The two different resins would be chosen so that one would supply toughness where toughness was required, and the other would supply stiffness where stiffness was needed [15, 16].

Mostly the properties of interest in composites are mechanical properties. There are many naturally occurring composite materials. For example, tissues in the body, wood, bamboo, muscles, etc. They exhibit high strength in addition to flexibility. In synthetic composites, the aim is to achieve optimum mechanical properties required for specific applications. Three types of composites may be distinguished: Macrocomposites, Microcomposites and Nanocomposites.

There are two types of macrocomposites: Large particle composites and fiber-reinforced composites [17–20]. In large particle macrocomposites big sized particles of one type of material is uniformly dispersed in a matrix material. The matrix may be metal, polymer or ceramic. Concrete is a typical example of large particle composite in which the cement matrix is mixed with particulate of sand and gravel. Cermets are large particle composites in which ceramic particles are embedded in a metal matrix. Other examples of large particle composites are carbon particles added to vulcanized rubber matrix. This enhances the tensile strength and toughness of the rubber material. These materials are used for automotive tires. For effective reinforcement, the particles should be small and must be uniformly distributed throughout the matrix. The particle should form strong adhesive bond with the matrix. Fiber reinforced composites are designed to increase the strength and elastic modulus of the material without increasing its specific gravity. High strength and low weight is the main characteristic aimed at in the design of fiber reinforced composites [21–23].

Carbon black has been used for the reinforcement of rubber compounds since the beginning of the twentieth century, and has a global production rate of approximately 10 million tonnes/year. Carbon black is produced by incomplete combustion of oil under specific conditions, with a long history of safe production and use. Several parameters are controlled in the process in order to achieve the

specific characteristics of the finished carbon black products. Specifically, the oil is injected at high speed, approximately 900 m/s, into a reactor where it is pyrolysed at high temperature (approx. 1800 °C). The combustion reaction is controlled so that the oxidation remains incomplete and therefore carbon black is formed. The reaction is intentionally stopped by spraying water (quenching). The carbon black obtained is filtered and then compressed into pellets of millimetre dimension. During the first split second of the above combustion reaction carbon nodules are formed with dimensions from 20 to 100 nm, depending on the grade of carbon black. On the basis of the proposed definitions these nodules may be considered nano-objects. However the lifespan of these nodules is very short as they immediately and irreversibly cluster together to form aggregates of sizes between 100 to 500 nm. These aggregates then subsequently combine together to form very solid entities: agglomerates (Fig. 1).

These agglomerates measure between 1 and 50 microns. The aggregates and agglomerates however, may meet the proposed definition of nanostructured materials. In aggregates, covalent bonds exist between particles; in agglomerates the bonds between aggregates are electrostatic. Aggregates cannot deaggregate at all. Agglomerates cannot de-agglomerate during standard handling conditions. After the agglomeration reaction, the agglomerates pass through the pelletiser to compact the carbon black into a pellet form of millimetre dimension [24].

Amorphous precipitated silica apart from being used to produce rubber articles is used in many other applications, e.g. cosmetics, paper and many other applications related to nutrition and health. The world production of amorphous precipitated silica is 1.4 million tons of which 1/3 is used in tire production. Silica has been used in the treads of tires for more than twenty years in order to reduce the fuel consumption of vehicles, thus contributing to a reduction in vehicle emissions of greenhouse gases. Amorphous precipitated silica is produced by a two step process: obtaining silicate, and then the production of precipitated silica. To make the silicate, very pure sand is mixed thoroughly with sodium carbonate. The homogeneous mixture is transferred to a glass oven, heated above 1000 °C, so that

**Fig. 1** Carbon black pellets [24]



glass, vitreous silicate, is formed. Then rapid cooling causes solidification and fractionation of the silicate into small granules, a few cubic centimeters in volume. The vitreous silicate is dissolved in water and transferred to a reactor in which, through acidification and under agitation, amorphous silica is precipitated out. During this precipitation, as is the case with carbon black, there is an instantaneous initial formation of elementary particles, from 5 to 40 nm, of a very short lifespan. These also may be considered *nano-objects* according to the above definition (Fig. 2).

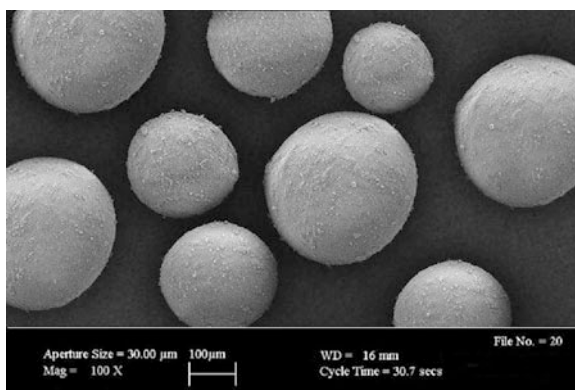
These particles, however, immediately and irreversibly cluster to form non-dissociable aggregates, from 50 to 300 nm in size, which subsequently bind together to form agglomerates from 1 to 50 microns. The aggregates and agglomerates meet the above definition of nanostructured materials. In aggregates, covalent bonds exist between particles; in agglomerates the bonds between aggregates are electrostatic. Aggregates cannot de-aggregate at all. Agglomerates cannot deagglomerate during standard handling conditions [25, 26].

## 2 Elastomer Based Macrocomposites

### 2.1 Elastomeric Matrices

The Elastomeric Matrices (EM) consists of compounds of natural or synthetic rubber with a variety of ingredients to confer the required properties. The natural rubber (NR) forms as a latex, a suspension in water of rubber particles coated with a natural surfactant [27]. The synthetic rubbers (SR) have been developed for specific purposes, and are made by polymerization of the monomers under pressure and heat in the presence of a catalyst either in suspension, to form latex, or in solution. The elastomers may be defined as long-chain organics, often polyolefin molecules, consisting of repeating units of one or more monomers, which exhibit very high extensibility combined with an ability to return to the original

Fig. 2 Silica micro pearls



configuration. Analysis showed that their high extensibility was due to uncoiling of the linear polymer chains from an initially random configuration to one of general alignment. There are several natural limits to both the elastic extension and the permanent set in raw elastomers:

- (i) Chain entanglements, which result in stiffening at very high elongations, an effect that increases with molecular weight [28–31].
- (ii) Crystallinity, which in elastomers requires high purity and very regular chain structure, e.g., in polybutadiene better than 98 % cis content, percentage of covalent bonds in the main chain. This level is unrealizable in cross-linked material. Spherulitic crystallinity develops in unstrained polymers e.g., NR or polychloroprene at low temperatures, thus increasing their stiffness. Crystallinity can also develop at high extension levels as fibers align along the stretching direction, where it increases both stiffness and strength [32–34].
- (iii) Second-order transition temperature [35, 36].

Since elastomers owe their elastic properties to thermal agitation, they are naturally sensitive to temperature variations. In general, their stiffness increases as the temperature is reduced, until a temperature is reached where the material assumes a glass-like consistency, with a corresponding increase in hysteresis, internal viscosity. The temperature at which this occurs, at the glass transition temperature,  $T_g$ , increases with the number and size of the side groups on the polymer chain, for example vinyl groups, benzene rings, chlorine, and the tendency is thus for high glass transition temperature to be associated with high hysteresis and incidentally low air permeability and high friction. Elastomers are usually mixed with several different ingredients to form a compound, the ingredients being chosen to optimize the physical properties of the compound in order to meet the specification for a particular application.

Studies have shown that the process causes sulfur cross-links between two and eight atoms long to form at irregular intervals between chains, by breaking the covalent bonds which are a feature of the polyolefin structure. Efficient vulcanization systems, having short cross-links, tend to have higher modulus and lower extension at break. The cross-link density can be deduced from swelling tests in solvents, and is usually defined in terms of the molecular weight between cross-links,  $M_c$ , typical values being around 100,000, compared with 78 for the polyisoprene monomer unit, or 26,106 for a natural rubber molecule. Where the main elastomer chain contains no covalent bonds, it is necessary either to provide such sites by copolymerization with an olefin, or to form cross-links directly between carbon atoms on the chains without using sulfur by radiation or organic peroxides. It was found that some materials, typically sulfenamides or thiazoles, can catalyze cross-linking reactions and are added as accelerators to reduce the reaction time. In some applications, the reaction rate needs to be reduced and a retarder (e.g., phthalic anhydride) is then added. All these additives comprise the curative system. The amounts of each ingredient vary, but rarely exceed 5 % by weight.

## 2.2 *Fillers*

Elastomers are relatively expensive materials, and it became common practice to add cheap mineral powders, e.g. silica or calcium carbonate to reduce the cost, the effect being to increase the elastic modulus of the cured compound with little effect on the strength or other properties. However, it was soon found that very fine powders, particularly carbon black, manufactured by burning oil or natural gas in controlled conditions, could result in a large increase in both strength and modulus, albeit with an increase in hysteresis [37–40]. The reinforcing effect increases with the amount added; up to about 30 % by volume, and also with reduction in particle size or increase in the structure the tendency of the particles to form chains. The particle size and structure are defined by an internationally accepted system, ASTM Standard, D-1765, thus N330 black ca. 30 mm, medium structure is made under a variety of trade names by various manufacturers. Reinforcing silicas having similar particle size, but with special surface treatments, have appeared, which appear advantageous in terms of hysteresis. Another means of reducing cost is to add oil to the compound, which may also improve processability, but usually with a small reduction in physical properties. Except in racing tire treads it is rarely used in quantities greater than 5 % by volume. By using highly aromatic oil, it is possible to raise the glass transition temperature,  $T_g$ , of the compound, which is found to improve the wet grip of tires, while aliphatic paraffinic oils tend to reduce it. Soon after the development of cross-linking systems, it was observed that rubber compounds deteriorate with time, an effect that is typically manifest as cracking or crazing of the surface. This is usually due to oxygen or ozone attack on the covalent bonds in the elastomer chains, a process perpetuated by the formation of free radicals. There are a variety of means of reducing the deterioration, e.g., the addition of waxes which bloom to the surface to form a protective skin, or the addition of small amounts of antioxidants or antiozonants which act as free radical acceptors, thus breaking the chain reaction. In addition to reducing the cracking, these materials may also affect the cross-linking reaction, hence necessitating an increase in the amount of accelerator used.

Where rubber is required to adhere to a polymeric or metal substrate e.g., cords, special compounding techniques are used. In some cases, one or more bonding layers such as latex resin mixtures are interposed between the substrate and the rubber, which bond well to both surfaces, while in other cases special compounding ingredients e.g., organic cobalt salts are added to promote adhesion. The cord reinforcement acts as the main load bearing component of the composite and enables it to withstand the variety of loads that it is subjected to in its service life while maintaining an acceptable degree of dimensional stability. Cords are made by twisting together a parallel array of fibers to form a singles yarn and then twisting together two or more of these yarns together to form the cord. Many different materials can be used as the cord reinforcement, the main requirement being that it is strong in a longitudinal direction and sufficiently flexible to withstand the forces imposed upon it in service. Initially cords were made from

natural fibers such as cotton, flax, etc. The development of regenerated natural fibers such as rayon and manmade fibers such as nylon, which have a much greater tensile strength, enabled the performance of cord reinforced elastomers to be greatly improved. In addition to organic polymer materials, some inorganic materials such as glass and steel are also used for cord reinforcement. Rayon is produced from regenerated cellulose. Cellulose is the main structural material of many plants such as trees, grasses, and cotton. The main source of cellulose for rayon production is wood pulp derived from spruce wood. Nylon was the first commercially successful synthetic fiber, the raw materials being derived from coal or oil. Nylon is a generic name for polyamide fibers composed of linear polymers, the monomer units being linked by amide groups. Polyester is the generic name for polymers with the monomer units joined by ester linkages formed by reacting an acid with an alcohol, the raw materials being derived from petroleum. Aramid fibers are aromatic polyamides formed from an aromatic acid such as terephthalic acid or an aromatic dichloride such as terephthaloyl dichloride and para-phenylene diamine. The performance of cord reinforced elastomers has improved dramatically, particularly when used in tires, mainly due to the service requirements of car manufacturers. In order to enable these demands to be met there has been continual research and development in polymer chemistry to find new fibers with improved properties. Two fibers which are new to the marketplace are polyethylene naphthanate and polyolefin ketone. Steel wires of higher tensile strength have been developed; these wires have a slightly higher carbon content and are known as high tensile and superhigh tensile. Steel cords, which are made from a number of steel wires, were first used in radial car tires as the tread stabilizing layer. In a similar way that steel would not normally be considered as a textile material, glass when extruded as a filament and drawn down fine enough can be processed similarly to a normal textile material. Glass is spun into air from the molten state, it is then rapidly quenched and attenuated to prevent crystallization and coated with size to aid future processing. Carbon fiber is virtually 100 % carbon with a highly orientated graphitic structure. Its main properties of interest as tire reinforcement are similar to those of glass but it is lighter and has even higher modulus and strength.

Rubber is a widely used material having properties of flexibility, strength and elasticity. The basic raw material, either natural rubber or synthetic rubber, is in latex or solid form, and processed into many different products. The raw rubbers, composed essentially of long polymer chains, are joined together with “cross-links” in a process called vulcanization to give the final material its characteristic properties. Natural rubber hardens below 0 °C and softens and weakens above 80 °C, losing its strength and becoming tacky. In between these temperatures it can flow under stress and permanent deformation occurs under prolonged strain. These undesirable properties are reduced by vulcanization, in which the reactivity the double bonds impart to the molecule is utilized to make it react with added material to form crosslinks between the chains. The crosslinking increases the useful temperature range of the rubber and hardens the rubber so that it becomes much stronger and does not creep but returns to its original shape on release of

stress. Its surface properties are improved and its solubility decreased. Sulphur is still the most important vulcanizing compound for natural rubber, but not the only one. The raw rubbers include butadiene rubber, butyl rubber (isobuteneisoprene copolymer), synthetic isoprene rubber, ethylene-propylene rubbers, chloroprene rubber (the methyl group of isoprene is replaced by chlorine), nitrile rubbers (acrylonitrile butadiene copolymer), styrene-butadiene rubber, and silicone rubbers which are polysiloxanes.

Compounds added to the raw latex must be in the form of emulsions or dispersions. They are prepared by milling the substances with distilled or softened water in ball or gravel mills which revolve for anything from a few hours up to several days. Gelatin, casein, glues, soaps etc. are used as wetting or dispersing agents. Substances added are softeners, fillers, pigments for color, the vulcanizing agents and antioxidants. The latex itself has to be stabilized with surface-active agents to prevent coagulation which can be irreversible. These agents act by imparting a charge to the surface of the minute rubber particles or by holding an envelope of water around the particle, thereby preventing any mixing. The compounding materials and the latex are mixed and are then ready for dipping, molding, foaming or spreading. The production sequence is mixing, forming and vulcanizing. The solid rubber and the other materials have to be mixed. This is done with two basic machines, a two-roll mill in which the material is passed between two heavy metal rollers mounted horizontally, and a Banbury mixer, an internal mixer in which the materials are sheared between the internal rollers and the inside of the casing. There are four basic methods of forming the material to the required shape; spreading onto fabric from solution, extruding, calendering and molding.

Sulphur vulcanization, the most common form, involves the formation of polysulphide crosslinks between the chains. If sulphur only is used, curing times of 8 h are necessary. Modern methods using “activators” and “accelerators” reduce the curing time, eliminate cyclic structures and can shorten the sulphur links down to one or two sulphur atoms. Shorter sulphur links give greater stability to heat and improve the ageing properties.

Fillers range from inert dilutants such as whiting, talc, clays,  $\text{CaCO}_3$ , etc. which “cheapen” the product and make it go further, to reinforcing fillers which increase tensile strength and abrasion resistance. Carbon black is a most important reinforcing agent in tires and tubes and is usually produced by burning oil or natural gas in a limited supply of oxygen. Protective agents prevent ageing or deterioration, which comes about mainly by oxidation. Softeners and lubricants, in the form of Stearic acid, waxes, mineral oils, tars, etc. are added to plasticise or increase self-adhesion of the rubber mix. Certain resins increase the tackiness of the rubber for use on adhesion tapes. Elastomers are polymers that will elongate when subjected to a tensile force. They will return to the original shape when the force is removed. Rubber is an elastomer. Natural rubber is composed of isoprene units. Isoprene is polymerized into polyisoprene. Natural rubber is soft and tacky when hot. Reacting it with sulfur cross-links the polyisoprene and makes the rubber harder. This process is known as vulcanization. Synthetic rubber is similar to



polyisoprene. One example is polybutadiene. Neoprene is very similar to polybutadiene, but contains chlorine instead of one CH-group. It is more resistant to solvents like oil and gasoline. Another synthetic rubber is styrene-butadiene rubber (SBR). SBR is a copolymer of styrene (25 %) and butadiene (75 %). It is tougher and more resistant to oxidation than natural rubber, but its mechanical properties are less satisfactory [41–46].

Addition of filler increases hardness of the cured product. All fillers are not created equal, so that there is a range of reinforcement from very high to very low, corresponding to the primary size of the filler particle, from around 10 nm for very fine particle carbon blacks giving high reinforcement, to greater than 300 nm for some calcium carbonate which give low reinforcement. Use of the latter reduces compound cost. The shape and surface chemistry of the filler particle also play an important part in reinforcement. Some popular fillers are, in order of decreasing reinforcement, carbon blacks and silicas, clays and then whittings. Carbon black is a material of major significance to the rubber industry, so it is no surprise that most rubber products we see in the market place are black in color. There are two common methods of producing carbon black today. Heating natural gas in a silica brick furnace to form hydrogen and carbon produces a moderately reinforcing material called thermal black. Alternatively, if we incompletely burn heavy petroleum fractions, then furnace blacks are produced. These are the most important blacks in terms of quantity used and available types. Carbon black consists of extremely small particles from around 10 to 300 nm. This gives two primary properties allowing a whole range of grades designated by both a particular particle size (surface area) and a specific level of structure [47–50].

### 3 Recent Advances in Elastomer Macrocomposites

The effect of rubber wood on curing characteristics and mechanical properties of epoxidized natural rubber (ENR) has been investigated in the loading range of 0–50 phr. Results indicate that the scorch and cure times decrease with increasing rubberwood loading. Tensile modulus and hardness of the composites increase with increasing rubberwood loading whereas tensile strength and tear strength show a decrease. SEM studies and rubber-rubberwood adhesion measurements indicate that the increasing rubber wood loading has weakened the rubber-rubber wood interactions [51]. Properties of natural rubber (NR) filled with various loadings of ultra-fine vulcanized acrylate rubber powder (ACMP) have been investigated. ACMP loading was varied from 0 to 20 phr and, after compounding, the compound properties have been determined. Results reveal that increasing ACMP loading leads to improved processability, as evidenced by the reduction of both mixing energy and Mooney viscosity. ACMP, however, has negative effect on cure, that is, both scorch time and optimum cure time are prolonged while the state of cure is reduced with increasing ACMP loading. Due to the reinforcing effect of the fine ACMP particles, both modulus and hardness are found to increase

consecutively with increasing ACMP loading. The tensile strength is also found to improve with increasing ACMP loading up to 10 phr. However, due to the cure retardation effect and the high thermoplastic nature, the presence of ACMP causes deterioration of elasticity. As ACMP is highly polar and fully saturated, the addition of ACMP enhances the resistance to oil and thermal aging of the NR vulcanizate. Significant improvement of thermal aging resistance is found when 10 phr or more of ACMP is added [52].

The puncture and burst properties of short-fiber reinforced polychloroprene rubber under various conditions has been investigated to yield the best mechanical properties. In addition to five types of interphase conditions, four types of fiber aspect ratios (length of fiber/diameter of fiber) and three different fiber contents have been studied for their roles in the puncture and burst properties of rubber products. Certain interphase conditions and higher fiber aspect ratios have shown to provide higher puncture and burst stresses at a given fiber content. Since both testing methods measure biaxial properties of reinforced rubber, the relation between the two properties have studied. The discrepancy between regressed puncture and burst force is explained based upon the rubber stiffness due to reinforcing parameters and the stress concentration upon sharp edge. Overall, it was found that the interphase condition, fiber aspect ratio, and fiber content have an important effect upon puncture and burst properties [53].

Mica or carbon black was used as filler in composites of acrylic rubber. The fillers differ not only in nature, mica being a mineral material and carbon black being organic, but also in form and particle size. The content of filler varied from 0 to 50 phr and its influence on acrylic rubber was evaluated based on cure parameters, mechanical, and swelling properties. The cure parameters allow the conclusion that the presence of mica does not have a negative effect on the cure or processability; the swelling results indicated a weak interaction between acrylic rubber and mica even though the mechanical properties of acrylic rubber composition with 40 phr of mica were found to be similar to those of 20 phr carbon black. As a result of mica being less expensive than carbon black, is light colored and easily processible, these properties are of industrial importance. All properties analyzed have been compared with gum type composition without filler [54].

A networked silica prepared by interconnecting silica particles with polymeric methylene diphenyl diisocyanate has developed for use as a highly effective reinforcing material for rubber compounds without the need to add silane coupling agents. Methylene diphenyl diisocyanate incorporated onto the silica surface formed networks among neighboring silica particles with urethane linkages and produced networked silica at low cost. The TEM photographs illustrated the improved dispersion and formation of openings among the silica particles, which could allow easy intrusion of rubber molecules. The networked silica has showed a high reinforcing performance for styrene-butadiene rubber (SBR) compounds, suggesting the possibility of replacing the silica reinforcing systems with coupling agents. Due to the absence of any silane-containing coupling agents, the networked silica does not suffer the disadvantages associated with coupling agents. Since the networked silica reinforces rubber compounds by the physical entanglement

between rubber molecules and the methylene diphenyl diisocyanate chains, high loading of the networked silica is more effective in enhancing the mechanical properties of rubber compounds [55].

Different elastomer-based composites for microwave absorbers are developed. The influence of chemical character and structure of the polymer matrix and chemical nature and concentration of fillers with high values of the imaginary part of the complex dielectric permittivity and magnetic permeability on the microwave properties of the absorbers is investigated. Natural rubber, styrene butadiene rubber, butadiene rubber, chloroprene rubber, nitrile butadiene rubber have tested as polymer matrix. Graphite, furnace carbon black, acetylene carbon black and active carbon are used as fillers with high dielectric losses; natural magnetite is used as filler with high magnetic losses in the experiments. Some more important microwave parameters of the absorbers as function of frequency and composition (mass ratio filler/rubber) are measured [56].

The production of hydrosilylated impact polypropylene (PP) copolymer has been demonstrated in a co-rotating twin-screw extruder. This has been accomplished through a two-step reactive extrusion process that involves: (i) the formation of terminal double bonds on a commodity polypropylene copolymer through peroxide initiated degradation reactions, and (ii) the melt-phase functionalization of these double bonds with hydride-terminated polydimethylsiloxane (PDMS). Spectroscopic analysis of the peroxide degraded polypropylene and the purified hydrosilylated polypropylene has been performed to confirm the attachment of PDMS onto the polypropylene chains. In addition, the hydrosilylated polypropylene has been characterized in terms of molecular, rheological, surface, and mechanical properties. It has been found that the two-step hydrosilylation reaction decreases molecular weight, imparts formation of branching/chain extension, decreases impact strength, and improves surface hydrophobicity. Finally, oscillatory shear measurements exhibit an unusual up-turn in the viscosity curve at low frequencies [57]. A theory for incompressible, rubber-like shells of arbitrary geometry undergoing finite rotations and finite strains, including transverse normal strains but neglecting transverse shear strains, is presented [58].

The effect of fillers on the mechanical properties such as stress-strain behavior, tensile strength, percentage strain at-break, Young's modulus and tear strength has been investigated. Different filled crosslinked thermoplastic elastomers of styrene butadiene rubber (SBR)/high density polyethylene blends (HDPE) blends were prepared using silica, HAF-carbon black, china clay and  $\text{TiO}_2$ . The reinforcement ability of the filler was increased in the order of silica > HAF-black > clay >  $\text{TiO}_2$ . The nature of the filler and filler loading has a dramatic effect on the mechanical properties of SBR/HDPE blends. Filled blends showed improved mechanical properties such as enhanced of strain at-break, when fillers are incorporated. The initial trend of properties for all filled system is the enhancement of properties. When HAF-black is used as the filler, at higher loading strain at-break is found to decrease due to the stiffness of the matrix. In the case of clay, there is a deterioration of properties occurs on higher loading, which is attributed to dilution effect and all  $\text{TiO}_2$  filled system have lower elongation at break than the base polymer.

Theoretical models namely Guith's and Kerner's model have been compared with the experimental values of Young's modulus of filled system. The experimental values of modulus are found to be higher than the theoretical values indicating strong interaction between the filler and the matrix. SEM studies of the tensile and tear fractured surfaces of the filled blends have been carried out. The variation in properties was correlated with the morphology of the system [59].

The use of the sol-gel process on general-purpose grade rubbers has reviewed in the absence or presence of silane coupling agents. The sol-gel reactions of tetraethoxysilane in epoxidized natural rubber (ENR), styrene-butadiene rubber (SBR) or butadiene rubber (BR) vulcanizates produced silica generated in situ. This silica was found to be a good reinforcing agent by investigating tensile and dynamic mechanical properties and morphology observation by transmission electron microscopy (TEM). The amount of silica formed was limited by the degree of swelling of the rubber vulcanizate by of tetraethoxysilane which was the precursor of the silica. However, the dispersion of silica generated in situ was better than conventionally added silica due to its formation in place. Also, it was noted that the diameter distribution of in situ silica was monodispersed. Silane coupling agents, such as mercaptosilane, aminosilane, and bis (3-triethoxysilyl-propyl) tetrasulfide, were compounded in the vulcanizates and their effects on silica generated in situ were evaluated. Their effects were significant. The dispersion of the silica in the rubbery matrix became better and the particle size became smaller and monodispersed, as observed by transmission electron microscopy, which improved mechanical properties. The superior properties of silica generated in situ have studied further to elucidate the mechanism of reinforcement [60].

Fatigue life prediction and evaluation are the key technologies to assure the safety and reliability of automotive rubber components. Fatigue life prediction methodology of vulcanized natural rubber was proposed by incorporating the finite element analysis and fatigue damage parameter determined from fatigue test [61]. Heat-aging effects on the fatigue life prediction of natural rubber were experimentally investigated. Fatigue test were performed using the 3-dimensional dumbbell specimen, which were aged different amounts. The Green-Lagrange strain at the critical location determined from the finite element method used for evaluating the fatigue damage parameter. Fatigue life prediction equation effectively represented by a single function using the Green-Lagrange strain. According to fatigue life prediction equation, fatigue life ambient temperature was longer than at 70 °C. Predicted fatigue lives of the rubber component were in fairly good agreements with the experimental fatigue lives within factor of two [61].

The relationship between the variation of hydrogen bonding and macroscopic properties of composites composed of hydrogenated nitrile butadiene rubber (HNBR) and 3,9-bis {1,1-dimethyl-2 [ $\beta$ -(3-tert-butyl-4-hydroxy-5-methylphenyl) propionyloxy] ethyl}-2,4,8,10-tetraoxaspiro [5, 5]-undecane (AO-80). Hydrogen bonding of the composites was studied by Fourier-transform infrared (FT-IR) and ultraviolet (UV) spectroscopies. FT-IR spectra at room temperature revealed that the stretching vibration peak of O-H and C = O of AO-80 red shifted with

increasing AO-80 content, whereas that of  $C \equiv N$  of HNBR blue shifted only when the AO-80 content exceeded 10 parts per 100 resin (phr) [62].

Miscibility and dynamic mechanical properties of hydrogenated nitrile butadiene rubber (HNBR) and 3,9-bis{1,1-dimethyl-2-[ $\beta$ -(3-*tert*-butyl-4-hydroxy-5-methylphenyl) propionyloxy]ethyl}-2,4,8,10-tetraoxaspiro [5, 5]-undecane (AO-80) composites have investigated. The composites with low-AO-80 content have showed the incomplete miscibility, and a part of AO-80 dissolved into HNBR, while the rest was dispersed into HNBR in the form of deep-submicron-sized microspheres based on the micromorphological and thermal analyses. However, with the increasing AO-80 content, the system became completely miscible. When blending with AO-80, the resulting composite exhibited the remarkably improved dynamic mechanical property. The loss tangent peak of the composites gradually shifted to room temperature with the increasing AO-80 content [63].

## 4 Manufacturing of Elastomer Macrocomposites

### 4.1 Introduction of Processing Rubber Compounds

Most products are made from dry rubber. The successive operations for natural rubber being [64–71]:

- (i) Tapping the rubber tree to collect the latex in cups, to be followed by screening to remove contaminants.
- (ii) Coagulation, using acetic acid to neutralize the surfactant charge.
- (iii) Consolidation squeezing out the excess water in a mill, followed by drying.
- (iv) Shipping, usually in the form of 50 kg bales, during which crystallization may develop.
- (v) Softening, by passing the rubber between the ridged rollers of a Breaker Mill, so reducing the molecular weight and crystallinity.
- (vi) Internal mixing, where the rubber is sheared by rotors within a heated chamber while the compounding ingredients are added. A few minutes mixing are typically required to achieve good dispersion of the filler, which may be accomplished in two or three stages to avoid overheating and the risk of 'scorch' (premature cure). The cross-linking ingredients are naturally always added last.
- (vii) Sheetting-out to a required dimension by passing the compound between the heated rollers of a two-roll mill or (with more precision) a three- or four-roll calendar.
- (viii) Extrusion, which involves forcing the compound through a shaped die to achieve the desired profile by means of a ram or screw feed.

- (ix) Vulcanization, by heating to  $130 \pm 180$  °C for a period of  $2 \pm 120$  min (depending on the thickness), to promote the cross-linking reaction. In normal rubber manufacture a slug of compound is usually placed in a mold of the required shape, and loaded into a press, which applies external load to prevent the mold opening or internal porosity developing in the rubber. Narrow vents (spew holes) are provided to allow the slight excess of rubber to escape.

Textile and glass cords are usually processed using the traditional spinning and weaving route to form a fabric prior to calendering but steel cords are usually fed from a creel situated in front of the calendar. After spinning the bundle of continuous filaments, these are brought together to form the yarn. This is then given a spin finish and a small amount of twist to aid processing and wound onto a cylindrical shaped center to form a cheese. The starting material of a steel cord is a hot-rolled wire rod, usually 5.5 mm in diameter, which has been specially cooled. The main production process consists of a series of drawing and heat-treatment stages during which the steel rod is reduced in diameter to give a flexible wire suitable for use as a textile material, and also having the desired crystalline structure to give a high-modulus, high-tensile wire. After the final wire drawing stage, several wires are brought together and twisted to form a strand, and for heavier cords, such as those used in truck tires, several of these strands are twisted together to form a cabled cord or further layers of wires are wrapped around a core strand to form a layered cord. The great majority of products made from cord reinforced elastomers, whether they be tires, hoses, or conveyor belts, are assembled from layers of uncured rubber/cord fabric to form the final article. There are several ways of making this fabric, the most common by far being calendering, but spreading and extruding methods can also be used. Another technique of making a cord/rubber fabric is that of extruding a sheet of cords and rubber through a die to produce a tape. The process for doing this with steel cords is called the Steelastic process, although a similar process can be used to produce textile cord fabric. The benefit of this technique is that it requires much less space and resources to set up, and produces much less waste material.

In the rubber industry, for the design and production of a commercial material that satisfies precise technical requirements, it is necessary to:

- (a) Select the right raw materials;
- (b) Blend them in the appropriate proportions in suitable equipment;
- (c) Form the resultant blend into the desired shape; and
- (d) Render the finished product dimensionally stable.

The first stage, known as compounding, refers to the formulation of a blend of rubber and various additives. These are first thoroughly mixed and then formed. All the operations inherent to the blending of the various ingredients and their forming constitute the processing. The physical properties of an unvulcanized elastomer do not allow a manufactured item to retain its dimensional and mechanical characteristics over time; therefore, it is necessary to generate a stable

molecular network, making use of a chemical reaction capable of joining the polymer chains one to the other. This process is known as vulcanization. Finally, it should be recalled that the definition of the physical and chemical properties of elastomers has been the subject of standardization carried out by the American Society for Testing and Materials (ASTM). The standard methods of measurement are continually updated and adapted to new instrumentation and needs, verifying their reliability through cross-tests between different laboratories. Once the characteristics of the finished product have been established, the basic elastomer and the package of ingredients necessary to obtain the properties required are selected. The recipe of the blend consists of a list of the various ingredients, and instructions on how to mix them to prepare the blend. The unit of measurement used for the quantities by weight of the various constituents of the recipe is phr (per hundred rubber), which indicates the quantity of additive required per 100 parts of rubber.

## ***4.2 The Materials Needed for the Preparation of a Blend***

The materials needed for the preparation of a blend belong to the categories indicated below:

- Base polymer (raw elastomer, gum rubber). This is the main ingredient and can consist of natural or synthetic rubber, or thermoplastic elastomers.
- Vulcanizers. These are the substances needed to generate the three-dimensional network that gives the rubber its typical characteristics (except in the case of thermoplastic elastomers that do not need to be vulcanized); a typical vulcanizer is sulphur, used in quantities in the range of 0.5–3 phr.
- Accelerators. They are the substances that interact with the vulcanizer to reduce the time of vulcanization; they are used in quantities in the range of 0.5–1.5 phr.
- Activators. Activators are made up of metal oxides (such as zinc, lead and magnesium), of carbonates and of alkaline hydroxides; they are added in quantities of 2–3 phr, form chemical compounds with the accelerators and modify the speed of vulcanization and the number of links between the different macromolecules (density of cross-linking) unlike diamonds and graphite, is not found in nature. It is the generic term used to indicate a family of materials made up of elementary carbon in the form of aggregated spheroidal particles, obtained by the thermal decomposition of hydrocarbons in a shortage of air. Carbon blacks are produced using different technologies, from which the various types take their names: furnace blacks and thermal blacks make up 95 and 4 % respectively of the world market. These particles, which have an average diameter from 10 to 100 nm (the size depending on the preparation technology), are aggregate forming larger structures (60–200 nm); their surface area is as much high as 150 m<sup>2</sup>/g, and on the surface there are phenol and quinone groups, carboxylic acids and lactones, in different numbers and quantities according to the type of carbon black.

- **Vulcanization retardants.** These are substances that interact with the vulcanizer-accelerator-activator system, creating a period of time during which vulcanization does not take place. They thus ensure the completion of the various transformation operations thereby avoiding pre-vulcanization; they are used in quantities in the range of 0.1–0.3 phr.
- **Organic acids.** Their reaction with the activators provides the cations necessary for the formation of chemical complexes with the accelerators. Monobasic acids with high molecular weights, such as stearic, oleic, lauric, palmitic, and myristic acids, and hydrogenated palm, castor and linseed oils are used in quantities of 1–3 phr.
- **Antioxidants.** Added in quantities of 1–2 phr, they protect the rubber from oxidation, accelerated by light and ozone, which generally causes a structural modification to a lesser or greater degree in the polymer chain with consequent variations to its mechanical properties. This category includes secondary amines, which exhibit a high tendency to coloring, phenols hindered by *t*-butyl groups in the ortho-position (primary antioxidants, they reduce the peroxide radicals) and organic phosphites (secondary antioxidants, they reduce the hydroperoxides). The primary and secondary antioxidants are used in synergic combinations.
- **Fillers.** Initially they were added to rubber in the form of small particles for economic reasons. The addition of carbon black to natural rubber had a reinforcing effect, improving some characteristics such as resistance to abrasion and tear, and increasing the values of the elastic modulus and of the tensile strength. Fillers are subdivided into two groups: the first includes reinforcing fillers and the second inert fillers. The inert fillers (kaolin, barytes, carbonates of calcium and of magnesium, of iron and of lead), powdered to dimensions of 0.1 mm, are used to modify some technological characteristics of the vulcanized elastomer such as its hardness, its density or its electrical properties. The reinforcing fillers (carbon black and silicas), instead, have a major effect on the mechanical and dynamic characteristics of the vulcanizate in that, by interacting with the macromolecules, they take part in the elastic network.
- **Carbon black** is an allotropic form of carbon that, unlike diamonds and graphite, is not found in nature. It is the generic term used to indicate a family of materials made up of elementary carbon in the form of aggregated spheroidal particles, obtained by the thermal decomposition of hydrocarbons in a shortage of air. Carbon blacks are produced using different technologies, from which the various types take their names: furnace blacks and thermal blacks make up 95 and 4 % respectively of the world market. These particles, which have an average diameter from 10 to 100 nm (the size depending on the preparation technology), are aggregate forming larger structures (60–200 nm); their surface area is as much high as 150 m<sup>2</sup>/g, and on the surface there are phenol and quinone groups, carboxylic acids and lactones, in different numbers and quantities according to the type of carbon black.
- **Plasticizers.** These are materials capable of improving processability, of reducing the hardness of the vulcanizates and increasing their elasticity and cold



flexibility, without undesired effects on their more important physical properties. They belong to two main classes: extender oils, derived from the petroleum refining industry, which are suitable for diene-based rubbers (SBR, NR and BR), and esters, which are recommended for polar rubbers such as NBR rubbers. Extender oils are, in turn, classified (the paraffin content is indicated in brackets) as highly aromatic oils (5–15 %), aromatic oils (15–32 %), naphthenic oils (48–56 %) and paraffinic oils (60–75 %); the choice of the most suitable plasticizer is made based on a criterion of compatibility.

- Processing auxiliaries. These are additives of different sorts introduced to facilitate the incorporation of other ingredients (peptizers, adhesion promoters, dispersants), to regulate the process (lubricants), or to facilitate the separation of the vulcanized article from the mould (release agents). Among the peptizers of natural rubber is thio-b-naphthol, which is used in quantities of 0.6 phr during the mastication phase, di-o-tolylguanidine and diphenylguanidine for polychloroprene and zinc laurate for SBR rubber.
- Various additives. They are substances of various types that are added in varying quantities and proportions—flame retardants (aluminium hydroxide, antimony oxide, zinc borate), antistatics (metal powders or fibres, carbon black), colorants (metal oxides) and substances that increase adhesion to metals during the molding or extrusion phase (resorcinol–formaldehyde resins and derivatives of isocyanates).

### 4.3 *Mixing*

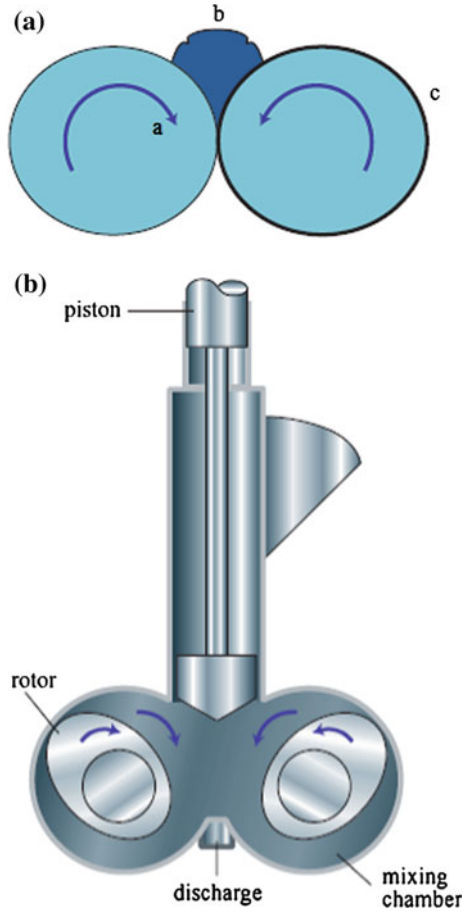
The final properties of a vulcanized elastomer depend not only on its intrinsic properties, composition, primary structure, but also on the degree of homogeneity with which the various fillers have been dispersed within it. The mixing of solid particles with highly viscous material is a very complex operation, which can be split into three successive stages: incorporation, dispersion and distribution. During the incorporation stage, starting with the separate ingredients of the compound, a homogeneous mass capable of flowing is obtained. Within this stage there can be three further distinct phases:

- encapsulation, during which the free surface of the elastomer wraps around the fillers,
- subdivision, during which the reciprocal distances and dimensions of the encapsulated fillers are reduced, deformed in shear or elongation; and, finally,
- the immobilization of a considerable fraction of the rubber inside the voids contained in the filler aggregates, with the important consequence that shielded polymer plays no part in the flow behavior. If the compound is subjected to moderate strain, the whole filler agglomerate and the associated entrapped rubber behave as if they were a single unit of filler.

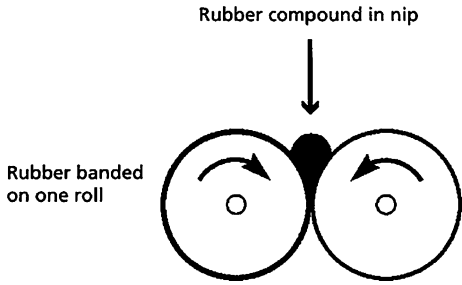
Since, when a polymer is mixed with a rigid additive, the viscosity of the compound increases with the volumetric fraction of the additive and its elastic memory diminishes, a *blend* with a less than optimal dispersion possesses an ever-increasing viscosity and an ever-decreasing post-extrusion swelling as compared to a material in which the filler has been effectively dispersed. The use of plasticizers and oils, which produce greater molecular mobility, allows the polymer to quickly exit the voids of the reinforcing filler aggregates, thereby diminishing the proportion of entrapped rubber, reducing the viscosity of the mass and favoring the subsequent phase of dispersion. A suitable parameter for describing the effectiveness of mixing is the amount of power applied, usually correlated linearly with the rate of dispersion. During mixing, the temperature rises notably and the viscosity decreases along with the amount of applied power; the mixing time should therefore be increased, but not beyond certain limits in order to avoid early vulcanization. The time interval, measured from the moment that the compound containing vulcanizing agents is heated to the moment at which the reaction of cross-linking starts, is called the scorch time. This time can be modified by using retardants as well as by the choice of vulcanizer and accelerator. From the technological point of view, while for thermoplastic materials broad use is made of continuous mixing, for the processing of rubber, batch mixers are mainly utilized, consisting typically of open mixers (two roll mills) and of internal mixers. The reasons for this derive from the lack of availability of rubber in free-flowing granules at a cost comparable to that of rubber in bales, from the difficulty of accurately feeding a large number of ingredients and from the impossibility of adapting continuous mixers to the processing of different types of rubber and formulations without heavy changes. In an open mixer, there are three zones: one is located between the high powered (internally cooled) rollers (a); another, the bench (b), acts as a reservoir to feed the region between the rollers where the process of encapsulation takes place; the third, the belt (c), carries the rubber from zone a to zone b. The rollers rotate in opposite directions at different speeds with a ratio that varies between 1 and 1.1 (Fig. 3).

Due to its versatility (the ability to mix a great variety of elastomers with the same setting), and due to its ability to accept rubber in bales, the internal mixer is the machine most used in the rubber industry. Figure 4 contains a diagram of the two counter-rotating rotors, of the piston, which allows for the introduction of the various ingredients of the blend into the mixing chamber when lifted, but which keeps the rubber in the mixing area when lowered, and of the discharge door. Cooling water passes through the rollers, the walls of the chamber and the discharge door. Observing the mixing of rubber in a roll mill makes it possible to identify two limiting situations: a dry behavior, which shows a critical factor relating to the shearing of the elastomers (the rubber breaks up); and a cheesy behavior, typical of materials characterized by poor elastic behavior and poor tensile properties, mainly related to the absence of high molecular weight fractions. Aside from these two limiting cases, the behavior considered to be good is that characterized by the formation of a continuous belt between the rolls. The scale of visual evaluation is associated to a behavior that can be related to the

**Fig. 3** Open mixer (a) and internal mixer (b)



**Fig. 4** Conceptual view of rubber mill rolls



extensional rheology of the unfilled polymer, which is particularly sensitive to its molecular structure. The principle stems from the theory of the elasticity of rubber at high deformation, and is based on the calculation of the elastic (recoverable) and viscous (non-recoverable) contributions of the polymer used in the blend.

## 4.4 Mills

These were used at the beginning of the rubber industry and are still an essential piece of rubber processing equipment. A mill consists of two horizontally placed hollow metal cylinders rotating towards each other (Fig. 4). The distance between the cylinders (mill rolls) can be varied, typically between 0.25 and 2.0 cm. This gap between the rolls is called a nip.

Raw gum elastomer is placed into the gap between the two mill rolls, the mill nip. It then bands, as a continuous sheet, onto one of the rolls. The speeds of the two rolls are often different, the back roll rotating faster than the front. The difference in speed between the two rolls is called the friction ratio and allows a shearing action (friction) at the nip to disperse the ingredients and to force the compound to stay on one roll, preferably the front one.

### • Mill processing

The following description relates primarily to compounds which use sulfur as the crosslinking agent. The key to mixing (in a Banbury mixer or a mill) (Fig. 5) is to maintain sufficient viscosity to ensure an adequate shearing action, to distribute the non-rubber ingredients into the raw gum elastomer, or to force the raw gum elastomer into the microscopic spaces of each filler particle. Both mechanisms have been hypothesized and one typical mixing sequence might be as follows: The raw gum elastomer is placed into the nip and allowed to band onto the front roll

### • Internal mixing machines

If the rolls of a mill are twisted to produce a corkscrew effect and then a block of steel is placed over the mill nip with the block connected to a steel rod above it, this would be called a ram. The ram would move up, to allow addition of ingredients to the nip, and it would move down to force the compound ingredients into the nip. If the whole thing is surrounded in a heavy metal jacket with a chute at the

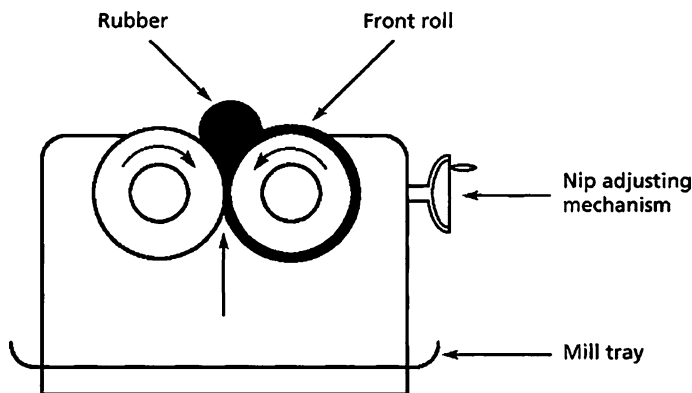


Fig. 5 Mixing in a mill

top to put ingredients in and a door at the bottom, to let the mixed material out, the result will be an internal mixing machine. Raw gum elastomer is dropped through the hopper into the mixing chamber where it is mixed by the rotors. The ram, pressing on to the rubber mixture, is forced down by a pneumatically or hydraulically controlled cylinder, whose pressure is adjusted to give the best control of the mixing process. Oil may be poured in from the hopper, or injected through a valve in the hopper wall just above the mixing chamber. Mixing can occur between the rotors (intermeshing rotors) or between the mixing chamber walls and the rotors.

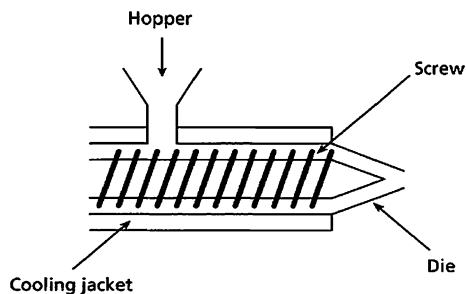
### • Processing

The mixing process will be discussed primarily with reference to unsaturated elastomers which are sulfur cured, unless otherwise stated. The mixing principles are similar to those for the mill. The raw gum elastomer is dropped into the hopper and the ram allowed to move down under pressure; the ram is raised for each addition of material and then lowered, to compact the mixture in the mixing chamber. Fillers are then added; large total amounts can be added incrementally and after most of the filler has been mixed in, any oil in the formulation may be then be introduced. If oil addition is delayed too long, the filler becomes totally 'encapsulated' by the elastomer and, the oil addition can cause a loss of shearing action, resulting in a slippery mess in the mixing chamber. During the mixing operation, feedback is received from the electrical power usage indicator, the temperature gauge, the time clock, and, for experienced operators, the sucking sound of the batch and the sound of the electrical motor driving the mixer.

### • Extruders

Extruders (Fig. 6) are conceptually a pump, consisting of a screw to move the material forwards, a barrel around the screw to contain the material, help it move, and provide part of the temperature control. The back end has a hopper, sometimes with feed rollers, to put rubber into the screw, and the front end has a 'head' to hold a die, through which the rubber extrudes. An alternative to the screw extruder is the ram extruder, a well known trade name being Barwell. The ram extruder pre-dates the screw extruder, but it is still used in certain specialized applications. Here, the screw is replaced by a ram, which forces the material through the die.

**Fig. 6** Conceptual view of a basic extruder



Since the process is discontinuous, a slug of rubber is placed in the barrel, extruded, then another slug introduced, it is suited to making preforms for further use, such as placing into the cavities of molds.

- **Die swell**

The die is designed to avoid sudden discontinuities, as the compound moves through it and thus often has a contoured lead section. As the extrusion exits the die, the extrusion can shorten in length and increase in cross section. This is known as die swell, which is dependent on die design, screw speed, i.e., shear rate, temperature and the compound's viscosity and its elastic component. In practice, die swell can be quite complex and it might be necessary to modify the die a number of times, before the required extrusion shape is achieved. This recognizes that even uncured rubber has complex elastic and plastic behavior. Like an elastic band it can undergo elastic recovery on exiting the die.

- **Recent extruder design**

A problem with traditional extruders is the potential for reduced interblending of material as it moves along the screw. This causes uneven temperature distribution in the extrudate, which translates to a variable viscosity and therefore a continuously changing die swell. Layers of compound move along without intermingling, i.e., in laminar flow.

- **Calendars**

A calendar can be crudely thought of as a very high precision mill, with the rolls stacked on top of one another, with anything from two to four rolls in various configurations. The distance between the rolls can be varied to control calendared thickness.

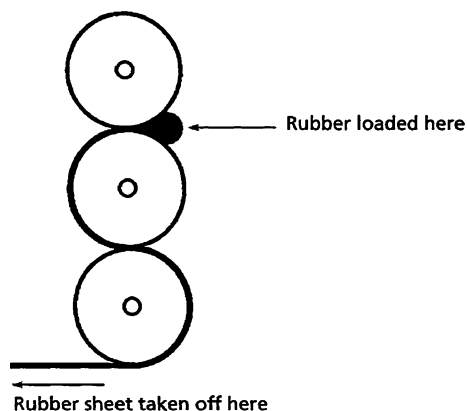
As with the extruder, the calendar (Fig. 7) further processes the compound after it has been mixed in the internal mixer or on the mill. Calendering is a useful technique, if the final product is to be a roof or tank lining, fabricated hose, expansion joint or indeed any further product which needs accurately dimensioned continuous sheet. Calendering is also used for applying rubber compound to textiles. Sheet from a mill will have a thickness which is much too imprecise, can have a rough surface and may contain some trapped 'bubbles' of air.

A three roll calendar is very popular, where the middle roll is fixed, while the ones above and below it can be moved vertically to adjust the gap between the rolls. A four roll 'S' configuration might be considered more 'state of the art'. Calendars are extremely robust and solidly built machines, and may provide service for many decades. Some of the rolls can be a substantial size, i.e., 90 cm in diameter and 250 cm in length.

- **Material thickness control**

The compound in the nip can generate very large reaction forces pushing against the rolls. A force of 43,000 kg/m of nip is possible for a product gauge of 0.25 mm, which is enough to deflect the surface of the rolls. Since the middle of

**Fig. 7** Three roll vertical calendar



the roll length is furthest away from a solid support it will deflect the most, resulting in a curve shaped deflection with a maximum at the middle which can be 0.13 mm or more. Even this apparently small variation can result in significant material wastage and complications in further processing. To counteract this, an opposing curve called a crown is put into the roll by grinding it. This only goes some way to solving the problem, since deflection forces vary with the compound used, and the thickness of the rubber to be calendared.

- **Feeding the calendar**

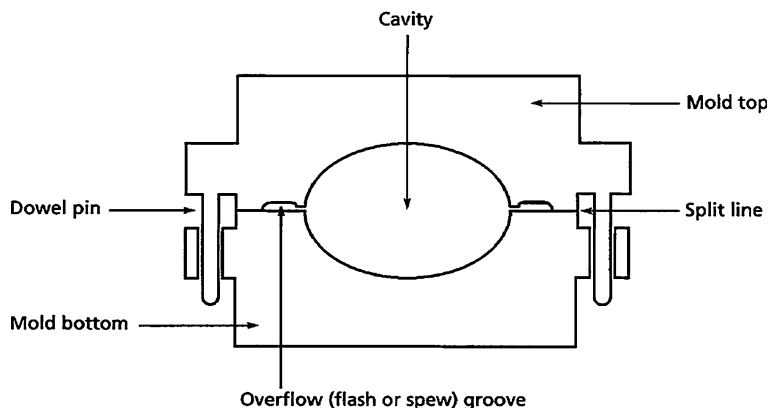
If cold, at room temperature, compound were to be fed to the nip, it would heat up erratically and produce a variable viscosity. This would cause uncontrolled deflection forces on the rolls and hence an unacceptable thickness variation and surface quality of the rubber. The simplest way to feed the calendar, is to 'roll' small pieces of compound off a mill and immediately put them in the nip. The pieces then spread along the length of the nip and form a 'rolling bank'.

- **Curing equipment**

The rolls of sheeting have been calendared, the extrusions have been made, the *Barwell* has produced its preformed pieces, and shapes have been cut from milled sheet. The final step is to provide sufficient heat to change the uncured compound from a somewhat plastic state, to a dimensionally stable elastic substance, and additionally, in the case of molding, to achieve a final shape.

## 4.5 Molding

A mold might be described simplistically as at least two pieces of material (typically steel), which when fitted together form a cavity, resembling the shape of the product. This would be a very basic mold. Molding is by far the most important



**Fig. 8** Closed empty compression mold

curing process, where uncross-linked rubber is placed into a heated mold, which gives it the final product shape, and then vulcanizes the material.

#### • Mold design

A basic compression mold design is illustrated in Fig. 8 which shows a cross section through the center. It is very important that the two halves of the mold register (fit accurately together). In this case, pins built into the top section fit snugly into holes drilled into the bottom half. Any looseness between the pin and the hole may cause the top half of the product to be out of alignment with the bottom half. If the fit is too tight, attempts to manually open the mold may prove difficult.

There are different ways of introducing compound into the mold, some of which involve modifications to the basic design in Fig. 9. They each confer certain advantages not found in the others.

(a) In the most basic design, (Fig. 10), compression molding, pieces of rubber compound are placed in the bottom cavity and compressed using the top half of the mold.

(b) The first modification is transfer molding, which can be visualized as drilling holes through the outside of the top mold half of a compression mold through to the cavity. Thus the mold can stay closed while rubber compound is introduced through these holes into the cavity by using the force exerted by the press platen.

(c) If a separate device is used, not related to the press platen, which injects the compound through the holes, this would be injection molding.

#### • Compression molding

This is the simplest, cheapest, and probably the most widespread of the three basic molding techniques. It is ideally suited to small quantity production, say, from around fifty to a few thousand of each product annually. Figures 10, 11, 12



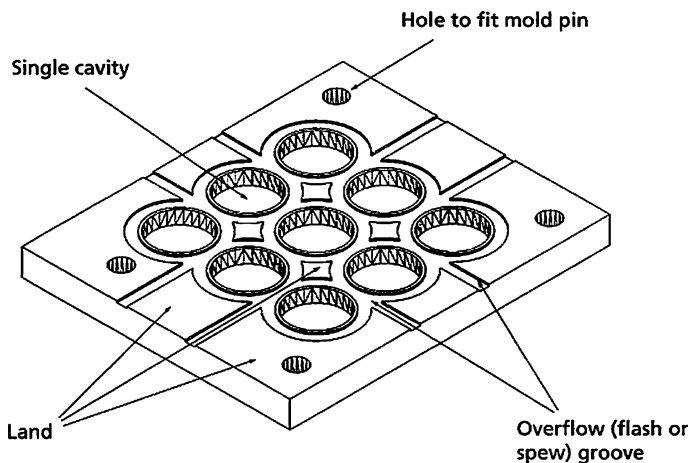


Fig. 9 The bottom half of a nine cavity mold

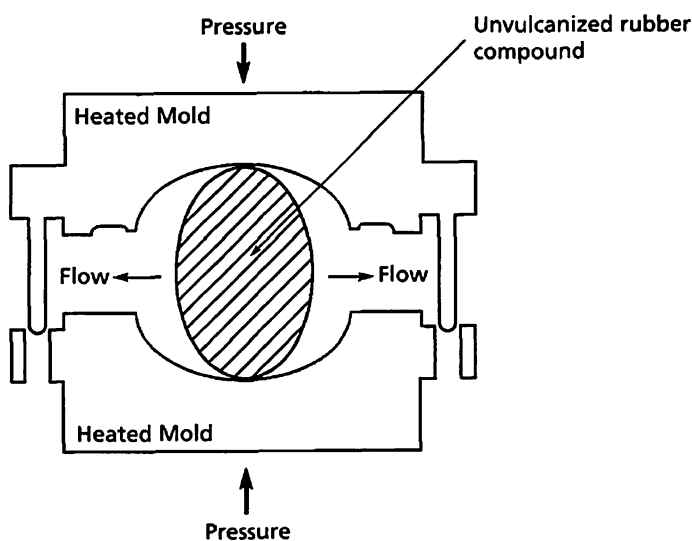


Fig. 10 A loaded mold closing

shows the various stages in the molding process. One of the keys to successful molding is adequate removal of air while the mold cavity is filling up with rubber.

The uncured pieces of compound placed in the mold are known-variously as preforms billets or load weights. For a ball, one might use an elliptically shaped extrusion, cut to an appropriate length from a *Barwell*. This shape is important and deliberately chosen so that air in the mold cavity will have a free path of escape when the mold begins to close.

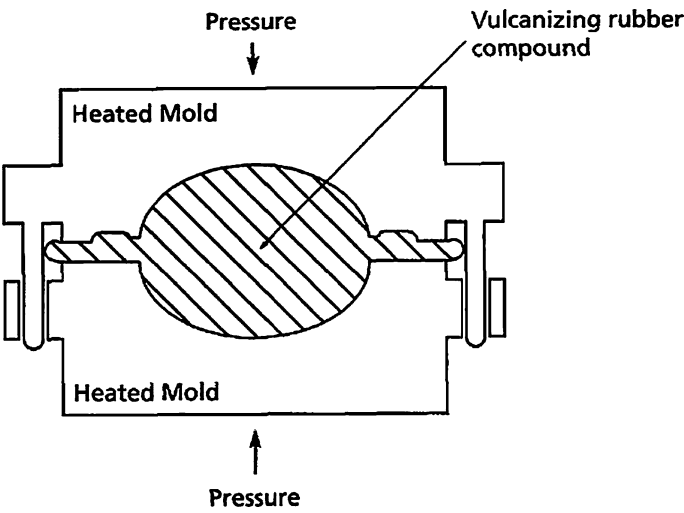


Fig. 11 A loaded mold, closed under heat and pressure

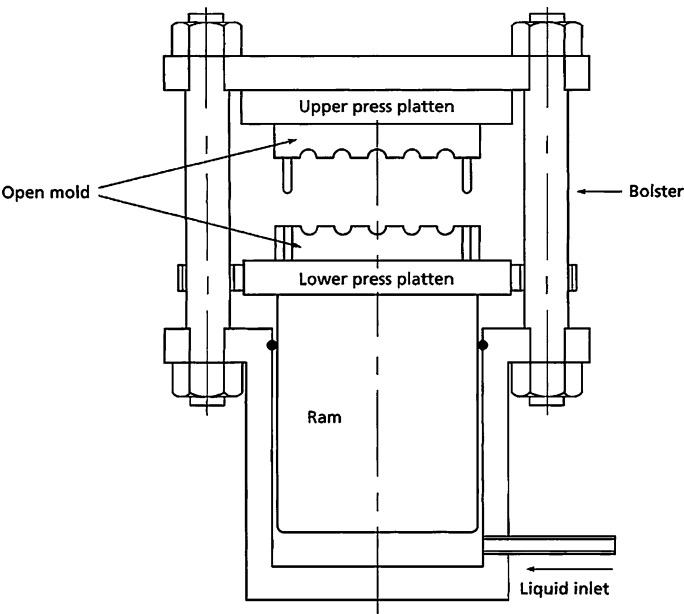


Fig. 12 A basic press for compression and transfer molding

As the press platens close the mold, excess compound begins to squeeze out into the flash grooves, taking air with it. Often, residual air remains and various methods have been devised to remove it. One method is to bring the mold pressure back down to zero and then return to full pressure by quickly lowering and raising

the press platens a number of times. This 'shock' treatment is called 'bumping'. An additional line of attack is to find where air is being trapped in the final cured product and drill a small diameter hole through the mold cavity in the equivalent area; these are called bleeder holes. They permit an alternative escape route for the trapped air together with some rubber. The shape of the preform and also its placement in the mold is important. The uncured rubber, placed in the cavity, might be a single piece or a number of pieces.

- **Backrind**

Once the compression mold has closed, the compound continues to heat up and attempts to thermally expand. Its coefficient of expansion can be a least fifteen times greater.

- **Heat transfer**

How long should it take to cure a compound in a mold? The rubber laboratory uses a rheometer to help determine these using small samples of compound. The rheometer might indicate a cure time to be 25 min at 150 °C. If this is then applied to a shop floor molding, it must be remembered that the 25 min is based on the entire compound in the rheometer being at 150 °C at approximately the beginning of the 25 min period. Rubber can be very poor at transferring heat, so that for a large bulky part in a shop floor compression mold, it may take hours for heat to be transferred from the mold to the center of the part. The rheometer estimate of 25 min must now be revised, to take into account a constantly changing temperature throughout the part as the cure progresses. Carbon black is significantly better at transferring heat than a raw gum elastomer, thus for the same bulky part, a carbon black filled compound will vulcanize, through to its center, much sooner than a non-filled gum compound.

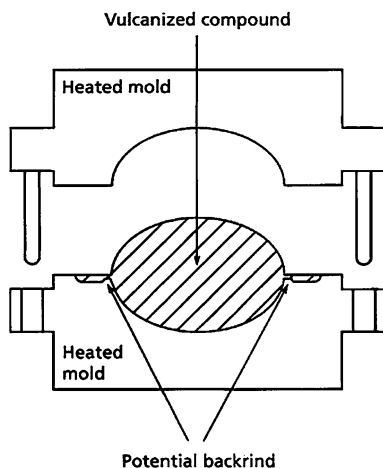
- **Transfer molding**

If we take the top half of a compression mold, then drill transfer holes through it and place a metal collar on the closed mold so as to surround all of the holes, we have in effect converted it into a transfer mold. All that is needed now is to put rubber compound into the pot and force it through the holes by placing a piston (plunger) into the pot and using the press platens to force the piston to push the compound down through the pot into the closed mold cavity. This conversion is used in the rubber industry. Alternatively, the transfer pot can be designed to be an integral part of the mold and the piston can be fixed to the upper press platen (see Figs. 13, 14, 15).

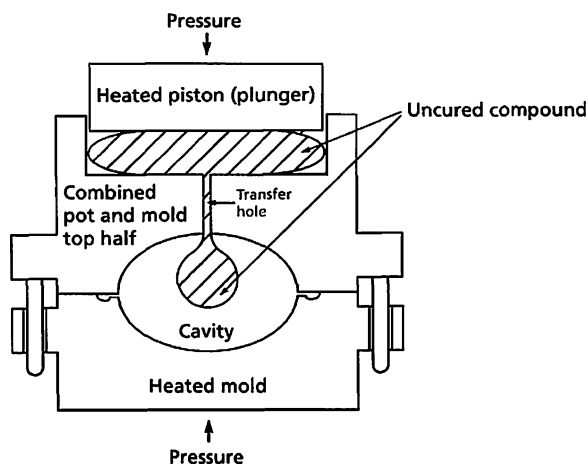
- **Injection molding**

Injection mold consists of a cylinder (injection barrel) with a ram or screw inside it, so that the rubber compound can be moved towards a nozzle at its end. The nozzle is then pressed against a hole made in the top half of a closed mold. This hole is then connected to smaller holes (gates and runners) which enter the cavities of the mold. The compound can be presented to the barrel as a continuous

**Fig. 13** An open mold after rubber curing



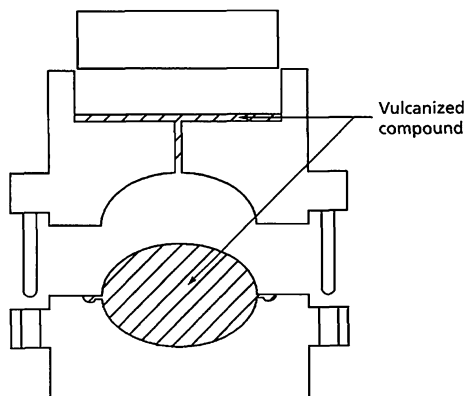
**Fig. 14** Conceptual cross section through a transfer mold—compound moving from pot to cavity



strip, or in granulated form through a hopper, as in plastics injection molding. A ram has a tighter fit in the barrel than a screw and therefore there is less leakage backwards through the barrel; it is also cheaper than a screw. The screw 'mixes' the compound as it moves towards the nozzle, creating more frictional heat and therefore higher temperatures which translate to easier flow and shorter cure times. A combination of ram and screw is popular.

#### • Autoclave curing

An autoclave is a cylindrical steel pressure vessel, used to cure extrusions, sheeting and all manner of hand fabricated parts. They can be very small or huge, for example, 30 m long and 3 m or more in diameter. The heat needed to cure is commonly provided by wet steam, often at 0.3 MPa, although some curing



**Fig. 15** Conceptual cross section through a transfer mold—transfer mold opened after cure. Since rubber can be considered a thixotropic non-Newtonian fluid, the shear between it and the walls of the transfer holes reduces its viscosity, thus allowing the compound to enter the mold cavity more easily. Shear also heats the compound which reduces viscosity and speeds up cure

processes might need pressures of 0.7 MPa or more. In special cases carbon dioxide or nitrogen might be used, either separately or in combination with wet steam, to provide higher pressures than the wet steam alone could produce at a given temperature. The pressure of wet steam is restrained by its temperature/pressure equivalence. Choosing 150 °C as the desired cure temperature would only generate 0.3 MPa from the wet steam. In cases where porosity in the product is a problem it might be advantageous to independently increase the pressure in the autoclave. If enough nitrogen is introduced to give an extra 0.6 MPa pressure then there is now a total of 0.9 MPa, which might significantly reduce any porosity problems encountered at the lower pressures.

The preparation of the blend is usually followed by a phase of molding and, subsequently, of vulcanization. The two phases can be simultaneous as in the case of compression molding, which consists in putting a part of the appropriately shaped blend into a mould. The closing of the mould and application of pressure bring about the adaptation of the rubber to the mould, while the elimination of excess material takes place through appropriate holes. Pneumatic tires are shaped and vulcanized by a similar technique. A technology for the shaping of thermoplastic elastomers, but also for vulcanizable elastomers, is that of injection molding, typical of the plastic industry, but adapted also for elastomers; in this case, the molding and vulcanization phases are also usually simultaneous. Instead, in the case of shaping by extrusion, which is used for the preparation of pipes or tapes, the vulcanization phase is separate and is effected continuously in high temperature baths (200–300 °C), in hot air tunnels or by means of continuous hot pressing systems (heated cylinders).

## 4.6 Vulcanization

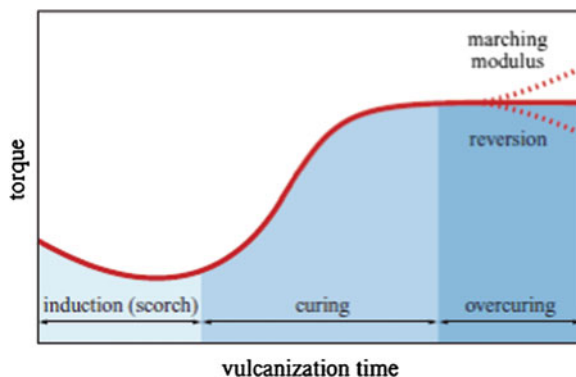
The process of vulcanization causes the formation, between the macromolecules, of bonds that are statistically randomly spaced along the molecular axis with a frequency of one link every 50–100 monomer units. The introduction of bonds between the macromolecules leads to important physical variations of the elastomer, which changes from a fluid soluble in solvents to an insoluble elastic solid characterized by mechanical properties that are technologically useful. The properties of the vulcanized elastomer depend on the number and type of the links that connect the molecular chains. The number and type of the links are, in turn, a function of the degree of advancement of the vulcanization and of the type of accelerator. As the density of the network increases, there is an increase in the static and the dynamic elastic moduli, at high frequency, and in hardness, while the permanent deformation values after compression decrease. The tensile strength, the tear strength and the fatigue resistance reach their maximum. The nature and the characteristics of the intermolecular bonds, as well as their number, have a great influence on the final properties of the vulcanized elastomer: short bonds, the thermal stability and the dynamic properties; improve tensile strength, fatigue resistance and tear strength. During vulcanization with sulphur, an evolution of the type and number of intermolecular bonds is observed, with consequent variations over time of the properties of the vulcanizate: polysulphide bonds steadily decrease as the vulcanization time increases, the monosulphide bonds increase and the disulphides remain constant (about 20 %). As vulcanization proceeds, the viscosity of the material increases and this increase is measured by the rise in the torque needed to keep the amplitude of the oscillation constant. Since the measurement is carried out at high temperature, it is assumed that the viscous effect of the material is negligible and that the increase of the torque is proportional to the number of links per unit volume of rubber. Figure 16 contains a typical vulcanization curve, which shows the trend of the torque as a function of time.

The first period (induction), in which the viscosity does not change (the retardant systems that inhibit the formation of the activator-accelerator complex are active) is followed by a period of torque rise and, subsequently, of stabilization of the torque value. A decrease in this value is symptomatic of breakage of the intermolecular bonds caused by the temperature (reversion), while an increase is linked to a further cross-linking of the material.

### 4.6.1 Accelerated Sulphur Systems

For many years, the adjustment of the scorch time was carried out by means of salicylic or benzoic acid or N-nitrosodiphenylamine until the first vulcanization inhibitors were introduced in 1968: they represent an important class of substances that make it possible to reduce the risk of prevulcanization without substantially altering the rate of the process. The principal and most common one is N-(cyclohexylthio)phthalimide (CTP), which is used in quantities of the order of 0.1–0.3 phr.

**Fig. 16** Vulcanization plot for an elastomer



A mold might be described simplistically as at least two pieces of material, which when fitted together form a cavity, resembling the shape of the product. This would be a very basic mold. Molding is by far the most important curing process, where uncross-linked rubber is placed into a heated mold, which gives it the final product shape, and then vulcanizes the material. It can vary in size from a clenched fist to that of an automobile, and can have a single cavity to make one product at a time, or enough cavities to make a hundred or more.

Most rubber molding is based on introducing a solid compound into a mold, although urethanes and silicones can be introduced as solids or liquids. It takes a fairly high mechanical pressure, to close the mold, and thus form the product shape; this pressure is provided by a press. Thus the mold must be strong enough to avoid being crushed. Tool steel hardened to a Rockwell C hardness of about 60 might be needed. A basic compression mold design is illustrated in Figs. 10–12 which shows a cross section through the center. It is very important that the two halves of the mold register fit accurately together. In this case, pins built into the top section fit snugly into holes drilled into the bottom half. Any looseness between the pin and the hole may cause the top half of the product to be out of alignment with the bottom half. If the fit is too tight, attempts to manually open the mold may prove difficult. Since a number of compound materials expand with heat by at least an order of magnitude more than steel, they will also shrink correspondingly as they cool when taken from the steel mold. The chemist plays his part in achieving a smooth flow of material in the mold, by striving to control the uncured compound viscosity. This needs to be high enough to create the back-pressure required to expel air efficiently as the mold closes, and low enough to permit completion of flow into all parts of the cavity before vulcanization begins. If we look at a low cured-hardness rubber, it usually contains little or no filler (NR & CR), or alternatively fillers plus a large quantity of oil. This can often make its viscosity too low for successful compression molding and the compounder may strive to increase its viscosity, by choosing a raw gum elastomer grade with a high Mooney viscosity. The flow of material in a mold is a complex process, especially in compression molding. The rubber in the cavity is undergoing large temperature changes, which translate to viscosity variations thus continuously altering the flow

characteristics of the compound. In recent years finite element analysis packages which describe the material flow patterns in the mold, have become available to mold designers. The use of such design aids is at an early stage in most of the rubber industry.

If we take the top half of a compression mold, then drill transfer holes through it and place a metal collar (transfer pot) on the closed mold so as to surround all of the holes, we have in effect converted it into a transfer mold. All that is needed now is to put rubber compound into the pot and force it through the holes by placing a piston into the pot and using the press platens to force the piston to push the compound down through the pot into the closed mold cavity. This conversion is used in the rubber industry. Alternatively, the transfer pot can be designed to be an integral part of the mold and the piston can be fixed to the upper press platen.

Raw gum elastomer is placed into the gap between the two mill rolls, the mill nip. It then bands, as a continuous sheet, onto one of the rolls. The speeds of the two rolls are often different, the back roll rotating faster than the front. The difference in speed between the two rolls is called the friction ratio and allows a shearing action at the nip to disperse the ingredients and to force the compound to stay on one roll, preferably the front one. A friction ratio of 1.25:1 is common. Powders, liquids, etc., are then added to the nip in a specific way. The process produces friction which creates heat. This excess heat needs to be removed, either by spraying or flooding the inside of the roll with cooling water or by passing water through drilled channels in the wall of the roll. A device is necessary to prevent the rubber from moving past the end of the rollers. This is accomplished by a piece of metal called a guide, positioned at each end of the roll, so as to almost touch the surface.

Rubber equipment and its use fall off the mill rolls, so a tray (mill pan) is provided to catch them, to be swept up and returned to the rolls. When all the ingredients are completely blended rotating knives, in the shape of a disc, can be automatically applied to the rubber covered roll (this method can eventually cause scoring of the rolls), to take off one continuous sheet. Alternatively the operator can use a hand-held mill knife, and take off individual sheets. The following description relates primarily to compounds which use sulfur as the crosslinking agent. The key to mixing (in a Banbury mixer or a mill) is to maintain sufficient viscosity to ensure an adequate shearing action, to distribute the non-rubber ingredients into the raw gum elastomer, or to force the raw gum elastomer into the microscopic spaces of each filler particle. Both mechanisms have been hypothesized and one typical mixing sequence might be as follows: The raw gum elastomer is placed into the nip and allowed to band onto the front roll. In the case of NR, it needs to move through the nip quite a few times to reduce its nerve (elasticity) and to lower its high viscosity (low viscosity grades are available). It then forms a smooth, more plastic, band on the roll. Normally most powders (other than accelerators and sometimes sulfur) are then added. If significant heat is produced, then cross-linking agents and accelerator addition will be delayed to the last part of the mixing process. In some cases, when excessive heat is produced, it may be necessary to remove the compound from the mill before the accelerator is



added, to avoid scorching (prevulcanization). The compound at this point is known as a *masterbatch*, defined in ASTM D 1566 as a homogeneous mixture of rubber and one or more materials in known proportions for use as a raw material in the preparation of the final compounds. The masterbatch is allowed to cool and subsequently returned to the mill for addition of the accelerator. If the rolls of a mill are twisted to produce a corkscrew effect (they would now be called rotors), and then a block of steel is placed over the mill nip with the block connected to a steel rod above it, this would be called a ram. The ram would move up, to allow addition of ingredients to the nip, and it would move down to force the compound ingredients into the nip. If the whole thing is surrounded in a heavy metal jacket with a chute at the top to put ingredients in and a door at the bottom (underneath the rotors), to let the mixed material out, the result will be an internal mixing machine. The Banbury mixer had modified rotors and the addition of a floating weight. The internal mixer rapidly became an essential part of the rubber industry. At the present time, mixers are available in sizes ranging from those capable of mixing a kg or so, to those that can mix more than 500 kg per load, equivalent to many large mills. The internal mixer is faster, cleaner, (produces less dust from powdery materials such as carbon black, silica and clay), uses less floor space, and is probably less operator sensitive. It has thus displaced the mill for most compounding operations. However, the variable nip opening on a mill, plus immediate visual feedback of the state of the mix, allows a good mill operator a high degree of control and consequently dispersion. The internal mixer has a fast mixing capability, from around two to ten minutes, and thus requires an efficient cooling system. This is provided by drilled channels in the walls of the mixing chamber, through which water passes to control the mix temperature. The rotors and discharge door can also be water cooled. The temperature of the compound being mixed is measured by a thermocouple in the side of the mixing chamber. Other parameters which can be measured and controlled during the mixing process are electrical power (amperage or watts) and time. The mixing principles are similar to those for the mill.

For natural rubber, the time taken to achieve coherence can be somewhat long, due to its high initial viscosity which needs to be reduced by mastication. Sometimes this involves a separate step, where the mixer is exclusively and completely filled with NR raw gum elastomer, which is worked to reduce its elasticity and increase its plasticity. It is then dumped from the mixer, and after resting, a portion of it is returned to be mixed with other compounding ingredients. Controlled, lower viscosity natural rubber is available which can eliminate this extra step. Compounds with larger quantities of reinforcing filler can often reach temperatures over 150 °C by the time they are mixed. They would therefore be dumped from the mixer, often without sulfur and definitely without any accelerators (called a first stage mix or masterbatch), as otherwise the vulcanization process could commence in the mixer. The masterbatch would then be cooled, prior to being returned to the mixer for the addition of these materials, allowing the batch to be dumped at a final temperature closer to 100 °C. Since the heat generated during mixing is often associated with reinforcing fillers, a compound

without this raw material (or with some non-reinforcing filler) can reach full mixing (complete dispersion and distribution) at a much lower temperature than a compound with reinforcing fillers. This temperature will generally be comfortably below that needed to initiate vulcanization. Thus it may be feasible to experiment with adding the whole cure system in the first stage, i.e., as a single stage mix. This would be done with due regard to the required compound scorch time and plasticity of the mix for further processing.

## 4.7 Extruders

Extruders are conceptually a pump, consisting of a screw to move the material forwards, a barrel around the screw to contain the material, help it move, and provide part of the temperature control. The back end has a hopper, sometimes with feed rollers, to put rubber into the screw, and the front end has a 'head' to hold a die, through which the rubber extrudes. An alternative to the screw extruder is the ram extruder, a well known trade name being Barwell. The ram extruder pre-dates the screw extruder, but it is still used in certain specialized applications. Here, the screw is replaced by a ram, which forces the material through the die. Since the process is discontinuous (a slug of rubber is placed in the barrel, extruded, then another slug introduced), it is suited to making preforms for further use, such as placing into the cavities of molds. Thus a rotating blade is fitted in front of the die to chop the extrusion into volumetrically accurate preforms. Extruders are used to make hose and general profiles such as window channels, coated wires, and preforms for further processing. They can also be used to produce sheet rubber, where a large extruder makes a tube, which is immediately slit, producing a continuous sheet.

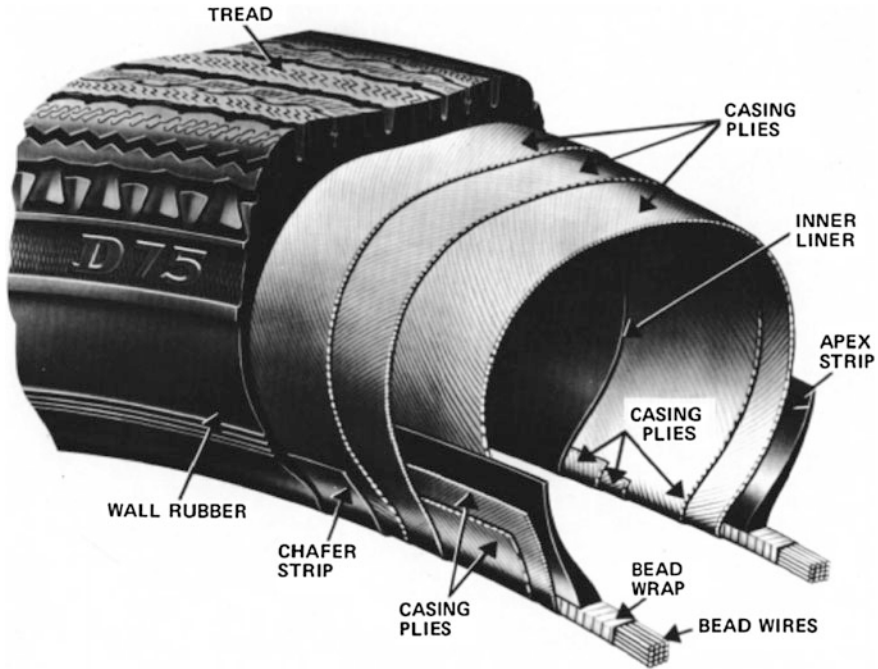
The die is designed to avoid sudden discontinuities, as the compound moves through it and thus often has a contoured lead (entrance) section. As the extrusion exits the die, the extrusion can shorten in length and increase in cross section. This is known as die swell, which is dependent on die design, screw speed (i.e., shear rate), temperature and the compound's viscosity and its elastic component. In practice, die swell can be quite complex and it might be necessary to modify the die a number of times, before the required extrusion shape is achieved. This recognizes that even uncured rubber has complex elastic and plastic behavior. Like an elastic band it can undergo elastic recovery on exiting the die. A problem with traditional extruders is the potential for reduced interblending of material as it moves along the screw. This causes uneven temperature distribution in the extrudate, which translates to a variable viscosity and therefore a continuously changing die swell. Layers of compound move along without intermingling, i.e., in laminar flow. A relatively recent idea, introduced in the 1970s, is to introduce pins protruding from the inside of the barrel towards the screw. This breaks up the layers, mixes them, reducing thermal variation and increasing homogenization. Such a machine is known as a pin barrel extruder. An extension of this concept is

called a Pinconvert extruder. After a conventional pin section, there is a portion which has hydraulically adjustable pins protruding into a helically grooved liner on the inside of the barrel. This gives it a high degree of flexibility for controlling temperature and output. The device described has an L/D ratio of 8:1, making it quite compact for a cold feed extruder. An alternative concept is to introduce small bowl shaped cavities into the end section of the screw and the inside of the barrel. This creates turbulent flow in the cavities and therefore increased physical and thermal blending. Such an arrangement would be added onto the end of a standard extruder, and is called a cavity transfer mixer.

## ***4.8 Pneumatic Vehicle Tires***

The initial patent for pneumatic bicycle tires dates from the middle of the nineteenth century, and had the objective of improving comfort by reducing the shock loads transmitted from the road to the rider, essentially by reducing the radial stiffness of the tire. The solid rubber tire, which carries load by compression, is replaced by an inextensible but flexible shell made of cord-reinforced elastomer. On inflation, the radial stiffness is much lower than the solid tire. It is an example of an invention which had to await the development of new materials to become viable. The concept was independently reinvented 40 years later, and has been much developed in the following 100 years, and applied to a variety of vehicles, ranging from bicycles and wheelbarrows to cars, trucks, aircraft, and earthmoving vehicles. The main requirements of most pneumatic tires are described in the following:

- **Tire shape.** On inflation, the tire must assume the desired shape without generating excessive internal stress, and any subsequent changes e.g., due to creep, should be minimal. It may be noted that the inflated shape of the tire is determined as much by the construction (the arrangement of the various cord-reinforced layers) as by the profile of the mold in which it was made.
- **Structural integrity.** Since a burst tire can lead to a major accident, and in some cases fatalities, this is a safety-critical requirement. The tire must survive repeated (several million) cycles of deflection, and in the case of truck tires one or more retreading processes, and continue to withstand the service conditions it is exposed to. These conditions can involve high values of speed, temperature, and deflection, inappropriate inflation pressure (high or low) and road surface roughness, all of which increase the technical demands on the tire.
- **Comfort.** Although the original objective of pneumatic tires was to reduce radial stiffness to improve comfort, it later became apparent that low longitudinal (i.e., circumferential) stiffness was also desirable. Tire uniformity is also important in minimizing the generation of vibrations.
- **Durability.** Apart from structural failure, tire life in service is likely to be limited either by penetration of the structure by foreign objects or by abrasion of the tread material. Since tires are relatively expensive to replace, maximizing the tread life is a major objective.



**Fig. 17** Various components of tires

- **Controllability.** During cornering or braking, frictional forces are developed at the road surface, whose limiting values are dependent on the road surface and also the tread pattern and material. These forces distort the structure of the tire, causing internal stresses. It is important that these forces increase progressively with steering or braking input, and that (for example) the slip angle for a required level of cornering force should not be excessive (Fig. 17).

#### 4.8.1 Compact Rubber Extruder with Gear Pump

Gear pumps with herringbone gearing in combination with compact extruders for precision technical profile production. Influenced only by its rpm, the gear pump generates an even, constant volume flow, a pre-condition for optimum production of hi-quality profiles.

- **Functional principle.** Filling of the tooth gaps, transport in the tooth gaps, discharging of tooth gaps (Fig. 18).
- **Extrusion Blow Molding.** The melt processible rubber can be processed on a range of extrusion blow molding machines to produce a variety of hollow rubber goods at low unit cost. The Extrusion Blow Molding Process Blow molding enables the production of hollow parts of complex design and variable internal

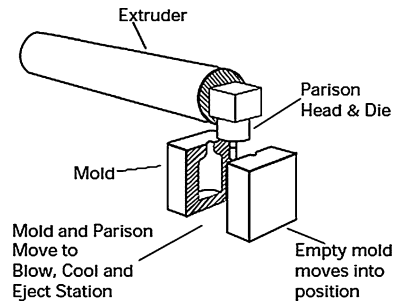


**Fig. 18** Compact rubber extruder with gear pump

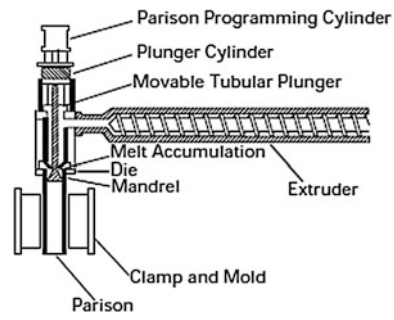
configuration from thermoplastic resins. The process involves forming a hot tube of molten or softened resin called a parison, and clamping it inside a cooled mold. As the mold closes, the parison is inflated with compressed air until it conforms to the mold cavity configurations. Thus, convolutions, texturing, and other fine details can be produced in the part. The finished part is ejected from the mold when it has developed enough strength (by cooling) to be removed without distortion. Blow-molded parts are prepared commercially by three processes:

- Continuous extrusion blow molding
- Intermittent extrusion blow molding
- Injection blow molding
- **Continuous Extrusion Blow.** In this process (Fig. 19), the melt is continually fluxed and extruded vertically downward through the parison die. The parison is formed, the mold closes and moves automatically to another station where the parison is blown and the finished piece is cooled and ejected. Meanwhile, an empty mold moves into position beneath the parison die head, a new parison is extruded, and the cycle is repeated. Continuous extrusion blow molding yields high production rates and is suitable for heavy weight parts. It is the preferred process for blow molding, because there is little opportunity for the melt to hold up in the machine and degrade.
- **Intermittent Extrusion Blow.** In this process the melt is fluxed and delivered to a reservoir, or accumulator. When enough melt has accumulated a ram or plunger forces it through the parison die. When the parison is completely formed, the mold closes and the parison is blown. Meanwhile, the ram retracts and the extruder plasticates more melt and delivers it to the accumulator for the next shot. There are three variations of the intermittent process:
  - The accumulator heat system (Fig. 20).
  - The ram-accumulator system (Fig. 21).
  - The reciprocating screw system (Fig. 22).

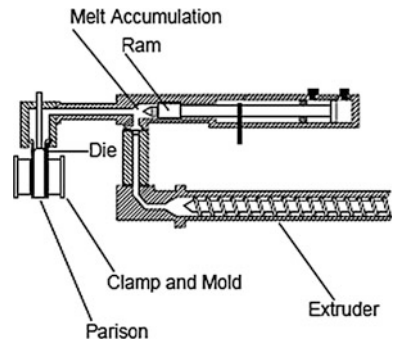
**Fig. 19** Continuous extrusion blow molding process



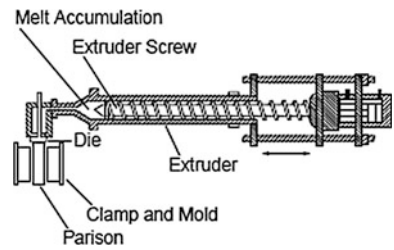
**Fig. 20** The Accumulator heat system



**Fig. 21** The Ram-accumulator system



**Fig. 22** The Reciprocating screw system



Intermittent extrusion blow molding is suitable for large parts and is economical for short production runs. It is best used with non-heat sensitive resins.

## ***4.9 Injection Molding***

The injection molding technique has to meet the increasing demand for a high quality product, which should still be economically priced. This is feasible only if the molder can adequately control the molding process, if the configuration of the part is adapted to the characteristics of the molding material and the respective conversion technique, and a mold is available which satisfies the requirements for reproducible dimensional accuracy and surface quality. Therefore injection molds have to be made with the highest precision. They are expected to provide reliable and fully repeatable function in spite of being under extreme loads during the molding process, and a long service life to offset the high capital investment. Injection molding is the most widespread technique for making 3-D configurations. In the simplest although most frequent case, the injection mold consists of two halves, which are directly mounted to the plates of a molding machine. These two basic elements, the stationary injection and the movable ejection half can be found in every mold regardless of its design. They are called the male and female half. Material under high pressure is forced to flow through a distribution system in the mold to the mold cavity. Pressure is applied until the mold is full and the part has cooled enough to prevent warpage. The pressure may be built up by an extruder equipped with a ram to force the polymer melt into the mold at the appropriate time in the cycle. The gate controls the flow of polymer melt into the cavity and prevents backflow of melt out of the cavity as the pressure is released and the melt is cooling. The runners distribute the melt to several different cavities and must be balanced to prevent some cavities from not getting enough melt to fill them. The factors, which dictate the dimensions of sprue, runner, and gate systems for injection molds, namely, pressure drop, temperature rise, and injection rate, are interrelated. The calculation of these dimensions is difficult, due to the need to solve coupled flow and heat transfer equations, and most mold manufacturers adopt a past experience approach. However, valuable guidance can be obtained from simplified flow analyses. In addition to the pressure drops and temperature rises in channels of constant or smoothly changing cross section, the transitions between them must also be taken into consideration, particularly when the change in cross section is considerable, as in the case for runners and gates. In the scheme of mold design, it is necessary to make an initial estimate of the number of cavities which may be included in the mold, the layout of the sprue and runner system required to feed them, and the volumetric flow rate for a desired injection time. The length of the flow path to each cavity should be the same wherever possible, to give an equal and simultaneous fill in each cavity. After setting the preceding parameters an initial selection of the sprue and runner cross sections is required. The dimensions of the nozzle and gates should also be included at this stage, since they are important parts of the total flow path during injection. The gate type and cross section is often fixed by the requirements of the product. The die, the male and female half, is split to allow removal of the product. It must be kept firmly shut during injection, with the aid of a large hydraulic cylinder, or hydraulically

actuated mechanical clamps, or a mechanical clamp combined with a shortstroke hydraulic cylinder. The clamping force is calculated from the projected area of the moldings and the recommended injection pressure. Shrinkage is the term used to describe the difference in the dimensions of the mold and the article produced from it, when both are measured at ambient temperature. Shrinkage factors must be determined for individual compounds if strict dimensional accuracy is required, and can be obtained by curing a standard test specimen at production temperatures. In general, linear shrinkage figures fall within the range 1.5–3.0 %, depending on polymer type and filler loading. Molding is the operation of shaping and vulcanizing the plastic rubber compound, by means of heat and pressure, in a mold of appropriate form. Fundamentally, all processes of molding are similar, the ways of introducing the material into the mold distinguishes one technique from another. The basic processes are compression, transfer, and injection molding.

In compression molding, chunks or sheets of material are placed in an open mold, which is then closed around it. After the part is formed, the mold is opened and the part removed. In injection molding, material is injected under pressure into a closed mold. After the part is formed and vulcanized, the mold is again opened and the part is removed. Transfer molding represents a combination of injection and compression molding in which rubber is injected from a reservoir into a compression mold. The main feature of injection molding, in which it differs from compression molding, is in the presentation of rubber to the mold at or near molding temperature. A large part of the cure time necessary to allow the whole of the rubber mass in the cavity to reach the vulcanizing temperature by conduction and convection, as in the case of compression molding, is eliminated. With compression and transfer molding, it is necessary to place a rubber preform into a compression mold cavity or into a transfer pot. A strip of rubber, or granulated rubber, automatically supplies an injection molding machine. Another difference is that systems for injection molding are much more complex than those for compression or transfer molding. There are several controls to adjust temperature, pressure and other variables during injection molding. These controls are not normally a part of compression or transfer molding systems. With compression and transfer molding, presses provide a force to close a mold. In injection molding, a press is referred to as a clamp. A clamp is an integral part of an injection molding machine. Injection molds are normally attached to the clamp and thus open and close with the clamp. One reason for attachment between mold and clamp is the need for accurate alignment between an injection molding machine and its mold. Injection molds must be capable of withstanding extremely high pressures without mold distortion. The pressure reached in an injection mold is about ten times greater than that for compression and transfer, i.e. injection pressures up to about 200 MPa (29,000 psi) are used. Therefore, high quality steel such as 4140 hardened to a Rockwell C of 28–32, is recommended for injection molds. The mold plates should be thick enough to resist bending at the high pressures encountered during injection molding. Injection molding can be combined with compression or transfer molding. With injection/compression molding, an injection machine pumps hot rubber into an open compression mold. Then the mold is closed, generally using much less



force to close it than is normally used in injection molding. This method was developed to protect shoe uppers from being torn apart or wrinkled by the strong forces typically associated with injection molding. With injection/transfer molding, hot rubber from an injection nozzle is placed in the pot of a transfer mold. Then a plunger transfers hot rubber from the pot to the mold cavities. With both injection/compression and injection/transfer molding, cycle times are shorter than for regular compression or transfer molding. Rubber entering the mold is preheated and this rubber therefore crosslinks in a shorter time.

### • Types of injection molding machines

The types of injection machinery available differ basically in the method of heating and pre plasticisation of the compounded rubber. The main difference usually arises between vertically oriented machines, which include both ram and screw-ram presses, and horizontally oriented machines, which are of the reciprocating screw type. In the former the mold temperature is maintained by conduction from the heated platens of the press, whereas the heaters are integral with the mold in the latter case. The configuration of molds for horizontal machines often result in large surface areas for potential convective heat loss and long paths for conductive heat flow from the press platens. The horizontal machine generates its own preplasticising heat by work on the rubber, which is fed into it in strip form, between the screw and the barrel. This heat is governed by a temperature-controlled fluid medium (water, glycol, or oil), which circulates around the barrel and, in larger machines, through the center of the screw. Progression of the rubber up the screw both heats and preplasticises it. The rubber, collected in front of the screw, pushes the screw back until a trip switch is operated, and the preplasticisation phase is completed. Final heating of the stock takes place during passage through a small die into the runner system of the mold. The second type of injection press uses the principle of vertical injection. This type of machine has a separate screw and injection piston in a V-head configuration situated near a vertical upstroking press. The preplasticising screw feeds into the injection chamber through a non-return valve where the compound is injected into the mold. There are many independently adjustable parameters of both the injection head and press unit. Molds for vertically oriented machines are usually larger in plan area, giving improved conductive heating, and also expose smaller areas for convective heat loss. A horizontal injection machine is shown in Fig. 23.

An injection mold consists of a cylinder (injection barrel) with a ram or screw inside it, so that the rubber compound can be moved towards a nozzle at its end. The nozzle is then pressed against a hole made in the top half of a closed mold. This hole is then connected to smaller holes (gates and runners) which enter the cavities of the mold. The compound can be presented to the barrel as a continuous strip, or in granulated form through a hopper, as in plastics injection molding. A ram has a tighter fit in the barrel than a screw and therefore there is less leakage backwards through the barrel; it is also cheaper than a screw. The screw 'mixes' the compound as it moves towards the nozzle, creating more frictional heat and therefore higher temperatures which translate to easier flow and shorter cure times.

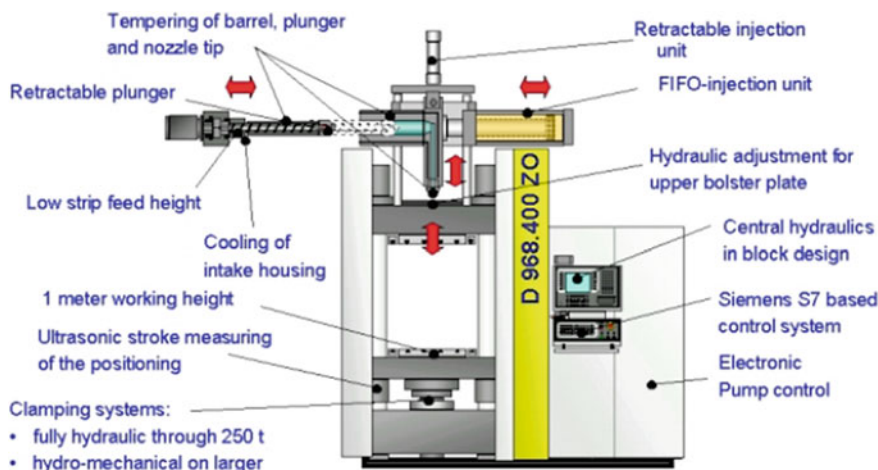


Fig. 23 Horizontal injection machine

## 5 Characterization of Elastomer Macrocomposites

Early structural characterization of polymers focused on solution properties and their relationship to molecular weight. Subsequently spectroscopic and chromatographic techniques were developed, and reviews are widely available. The chemical *elemental analysis* of polymers can often be carried out by the methods used for low molecular weight organic compounds [72–88]. This is particularly true when combustion of the sample is involved. Thus, C, H, and N can be determined on milligram samples by complete combustion followed by gas chromatographic analysis of the gases evolved. Accuracy is about 0.3 %. Sulfur and halogens are also easily determined after combustion, by titration of sulfate or SO<sub>2</sub> for S, and by potentiometric titration with AgNO<sub>3</sub> for halogens after treatment of the gases with NaOH and hydrazine sulfate, for example. Quantities as low as ppm metals can be determined quantitatively and quickly by x-ray techniques. For basic information, *infrared spectroscopy* (invariably Fourier transform infrared [FTIR]) is a straightforward technique, accessible to the nonspecialist. Thin films of elastomers can be measured directly, and obtained by casting or molding 20–30 mg of sample between polyester or aluminum foil (preferably Teflon-coated). Care must be taken to minimize oxidation if the molding is done at elevated temperature. Most analyses make use on the mid-infrared region at 4000 to 400 cm<sup>-1</sup>, with sample identification made through comparison, using widely available spectral libraries. If the polymer is crosslinked, sample-forming is more restricted. Raman spectroscopy yields analogous information, but is complementary to infrared absorption, in that vibrations which are infrared inactive are generally Raman active, and vice versa. For example, carbon–sulfur bonds are easily detectable via Raman measurements. Since the detected light is scattered from the sample, spectra are readily obtained on crosslinked specimens.

Interferences due to fluorescence are avoided by using a longer wavelength Source Pyrolysis of samples can lead to the production of characteristic fragments, which may be analyzed by gas chromatography (GC) or mass spectrometry (MS). Since the relationship between fragments and the original polymer is often complex, this technique is a last recourse, for insoluble polymers or samples not amenable to more facile and reliable characterization methods. Combined GC/MS has been used to analyze the volatile components in natural rubber. In ozonolysis, an unsaturated sample is reacted to form an unstable intermediate, ozonide, which is then further reacted for chemical identification. Ozonolysis of rubber is usually combined with GC analysis. In secondary ion mass spectrometry (SIMS), the sample surface is irradiated with an ion beam, followed by mass spectrometry of the emitted secondary ions. SIMS has found various applications in rubber, including surface analysis and studies of carbon black interaction. Pyrolysis can also serve as a fingerprinting technique for routine analyses. In thermogravimetric analysis (TGA), the polymer degradation by-products volatilize, whereby the residue provides a measure of the carbon black or other filler content.

Electron paramagnetic resonance (EPR), or electron spin resonance (ESR), can be used to detect types and quantities of free radicals. Such information is of value in studying the chemistry occurring during degradation and fracture of polymeric materials. EPR can also be applied to study carbon black and other fillers in polymers. The technique of temperature rising elution fractionation (TREF) has been developed to measure the compositional distribution of semicrystalline polymers. Polymer is dissolved off a substrate as temperature is raised through the melting region, so that discrimination is based on differences in crystallizability of the fractions. A similar method uses supercritical fluids. TREF can also provide information about the sequence distribution, since longer sequences of a monomer unit are more crystallizable. Different arrangements of the monomer units give rise to different chemical shifts and scalar couplings (splittings) in the NMR spectra. Using selection rules and empirical knowledge of chemical shifts, chemical structures can be assigned. Since chemical shifts in  $^{13}\text{C}$  NMR spectra are larger than in proton spectra, subtle structural differences can be seen for carbon atoms separated by up to five bonds from the point of reference. The viscoelastic response of amorphous polymers at elevated temperatures is governed to a significant extent by the average molecular weight,  $M_w$ , the presence of any long chain branching, and the MWD. The chain length distribution is usually presented as a plot of the mole fraction or weight average of molecules versus molecular weight. The various average molecular weights represent the moments of the chain length distribution. For low molecular weight samples, the preferred method is by vapor pressure osmometry (VPO). This technique is based on the decrease of vapor pressure of a solvent due to the presence of dissolved polymer. The different equilibrium vapor pressures cause a difference in condensation rate on two matched thermistors, contained in a chamber saturated with solvent vapor. One thermistor is coated with solvent and the other with a solution of the polymer. Membrane osmometry relies on the lowering of the activity (free energy) of the solvent by dissolution of a solute, to yield an direct determination of  $M_n$ .

When a polymer solution is brought in contact with pure solvent, the concentration gradient induces mixing by diffusion. If a semipermeable membrane is placed between the pure solvent and solution, the polymer is trapped but solvent can pass. Light scattering is another absolute technique for the determination of molecular weights ( $>103$  g/mol). (We are only concerned with static light scattering for structural information; however, inelastic light scattering is a powerful technique for studying polymer dynamics. Structural information can also be obtained from measurements of small angle neutron scattering (SANS). Scattering of neutrons is due to their interaction with nuclei. It differs from light scattering, in that contrast arises from differences in neutron scattering length, rather than refractive index differences. Neutron cross-sections are commonly expressed in terms of the relevant correlation function. Elastic, coherent scattering is proportional to the spatial Fourier transform of the pair-correlation function. The classical method of solvent-nonsolvent fractionation according to MWD and compositional distribution depends on solubility differences among the various species. The method is empirical and tedious, involving characterization of phase-separated “cuts” as they are recovered. The term field flow fractionation (FFF) refers to a family of one-phase chromatographic techniques, carried out in thin flow channels. In principle, FFF yield absolute molecular weights, although in practice calibrations similar to SEC are used. Long chain branching (LCB), defined as branches having molecular weights of at least a few times the entanglement molecular weight, is common in rubbers. Its most important effect is increasing the viscosity; LCB is present in some commercial rubbers in order to reduce cold flow (i.e., the room temperature creep of rubber during storage). Substantial LCB may require use of a low  $M_n$  polymer, in order to retain a viscosity low enough for processing; however, the consequent plethora of chain ends may entail sacrifice of cured properties, especially those relating to heat buildup or strength. Branching affects other properties, affording a means to characterize the degree of branching.

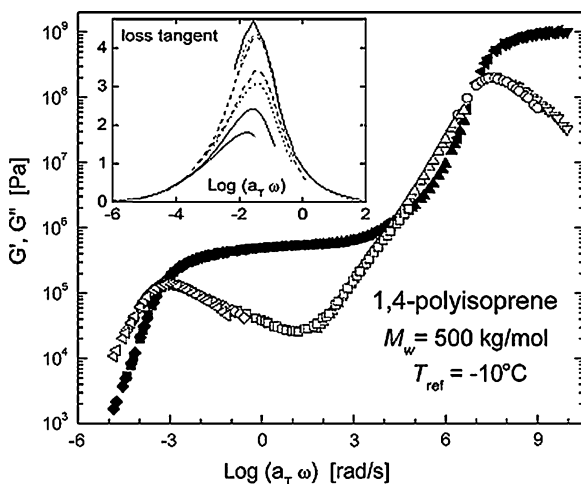
With light scattering measurement of the radius of gyration, direct comparisons of  $g$  values can be made. In  $Q$  solvents, the experimental  $g$  values generally agree with calculations, with some notable exceptions. Advanced SEC analytical techniques take advantage of online light scattering and viscometry [IV A]. With the SEC calibrated for the product of  $[\eta]$  times  $M$  versus elution time for a particular polymer species, together with  $[\eta]$  Br or MW Br measurements, one can calculate  $g$  factors as the ratio of the measured intrinsic viscosity to the value of  $[\eta]$  calculated for the corresponding linear polymer (i.e., linear polymer that would have eluted at the same time). When a measurement of polymer dynamics is made (using, for example, mechanical or dielectric spectroscopy, or dynamic light or neutron scattering), a maximum in the susceptibility (absorption peak) is observed for molecular motions transpiring on the timescale of the experimental variable (e.g., frequency of the applied stress or voltage). In the limit of small perturbations (for which the material response is linear), the relaxation directly reflects the equilibrium Brownian motion. Such correspondence follows from fluctuation dissipation theory, originally developed to explain Johnson noise in electrical conductors. The gigantic size of polymer molecules provides for an enormous

number of degrees of freedom, and thereby motion encompassing many decades of time overly a broad range of length scales.

The local segmental dynamics are associated with the rubber-glass transition, occurring at  $T_g$ . It is only in the glass transition zone of the viscoelastic spectrum that both chain modes and local segmental modes can be measured simultaneously at the same temperature, using conventional techniques. Since the chain modes and the local segmental dynamics have different temperature dependences, a breakdown of the time-temperature superposition principle is observed in the glass transition zone. Thus, master curves for the chain dynamics can be constructed, which extend from the end of the softening zone through the terminal relaxation, and master curves of the local dynamics are possible. However, in the softening zone, the shape of the viscoelastic spectrum changes with temperature (Fig. 24).

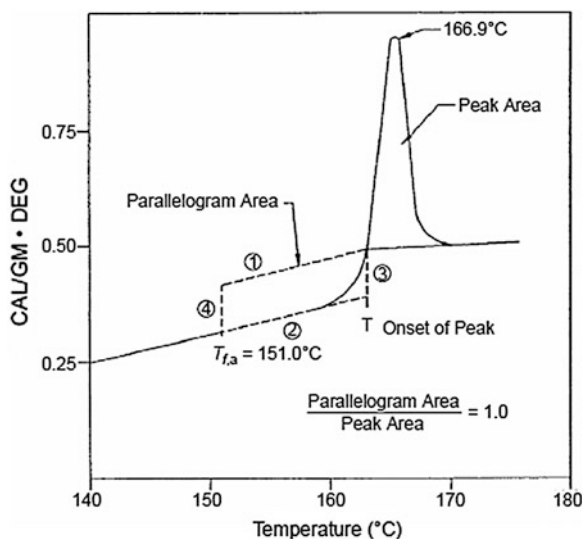
The most common means to assess  $T_g$  is via heat capacity ( $C_p$ ) measurements, usually carried out in a differential scanning calorimeters (DSC). The temperature of the sample changes at a fixed rate, with the heat flow monitored. An older, and less useful, variation is differential thermal analysis (DTA), in which heat flow is programmed, and the consequent rate of temperature change is measured.  $T_g$  in heat capacity. This is nearly equal to an alternative definition, the temperature of the intersection of the extrapolated baseline with the tangent of the maximum slope (Fig. 25).

Analyzing the morphology of an elastomer includes not only the characterization of the molecular structure of the polymer itself and of the compounding ingredients, but may also extend to the super molecular scale. Rubber elasticity arises from the orientation of chain segments, and the degree of this orientation underlies the mechanical properties. The most facile way to quantify the orientation is from the (optical) birefringence, defined as the difference in refractive indices for two perpendicular directions. When a material is semicrystalline, the observed birefringence is the sum of the  $\Delta n$  from the oriented amorphous phase and the crystalline regions. There is also a contribution due to form birefringence, arising from distortion of the light wave transverse the refractive index boundary between the amorphous and crystalline phases. Another method to characterize orientation is deuterium NMR. Deuterons have a spin quantum number equal to unity and therefore a nuclear quadrupole moment. Coupling between the quadrupole moment and the two possible NMR transitions (resulting from the three Zeeman levels of the spin = 1 nucleus) yields differences in the energy levels of the two transitions, giving rise to a doublet. The separation of this doublet is proportional to  $f_2(f)$ , which depends on the orientation of the chemical bond axis of the deuteron relative to the applied external magnetic field; thus, the magnitude of the observed splitting yields directly the orientation. Although many rubbers can be mixed to form an ostensibly homogeneous blend, the overwhelming majority of such mixtures have phase-separated morphologies. To form a useful elastomer, the components need only be sufficiently compatible that a satisfactory dispersion is attained. Actual thermodynamic miscibility, implying segmental mixing of the components, is rare, although it is important to recognize when is achieved. The phase size in a heterogeneous blend will depend on the compatibility of the



**Fig. 24** Apparent master curves (reference temperature =  $-10^\circ\text{C}$ ) for the storage (solid symbols) and loss (hollow symbols) moduli of cis-1,4-polyisoprene ( $M_w = 500,000 \text{ g/mol}$ ). The breakdown of time-temperature superposition, barely evident in the softening zone, is seen clearly in the loss tangent peak, shown in the *inset* for temperatures from  $-66^\circ\text{C}$  to  $-48^\circ\text{C}$

**Fig. 25** DSC of a cured epoxy resin. To determine the fictive temperature, a parallelogram is constructed to the low temperature side of the enthalpy peak, with horizontal sides parallel to the measured heat capacity. The onset of the peak defines the high temperature boundary, while the low temperature boundary (i.e.,  $T_f$ ) is chosen such that the area of the parallelogram equals the peak area



components and, to a lesser extent, on the mixing conditions. The simplest method of determining whether the phase morphology is homogeneous is by calorimetry. The observation of two transitions, corresponding to the respective  $T_g$  of each component, indicates a phase-separated morphology. However, a single transition does not guarantee thermodynamic miscibility, especially if the component  $T_g$ 's are close. NMR of swollen rubber has been used to determine crosslink

distributions in blends. Swelling enhances chain mobility, and the isotropic motion of nuclei averages local fields, thereby narrowing the spectral lines. This allows individual resonances to be characterized. Rubbery behavior—large, reversible extensibility—implies an absence of crystallinity, and this is usually the case for undeformed elastomers. However, small extents of crystallization may be present at ambient temperature in some elastomers, including EPDM with high ethylene content, epichlorohydrin rubber, and polypropylene oxide rubber. The crystallites in these materials can act as reinforcing agents. Many thermoplastic elastomers have crystalline domains which function as reversible crosslinks. It is well known that elastomers, like virtually all solid materials, have preexisting, “naturally occurring”, flaws. By intensifying local stresses, such flaws exert an influence on the failure properties of elastomers. More recently, interest in these flaws has increased, due to concerns about their potential for reducing the barrier performance of rubber films. The elastic behavior of rubber for large strains reflects the effect of topological interactions known as entanglements. Entanglements constrain the chains, suppressing lateral motions. The pseudo-network of entanglements gives rise to the characteristic plateau in the time-dependence of the mechanical response of uncrosslinked rubber. While the length (extent over time or frequency) of the rubbery plateau is determined by the molecular weight, its height,  $G_0N$ , reflects the concentration and effectiveness of the entanglements. The storage modulus varies only weakly with frequency, and is approximately proportional to the entanglement concentration. Such proportionality in the melt is purely entropic, and is not affected by energy differences between the conformers. The molecular weight between entanglements, depends on chemical structure, and thus is characteristic of the polymer species. The entanglement interactions govern the rheology of uncrosslinked polymers, influencing the viscosity, the dynamic modulus, and the recoverable compliance.

## **6 Applications of Elastomer Macrocomposites**

### ***6.1 Tire Manufacturing Process***

A tire is a black donut made of rubber, placed on a vehicle so the driver can transport himself and his cargo from point A to point B. The tire has to allow for easy steering, braking and cornering. It must provide for a comfortable, safe ride. It needs to be durable. Actually, a tire is an advanced engineering product made of a lot more than rubber. Fiber, textile, and steel cord are just some of the components that go into the tire's innerliner, body plies, bead assembly, belts, sidewalls, and tread. As you can imagine, the manufacture of this complex product is, well, complex. It requires the latest technology, heavy equipment, precision instruments and—most importantly—qualified people. Some of the activities that go on in the tire factory are the mixing of the rubber compound; preparation of the fabric cord, steel cord, and bead wire; “calendering” of the innerliner, steel belt and ply cord;

extrusion, or shaping, of the tire's sidewall and tread; and the actual building, curing, and inspection of the tires. Read on for a more detailed explanation and refer to the manufacturing flowchart for a visual reference to each process [89].

The two major ingredients in a rubber compound are the rubber itself and the filler, combined in such a way as to achieve different objectives. Depending on the intended use of the tire, the objective may be to optimize performance, to maximize traction in both wet and dry conditions, or to achieve superior rolling resistance. The desired objective can be achieved through the careful selection of one or more types of rubber, along with the type and amount of filler to blend with the rubber. In general, there are four major rubbers used: natural rubber, styrene-butadiene rubber (SBR), polybutadiene rubber (BR), and butyl rubber, along with halogenated butyl rubber. The first three are primarily used as tread and sidewall compounds, while butyl rubber and halogenated butyl rubber are primarily used for the innerliner, or the inside portion that holds the compressed air inside the tire [90, 91].

The most popular fillers are carbon black and silica, and there are several types of each. The selection depends on the performance requirements, as they are different for the tread, sidewall, and apex. Other ingredients also come into play to aid in the processing of the tire or to function as anti-oxidants, anti-ozonants, and anti-aging agents. In addition, the “cure package”—a combination of curatives and accelerators—is used to form the tire and give it its elasticity. Once the compound is determined, the next challenge is how to mix it all together. The mixing operation is typically a batch operation, with each batch producing more than 200 kg of rubber compound in less than 3–5 min. The mixer is a sophisticated piece of heavy equipment with a mixing chamber that has rotors inside. Its main function is to break down the rubber bale, fillers, and chemicals and mix them with other ingredients. The sequence in which the ingredients are added is critical, as is the mixing temperature, which can rise as high as 160–170 °C. The compound can be damaged, if the temperature is too high, so the mixing operation is typically accomplished in two stages. The curative package is normally added in the final stage of mixing, and the final mixing temperature cannot exceed 100–110 °C or scorching may occur [92, 93].

Once the mixing is completed, the batch is dumped out of the mixer and sent through a series of machines to form it into a continuous sheet called a “slap.” The slap is then transferred to other areas for bead wire assembly preparation, innerliner calendering, steel and/or fabric belt/ply cord calendering, tire sidewall extrusion, and tire tread extrusion. Because tires have to carry heavy loads, steel and fabric cords are used in the construction to reinforce the rubber compound and provide strength. Among those materials suitable for the tire application: cotton, rayon, polyester, steel, fiberglass, and Aramid [94, 95].

- **Fabric cord.** Fabric cord quality is based on its strength, stretch, shrinkage, and elasticity. The yarn used is first twisted, and then two or more spools of yarn are twisted into a cord. Before shipping the cord to the tire factory, the manufacturer pre-treats the cord and applies an adhesive to promote good bonding with the rubber. The temperature, humidity, and tension control are critical before the



fabric cords are calendared with rubber compound. For this reason, fabric cord is kept in a temperature-and-humidity-controlled room once it arrives at the factory.

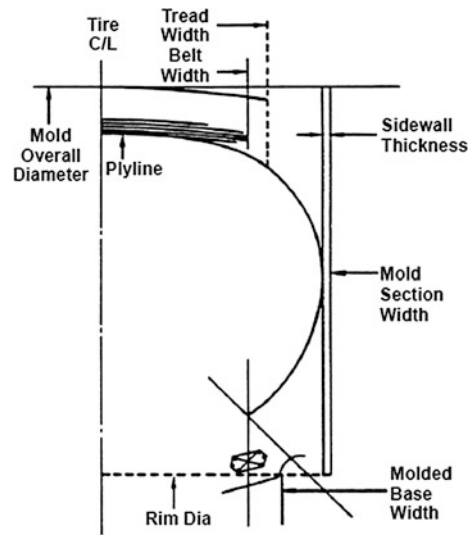
- **Steel cord.** Steel wire cord quality is based on tensile strength, elongation, and stiffness. It is manufactured from steel rod with high carbon content; and while the steel wires used have different configurations, all are brass-coated strands twisted together into cords. If the wire is used in a multi-ply tire rather than a belted tire, the fatigue performance will be important. If used in belted tires, then stiffness is of primary concern. Since the steel wire is brass coated, storage conditions are important to maintain the steel wire to rubber bonding properties. Therefore, the steel wires are also kept in a temperature and humidity controlled room once they arrive at the factory.

To produce fabric or steel belts, the fabric or steel cord must go through a calendaring process—an operation in which the rubber compound is pressed on and into cords. Because the bonding of fabric to rubber or steel to rubber is critical to performance, the calendaring process is an important step. The calendar is a heavy-duty machine equipped with three or more chrome-plated steel rolls which revolve in opposite directions. The roller temperature is controlled via steam and water. In this process, the rubber compound is applied to the cords [96, 97].

First, a pre-set number of fabric or steel cords under proper tension are continuously pressed through two steel rollers, and rubber compound is added to the opening area between the rollers. Then the rubber compound is pressed into, on top of and on the bottom of the fabric or steel cords. A continuous sheet of cord-rubber composite goes through several more rollers to ensure good penetration and bonding between the rubber and cords. Quality is measured by the thickness of the sheet, spacing between cords, the number of cords and the penetration of rubber into the composite sheet. The composite sheet is then cut into appropriate sizes, shapes, and angles depending on the desired contour of the tire.

Finally, the tire is ready to be built by a highly robotized machine which ensures quality and efficiency. All components—bead assemblies, calendared plies, belts and innerliner, tread and sidewall sections—are assembled and the building process begins. A typical radial tire is built on a flat drum in a two-stage process. In the first stage, the innerliner is wrapped around a drum and the first body ply is wrapped on top, followed by the second body ply. The bead assemblies are then positioned, and a bladder on the drum is inflated and pushed in from both ends of the drum, forcing the body plies to turn up to cover the bead assemblies. The sidewall sections then are pressed onto both sides. In the second stage of the tire building process, another machine is used to apply the belts, nylon cap, and tread on top of the first stage. At this point, the tire still needs curing because there is no tread pattern on it. A tire is essentially a cord–rubber composite. Tires have plies of reinforcing cords extending transversely from bead to bead, on top of which is a belt located below the tread. The belt cords have low extensibility and are made of steel and fabric depending on the tire application. The belt cords are at a relatively low angle, between 12° and 25°, and serve as restrictions to the 90° casing plies.

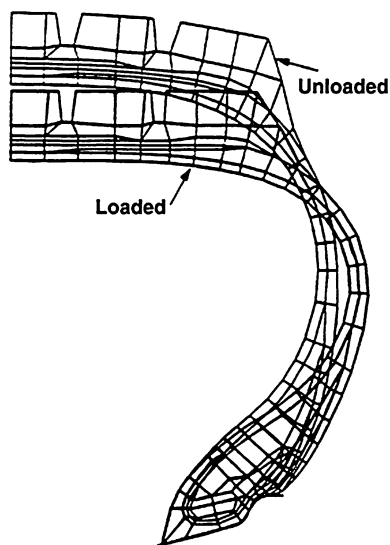
**Fig. 26** Ply line boundaries of the tire



Tire mold design initially begins with determination of the inflated dimensions of the required tire size. By use of inflated tire and growth characteristics of the tire, preliminary ply line and mold dimensions are computed (Fig. 26). Once the mold boundary dimensions, location of the ply line, and tread width and depth are known, the contours of the tread, shoulder, sidewall, and bead components can be established. These dimensions and contours are developed using computer-aided engineering techniques. Structural mechanical calculations such as finite-element analysis are used to analyze both the inflated and loaded deflected shapes of a tire cross-section and the resulting stress-strain relationships in the belt area. Such studies permit both quantitative analysis and qualitative comparisons of the range of belt configuration options. Figure 27 shows a heavy-duty truck tire in the loaded and unloaded states. The density of grids is designed so as to preserve the essential features of the tire cross-section geometry while maintaining the total number of grid points.

Steel wire used in tires are of various configurations, but all are brass-coated wire strands wrapped together to give cords of different characteristics, depending on the application. Steel tire cord is manufactured from high-carbon-steel rod which is first drawn down to a diameter of approximately 1.2 mm. A brass plating is then added to the wire before a final drawing to 0.15–0.40 mm. These filaments are next stranded to form a cord construction which is designed and optimized for a specific service requirement. Steel tire cord is manufactured from high-quality steel which is necessary because of the performance demands to which tires are subjected. The composition of a typical steel cord is illustrated in Table 1.

**Fig. 27** Finite-element structure of a heavy-duty truck tire



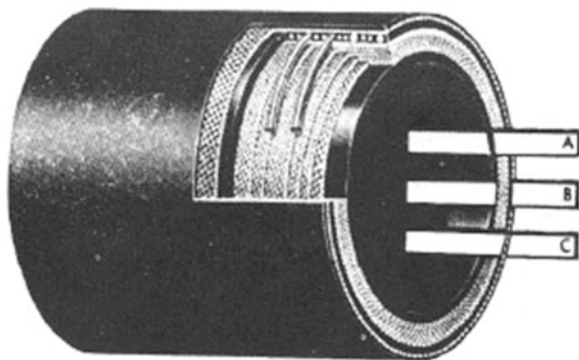
**Table 1** Composition of steel tire cord

Element	Composition (%)	Function
Carbon	0.65	Strength
Chromium	0.05	Strength
Copper	0.02	Strength
Manganese	0.60	Deoxidation
Silicon	0.25	Deoxidation
Sulfur	0.03	Machinability

## 6.2 Hoses

A hose is a reinforced, flexible conduit used to move materials from one point to another or to transmit energy. It is flexible to accommodate motion, alignment, vibration, thermal expansion and contraction, portability, ease of routing, and ease of installation. Most hoses are made up of three elements: (1) a tube, (2) reinforcement, and (3) an outer cover. Each of these components is usually adhered to the adjacent components by bonding agents or thin layers of specially compounded rubber. The tube is the innermost rubber or plastic element of the hose. Reinforcement can be textile, plastic, or metal, alone or in combination, built into the body of the hose to withstand internal pressures, external forces, or a combination of both. The type and amount of reinforcing material used depends on the method of manufacture and on the service requirements. For example, a residential garden hose does not need the same level of reinforcement as required for high pressure air hose used in construction and mining applications. The cover is the outer element and can be made [98].

**Fig. 28** Typical hose construction

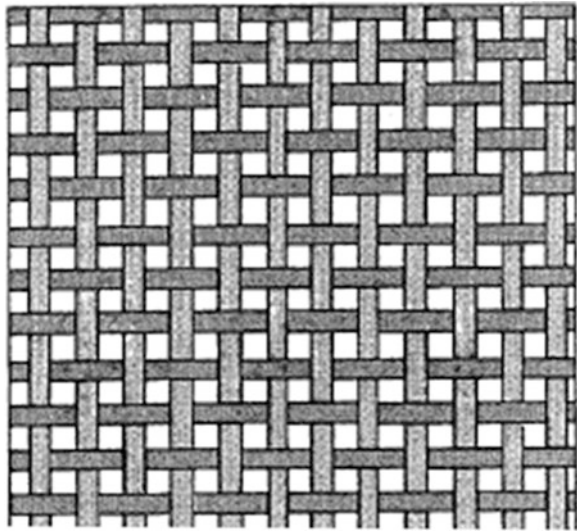


The prime function of the cover is to protect the reinforcement from damage and the environment in which the hose will be used. Covers are designed for specific applications and can be made to be resistant to oils, acids, abrasion, flexing, sunlight, ozone, etc. The basic materials in the manufacture of hose are rubber, plastics, textile yarns, textile fabrics, and metal in the form of wires and cables. Throughout this book, the term “rubber” will be used in its broadest sense. This will include all elastomeric materials that are compounds of natural or synthetic elastomers or combinations of these materials. To provide a wide range of physical properties for specific service needs, elastomers are mixed with various chemicals. Space does not permit discussion of the compounding ingredients or compounding methods, so only the basic elastomers will be discussed. There are many of these available to the hose manufacturer. In addition, many types may be blended in almost unlimited combinations to obtain the most desirable properties. A typical hose is shown in Fig. 28.

Textile fabrics used as reinforcement in hose construction provide the strength to achieve the desired resistance to internal pressure or to provide resistance to collapse, or both. The properties of a fabric depend on the construction and the material from which the yarn is made and on the type of weave used. One common hose fabric is woven from warp yarns, which run lengthwise, and filling yarns, which run cross-wise. Usually they are woven at right angles to each other. The most common weave is known as “plain weave”, Fig. 29.

Yarns are used in hose for reinforcement of the tube material to provide the strength to achieve the desired resistance to internal pressure or to provide resistance to collapse, or both. The basic yarn properties required for hose reinforcement are: adequate strength, acceptable heat resistance, dynamic fatigue resistance, and satisfactory processability for the various methods of reinforcing hose. Other special properties such as stiffness, adhesion, conductivity, etc., may be developed depending upon the specific hose application. Yarn is available in two basic forms: staple (sometimes referred to as spun yarn) and filament.

Staple yarn is made by twisting bundles of short fibers to form a continuous yarn. The staple obtains its strength from the binding effect of the twist imparted to the individual fibers. The base staple yarn is called a singles. It is made from fiber

**Fig. 29** Plain weave

bundles twisted together in one direction to form a single strand. If two or more single yarns are twisted together, usually in a direction opposite that of the single yarn, the result is a plied yarn.

Filament yarn is produced by extruding synthetic material through a spinnerette containing hundreds of orifices. The monofilaments from each of the orifices are brought together to form a multifilament yarn. Filament yarns have higher tenacity (strength per unit of weight -grams per denier), in the range of 2–3 times that of staple yarn on the same material type and size. Steel wire has strength, high modulus for dimensional stability, fatigue resistance, and low cost, and is the major reinforcement used in high pressure hose and in most suction hose. Under certain service conditions, carbon steel wire is not suitable. An *alloy wire* is used instead. One of the most commonly used is stainless steel which offers exceptional resistance to corrosion and heat. Where light weight is essential, alloys of aluminum are used. *Static wires* and other conductive materials are used in hose to prevent static electricity buildup. Wires can be made from many metals including copper, steel, monel, aluminum and tin-coated copper. Static wires may be solid, stranded, or braided.

Most hose is used for pressure service; however, some applications require the hose to resist collapse in suction and vacuum service. Such hose is subjected to crushing forces because the atmospheric pressure outside the hose is greater than the internal pressure. The hose can collapse and restrict the flow unless the hose is constructed to resist these pressure differentials. The most common method of preventing hose collapse is to build a helical wire reinforcement into the hose body. The size and spacing of the wire reinforcement depends on the size of the hose and the expected pressure differential for the application. In suction

applications approaching a perfect vacuum, most of the carcass plies are applied over the wire reinforcement. The hose is constructed with high adhesion between the tube and the carcass to prevent tube separation. Suction hose must be specifically designed for the service for which it is used.

Static wires and conductive rubber components are used in hose to help prevent static electricity build-up and subsequent a discharge as a spark. Electrical engineers differ in opinion on the effects of static electricity and the means of dissipating it. In handling gasoline and other petroleum-based liquids, recognized national associations and companies have conflicting opinions on the need for conductive hoses. In some specific applications, specially around high voltage electrical lines, it is imperative for safety that the hose be nonconductive. Unless the hose is designed particularly to be non-conductive and is so branded, one dare not conclude that it is nonconductive. Many black rubber compounds are inherently and inadvertently conductive. Nonconductive hose is usually made to a qualifying standard that requires it to be tested to verify the desired electrical properties.

Thermoplastic products such as vacuum cleaner hoses, used for very low pressure applications are often manufactured with blow molded or tape forming techniques. Blow molded products are shaped into a circumferentially corrugated profile at the tube extruder when the thermoplastic material is still in the molten state. The corrugations provide a tremendous improvement in product flexibility and stretch characteristics. The profiling is accomplished by injecting air into the tube pushing it into a series of metal die blocks corrugated with the intended profile. As the tube cools while traveling along the die block track, the tube becomes permanently corrugated circumferentially. A similar process, vacuum forming, uses the same technique of corrugated die blocks at the extruder, but instead of blowing air in the tube, a vacuum is drawn through the blocks pulling the molten tube into the corrugations. The appearance of the final product from each method is quite similar. However the vacuum forming process generally yields superior corrugation uniformity. The corrugated tube may be the final product or used in conjunction with other hose components. For instance, for higher pressure applications an adequate reinforcement may be applied and then a smooth cover extrusion. Combinations of rubber and plastic layers may provide the best appearance for a specific application.

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