

Principles of Vulcanization

It is essential to know first what qualities and duties are desired in a vulcanizate or a cured product, and to attain these properties what would be the problems involved. As a practical approach, vulcanization is considered a process whereby a material of different compositions and a poor conductor of heat is subjected to a heating process with the intention of producing a uniform product having the desired physical properties. That such a result is obtained regularly with either natural rubber or synthetic rubber is a tribute to improved compounding ingredients and techniques of formulating a compound, permitting a wide range of curing systems without any deleterious effect, and also engineering design that allows uniform heating. The possibilities of variables are many in the process of vulcanization and they are so serious that it is important that utmost control is exercised over the type and quality of raw materials, compound development, and the uniform dispersion of sulfur and other ingredients. Second, a precise control of curing time, pressures, and temperatures adopted in the operation is essential.

In so many applications the elastomeric component of the formulation design has proven to be absolutely critical to its overall performance and success. However, one scenario that a rubber chemist encounters time and time again is that proper understanding and development of this key material is so often overlooked by the whims and fancies of company management, or left to the last stages of the product development process forced by constraints of delivery deadlines. Doing so can have serious and adverse consequences for the durability and long-term performance of the product.

Unlike many other materials, rubber is often solely used as a result of its engineering properties. Additionally, it is almost always used in a highly compounded form to achieve the required physical properties. It is the physical and chemical properties of the compound that are the key factors to successful

performance, but to get the right properties the user must first negotiate the “black art” of rubber compounding and curing. Rubber compound development is no simple task.

With over 35 different rubber polymer types and countless material grades to choose from, plus the fact that the physical properties obtained can be modified greatly by compounding and curing technology, it can be very difficult for nonspecialists to select the most suitable rubber compound for their application. This is true even before the effects that improper compound processing could have on the final products and its functionalities can be considered. Therefore it is absolutely crucial to obtain impartial materials advice and consultations from a rubber technologist to enable the most appropriate rubber and grade to be chosen, rather than simply rely on a single source of supply and a misguided knowledge of materials as well as a misunderstanding of the performance specifications.

After the rubber compound has been properly mixed and shaped into blends for molding, calendaring, and extruding, fabricated into composites or hand formed, and lined on the tanks and vessels, etc., it should be vulcanized either in the autoclave or in molds. Molded components are made in hydraulic presses and different types of molding processes are adopted, such as transfer molding, injection molding, and vacuum molding. In innovative practice in the United States and Japan, moldless rubber components are made with proprietary technology.

Different Methods of Vulcanization

In the vulcanization of rubber-lined vessels, one of the following methods would be necessary depending upon the size of the equipment and the compound formulation:

- Autoclave curing,
- Open steam curing,

- Hot water curing,
- Self-vulcanizing,
- Cold bond lining, and
- Curing by using the vessel itself as an autoclave.

An autoclave is a pressure vessel capable of withstanding an internal pressure generated by steam. Fig. 8.1 shows a custom built large size autoclave with door closed. Autoclave processing is the most common method used for curing thermoset products. The curing of thermoset composites involves both mechanical and chemical processes. Mechanically, pressure is applied to remove trapped air and volatiles, and to consolidate the individual plies and fibers. Chemically, a crosslinking reaction must be initiated and taken to completion to form a rigid matrix. Crosslinking is most commonly initiated through the application of heat, though it also may be initiated by exposure to ultraviolet light, microwaves, or high-energy electrons (e-beam curing). In the autoclave process, high pressure and heat are applied to the rubber-lined equipment through the autoclave atmosphere. The cure cycle for a specific application is usually determined empirically and, as a result, several cure cycles may be developed for a single material system to account for differences in laminate thickness or to optimize particular properties in the cured part.

The typical autoclave cure cycle for a fabric-reinforced inflatable is a two-step process. First, vacuum and pressure are applied while the temperature is ramped up to an intermediate level and held there for a short period of time. The heat reduces the polymer viscosity, allowing it to flow and making it easier for trapped air and volatiles to escape. The plastic polymer also begins wetting the fibers at this stage. In the second ramp-up, the temperature is raised to the final cure temperature and held for a sufficient length of time to complete the cure reaction. During this step, the viscosity of the rubber compound continues to drop, but starts raising at temperature ramp rates and hold times, and then is stabilized at a level that permits adequate consolidation and fiber wetting, while avoiding excessive flow and subsequent polymer starvation. These control factors also slow the reaction rate, which prevents excessive heat generation from the exothermic vulcanization process. An autoclave-cured fabricated rubber inflatable acid storage tank is shown in Fig. 8.2.



Figure 8.1 A custom built large size autoclave for vulcanizing rubber lined tanks.

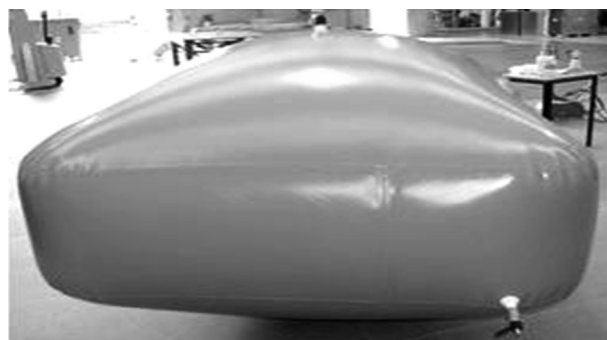


Figure 8.2 Fabric-constructed rubber inflatable storage tank.

For rubber-lined vessels, the working pressure in an autoclave is normally 4–5 kg/cm². The design and construction of the autoclave have to take into consideration these working pressure requirements. The autoclave selected for this purpose has to accommodate a fairly large proportion of chemical plant equipment, piping, etc. The size and layout of the autoclave in the factory are important considerations. The lined equipment is loaded onto a trolley and then pushed into the autoclave with the help of a winch motor. The boiler pressure is maintained at 100 psig and the steam pressure inside the autoclave is kept at 60 psig resulting in a constant temperature of 130–140°C, depending upon the type of compounds used for lining. The curing cycle time normally varies between 6 and 16 hours, depending largely on the compound used and the size of the vessel. After vulcanization, the autoclave is opened and the lined equipment and tanks are unloaded for finishing and inspection.

In the case of open steam curing and hot water curing, the rubber-lined vessel is to be insulated outside

to provide heat retention at the adhesive layer so that proper bonding of the rubber to metal is ensured. In the case of curing by using the vessel itself as an autoclave, the same is to be designed to withstand the temperature and pressure conditions of the curing process as well. This is to be ensured by the vessel/tank fabricator. It is good practice to insulate the outside of the vessel while the lining is cured with steam. The pressure in this case is usually 1 atm. Self-vulcanizing linings are not very popular except in the case of noncritical equipment. The cold bonding method involves the use of precured rubber and room temperature curable bonding adhesive. This method is mostly followed for large-sized tanks.

During vulcanization the following physical and chemical changes occur:

- The long chains of the rubber molecules become crosslinked by reaction with the vulcanizing agent to form a three-dimensional molecular structure. This reaction transforms the soft and weak plastic-like rubber material into a strong elastic resilient product.
- The rubber loses its original tackiness, becomes insoluble in solvents, and is more resistant to deterioration and degradation effects of heat, light, and aging.

The following vulcanization systems in the compounds are followed to effect the foregoing changes.

Sulfur and Sulfurless Vulcanization

The most common rubbers used in industry are the general-purpose synthetic types and natural rubber, which contain adequate unsaturation in the molecular structure. With these so-called diene rubbers, vulcanization with sulfur is possible. Sulfur is the most commonly used vulcanizing agent. With sulfur, crosslinks and cyclic structures of rubber molecules are formed. The total number of sulfur atoms combined in the crosslink and cyclic structure network is usually called the coefficient of vulcanization [1], and is defined as the parts of sulfur combined per 100 parts of rubber by weight. For most rubbers, one crosslink for about each 200 monomer units in the chain is sufficient to produce a vulcanized product. In an efficient accelerated curing system about one or two sulfur atoms

crosslink with little or no cyclic group being formed. In an inefficient sulfur curing system without the addition of an accelerator, the crosslinked sulfur is equal to 8 atoms. The amount of cyclic and crosslinked sulfur in the network governs the aging characteristics of the rubber products. Vulcanization can be effected without elemental sulfur by the use of thiuram disulfide compounds, which are accelerators of vulcanization, or with selenium or tellurium products, which are more resistant to heat aging. With the thiuram sulfides, efficient crosslinks containing one or two sulfur atoms are found and in addition to this, the thiuram accelerator fragments act as antioxidants. Therefore sulfurless or low-sulfur cures with such accelerators produce products with better aging characteristics.

Vulcanization With Peroxides

The saturated rubbers such as butyl or ethylene-propylene-diene-monomer cannot be crosslinked by sulfur and accelerators. Organic peroxides are necessary for the vulcanization of these rubbers. When the peroxides decompose, free radicals are formed on the polymer chains and these chains can then combine to form crosslinks of the type where only carbon-carbon bonds are formed, unlike in sulfur vulcanization. These carbon-carbon bonds are quite stable. Such bonds are also formed by vulcanization using gamma or X-ray radiation of compounded rubbers. Some rubbers can be vulcanized by the use of certain bifunctional compounds, which form bridge-type crosslinks, for example, neoprene with metal oxides or butyl rubber with dinitrosobenzene.

Vulcanization Conditions

It can be seen that every type of vulcanization system differs from every other type in kind and extent of the various changes that together produce the vulcanized state. In the vulcanization processes, consideration must be made for the difference in the thickness of the products involved, the vulcanization temperature, and thermal stability of the rubber compound. The word “cure” used to denote vulcanization is believed to have been coined by Charles Goodyear and this has been a recognized term in rubber industry circles [2]. The conditions of cure will vary over a wide range according to the type of vulcanizate required and the facilities available in a rubber factory. Many factors

must be predetermined including the desired hardness of the product, its overall dimensions, the production turnover required, and the pretreatment of the rubber stock prior to vulcanization. Hardness will normally be determined by the composition of the stock, but it can also be influenced by the state of cure.

Effect of Thickness

The thickness of the product is highly significant because of the necessity of providing heat in the interior of the rubber and preserving a uniform state of cure through the cross-section. Rubbers are poor conductors of heat and thus it is necessary to consider the heat conditions, heat capacity, geometry of the product in the case of moldings and autoclave-cured items, heat exchange system in the case of open steam or hot water-cured processes adopted for rubber-lined equipment, and the curing characteristics of a particular compound where articles thicker than about one-quarter of an inch are being vulcanized. It is a general shop floor practice to add an additional 5 min to the curing time for every one-quarter inch thickness in the molded articles. In the case of autoclave curing of lined tanks and vessels, a slow rise in temperature up to the curing temperature is the proper procedure when the thickness of lining is more than a quarter inch. For thicknesses larger than a quarter inch, say 2 or 3 inches as in the case of ebonite pipes and components, it is desirable to adopt a hot water curing technique. Two practical methods of dealing with thicker articles are (1) step-up cures where more than one temperature is employed and (2) slow external cooling in place of slow heating. Heat is discontinued before the cure is complete and the rubber is kept under pressure either in the mold or in the autoclave for atmospheric cooling. An increase in dimensions necessitates a reduction in curing temperature with increased time to obtain uniformity throughout the product. However, low-temperature cure in open steam may lead to plastic flow of the rubber, if onset of cure does not commence at that temperature. A suitable compounding technique is followed to offset this problem.

Effect of Temperature on Curing Time

The vulcanization temperature must be chosen to produce a well-cured product having uniform and optimum physical properties in the shortest possible

time. The term “temperature coefficient of vulcanization” can be used to identify the relationship between different cure times at different temperatures. With this information, optimum cure times at higher or lower temperature can be estimated for many rubber compounds with known coefficient of vulcanization. For most rubber compounds the coefficient of vulcanization is 2. This indicates that the cure time must be reduced by a factor of 2 for each 10°C increase in cure temperature or if the temperature is reduced to 10°C, the cure time must be doubled.

Effects of Thermal Stability

Each type of rubber has a definite range of temperature resistance, which has to be considered for vulcanization. These temperatures may vary somewhat but it is quite important not to exceed the maximum for each since some form of deterioration will occur. This effect is shown either by the appearance of the finished product or by its physical properties.

Techniques of Vulcanization

Many methods of vulcanization are available for manufacturing a rubber product. In the case of molded goods for process industries, the methods followed are similar to those for other products except that the former may have a different compound formulation. The methods used in most industries are based on universally followed standard techniques, which are briefly outlined next.

Compression Molding

This method or a modification of it as required by convenience utilizes the most common type of mold used in the rubber industry. This is the standard method followed throughout the world and a vast assortment of molded products known as general rubber-molded goods are cured in this method. Essentially, this method consists of placing or loading into a two-piece mold a precut blank or a composite material and then closing the mold. The pressure applied by the hydraulic press forces the material to fill up the cavity in the mold bringing the required shape into formation and the slight excess rubber in the blank flows out of the rims of the mold or through vents. This excess rubber is known as

flash. The common platen sizes range from 12"×12" to 32"×32" when the presses are operated by single hydraulic rams. When multirams are involved the platen size is unlimited and conveyor belts of more than 30 feet in length are produced in larger platens. Such belts are fastened at the ends and cured in the presses to make them endless. For higher productivity the presses will have multi-daylight platens. The usual hydraulic pressures applied during press cures range from 1500 to 2000 lb/inch. Steam is the most often used heating medium although electrical resistance heating also is used whenever high-temperature cures are required. For manufacturing rubber to metal-bonded components compression molds are preferred. Shrinkage of cured rubber is an important factor when designing molds. Shrinkage depends on the type of rubber compound, type of mold, and the temperature of the cure. An arbitrary figure of 1.5%–3% is chosen for general rubber-molded goods as shrinkage allowance.

Tires are normally cured in a modification of the compression mold where a bladder or an inflated airbag forces and holds the green rubber stock of the tire against the mold surface during vulcanization. This force reproduces the design of the tire tread and the heat from the steam is introduced into the bladder to effect the vulcanization. Small size rubber expansion joints used in piping systems are molded by compression molding, whereas larger sizes are hand built on molds and cured in an autoclave. Thick ebonite moldings are vulcanized by a step-up cure process.

Hand-formed moldings are also produced by molds made of cast iron or aluminum for products such as expansion joints for pipelines, flexible cell covers for caustic soda factories, and large-sized valve diaphragms. The products are hand formed by building up the stock of rubber manually along with fabric or steel reinforcement required in the case of some products and then cured in the autoclave.

Transfer Molding

Transfer molding involves the distribution of the uncured stock from one part of the mold, called the pot, into the actual mold cavity. This process permits the molding of intricate shapes or the introduction of inserts like metals in many composite products. These procedures are difficult in compression molds. Although molds are relatively more expensive than

compression molds the actual process permits shorter cure times through the use of higher temperatures and better heat transfer, which is obtained because of higher pressure applied to force the compound into the mold.

Injection Molding

This method is normally followed for plastic products. However, injection molding with modifications of equipment is adopted for the manufacture of small rubber components. By careful control of the feed-stock the rubber products can be vulcanized in less than several minutes. This method can be completely controlled by proper feed, injection, and demolding cycles resulting in low rejection rates and lower finishing costs.

Isostatic Molding

Isostatic molding is a unique process where molding pressures are applied evenly in all directions around the part being made. This differs from compression molding, which has pressure applied in only one direction. Isostatic molding lends itself nicely to making odd shapes such as cups and buckets. An isostatically molded part is made to near net shape. Because the part is molded to near net shape, significantly less material would be used as opposed to the more standard use of blocks and cylinders. After molding, the part would be suitable for final machining.

Tapered sleeves and closed end cylinders are common shapes that are often molded isostatically. Unlike extruded and compression-molded parts, materials isostatically molded will have highly consistent material properties. This method is followed for making polytetrafluoroethylene products.

Open Cures

Hot air ovens can be used to vulcanize thin articles and sheets that have been preshaped in the extrusion process or by calendering, or by a combination of precuring in a mold followed by postcuring. Postcuring is done to remove decomposition products from products cured with peroxides. This system is not very efficient because of the poor heat transfer of hot air. Longer cure times at lower temperatures

are necessary to prevent the formation of porosity or deformation of the unvulcanized or still-to-be-vulcanized rubber stock. Hot air cure is divided into open air cure at atmospheric temperature and cure at closed ovens. The usual conditions are an air cure rising from 80 to 120°C within 45–60 min. Hot air-cured vulcanizates give a glossy finish.

Open steam can be used in closed vessels such as autoclaves. The process involves using saturated steam under pressure. The saturated steam acts as an inert gas and better heat transfer is obtained, thus high temperatures can be employed and shorter cure times are possible making the process more desirable than hot air ovens. Dry steam under pressure is used in horizontal heaters. Hoses, cables, rubber-lined equipment, rubberized rolls, extruded profiles for various equipment as accessories, and calendered sheets are cured by this method. In the case of rubber sheeting for lining, a cloth liner is used as a backing while it is wound on drums. These liners are wet and exert pressure when dried up because of shrinkage. Sheets of 10–12 mm thickness are wound over hollow drums to a thickness as high as 40–50 mm and tightly wrapped with wet cotton cloth liner. This method has not been replaced by any other newer methods to any extent. The use of open steam for vulcanizing rubberized fabrics is the most efficient method. During cure the inflated fabrics are kept in their normal inflated shape. The inflated pressure is maintained to balance the internal and external pressure of the steam. Near the completion of the cure, air is allowed into the steam to give a steady and slow drop in pressure.

Hot water cures can be used for articles that are not affected by immersion in hot water. This method is useful for thick-walled articles and rubber-lined equipment and is especially most suitable for ebonite compositions. Direct contact with water produces better heat transfer than with hot air or steam. Consequently, this system gives less deformation of products during cure.

Continuous Vulcanization System

This system involves the use of some form of heating by air or steam in a chamber in a manner such that the vulcanization occurs immediately after the rubber is formed in an extruder or calender. This is a suitable process for extruded profiles and calendered sheets and conveyor belts. The liquid curing method is also

a continuous process that involves the use of suitable hot liquid baths through which extruded profiles can be passed and vulcanized continuously. Items can be cured rapidly at temperatures from 200 to 300°C; however, the compounds must be suitably designed to prevent porosity because this is a common problem with any extrudate. Suitable materials for curing medium include bismuth-tin alloys, a eutectic mixture of potassium nitrate and sodium nitrate (a eutectic is a mixture of two or more constituents that solidify simultaneously out of the liquid at a minimum freezing point), polyglycols, and certain silicone fluids. Fluidized beds consisting of small particles (glass beads) suspended in a stream of heated air is an efficient vulcanization system. This is normally used for continuous vulcanization of extrusions. The heat transfer is approximately 50 times greater than with hot air alone.

Cold Vulcanization

Thin articles may be vulcanized by treatment with sulfur monochloride by dipping in a solution or exposing them to its vapors. This process has been replaced by using ultra accelerators, which are capable of curing at room temperature.

Cure With High-Energy Radiation

Systems using either gamma radiation from cobalt 60 or electron beams have been used for vulcanization. The electron beam method has been used for curing silicone rubbers.

Optimum Cure

Determination of optimum cure and rate of cure are essential prerequisites in the selection of stocks for a particular finished product. These are generally obtained by first curing the samples at say 140°C and determining the modulus, tensile strength, and hardness at various cure times. The optimum cure is normally fixed by plotting modulus, tensile strength, and hardness against various cure times. Optimum cure may also be fixed on the basis of other properties such as tear strength, abrasion resistance, or resistance to flex cracking. In the United States the optimum cure is mainly based on optimum modulus. In the United Kingdom optimum tensile strength is

the one followed for determining optimum cure. A cure rate chart of practical vulcanization is shown in Fig. 8.3 comprising three curves based on three physical determinations, namely, ultimate tensile strength, 300% modulus, and hardness together with one based on chemical determination, namely, free sulfur in the vulcanizate. The point of optimum cure is taken from the three physical properties in the graph.

Tensile Strength

The point on the curve that has a tangent based on a slope of 10lb increase in tensile strength per minute of cure denotes an optimum cure time of 46 min.

Modulus

The point on the curve that has a tangent based on a slope of 20lb increase in modulus per minute of cure denotes an optimum cure of 43 min.

Hardness

The point on the curve that has a tangent based on a slope of 0.2 degree (1/5 degree) increase in hardness per minute of cure denotes 48 min. Hardness is less specific than other constants and because of this is less frequently used.

The optimum cure of such a stock is quoted as 45 mts at 138°C.

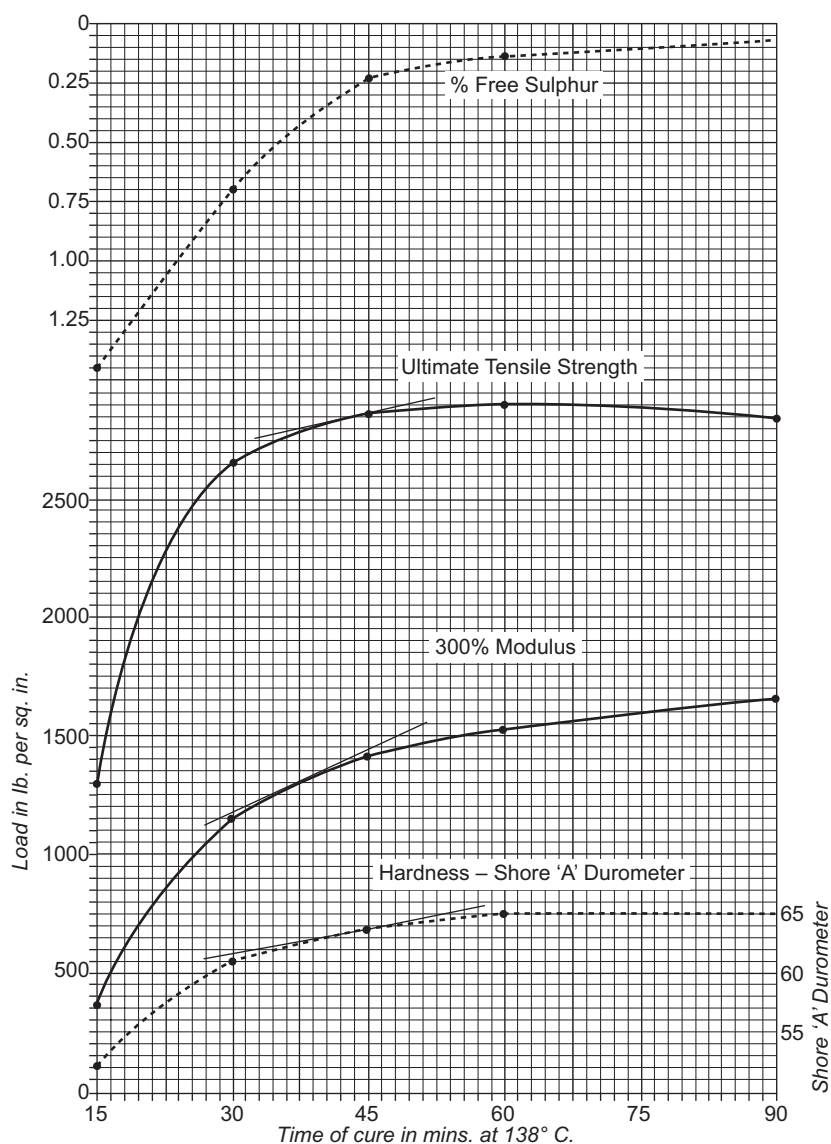


Figure 8.3 Practical vulcanization chart for optimum cure.

The aforementioned details on optimum cure are related only to natural rubber and do not apply to styrene-butadiene rubber (SBR) in which case hardness and modulus continue to increase beyond the optimum cure point. However, this gives an indication of the cure state of the SBR compounds. Tear resistance, cut growth, and permanent set, however, have been used to determine the optimum cure of SBR.

Control of Production Cures

- Specific gravity, which can be easily determined, is not strictly a check on cure state but on materials that may affect cure.
- The simplest check on cure is by a hardness determination, which is to be done after the vulcanizate is sufficiently cooled to room temperature; the test is best done after 24 hours of cure.
- Reducing scraps can be caused by undercure or air trapping.
- Fixing of thermocouple can be done at various locations in the vulcanization equipment as well as monitoring the temperature of cure accurately.
- Adhesion tests of rubber to metal or rubber to fabric are to be done in counter samples kept along with the products in the curing equipment.
- Chemical analysis of free sulfur provides one of the most generally accepted methods of determining the state of cure, which is also appropriate for the compound batch.
- A swelling test indicates the degree of vulcanization.
- Samples can be cut and prepared from the product itself and tests should be conducted on them for tensile strength, modulus, and hardness.

Curing Time

The total time of vulcanization is split into two steps:

1. The time taken to heat the rubber to curing temperature, and
2. The time taken to cure the rubber after the curing temperature has been attained.

The latter is predetermined and fixed for a given temperature, and the former is the time for warming up the stock and can be referred as the warming or preheating time. A shorter curing time does not necessarily mean the use of steam since the unit weight of rubber requires a definite quantity of heat. In open cures involving air, the cure time can be reduced considerably by circulating the heating medium as the cold rubber cools the air in direct contact with it and then acts as an insulator. Where saturated steam under pressure is used for curing lined vessels and tanks, the cold rubber surface causes steam to condense, at the same time giving up its large content of latent heat. The condensation causes a reduction of pressure to attract more steam at that point of contact.

No one curing process possesses all the virtues and those that may appear to be most desirable may be rejected on the grounds of initial cost and maintenance of the equipment. For example, even an autoclave-curable rubber-lined vessel can be cured in open steam at atmospheric pressure and this method can be adopted while the autoclave is down for repairs or maintenance.

Common Defects in Vulcanizates

Most of the defects in the finished products are attributed to improper mixing of the compound. Assuming that proper mixing has been done, the following product defects can be caused by deviations in the conditions prescribed for vulcanization, such as pressure and temperature as well as the process of vulcanization itself. Some of the most commonly occurring defects, their probable causes, and remedial measures are given next.

Air Blisters

Air blisters generally occur because of trapped air during the processing of the rubber in the calender or extruder or during hand building up of the products. The remedial measures to be undertaken are:

1. Modify process temperature or pressure,
2. Feed the calender or extruder with adequate rubber stock,
3. Prick out visible blisters when the compound is in an unvulcanized state, and

4. Use bleeder cords between metal and the rubber sheets applied at the welded places in the rubber lining process.

Tearing

This is caused by overvulcanization. The remedy is to reduce cure times and temperatures or modify the compound formulation to reduce the speed of cure. Tearing can also be caused by method of removal of the product from the mold while it is in hot condition. Tearing can be eliminated by removing the products from the mold after sufficient cooling or by careful and slow removal.

Porosity

Volatile substances in the rubber or compounding ingredients or moisture can cause porosity. Insufficient stock of rubber in the mold and undercure also cause porosity. To prevent this defect from occurring, avoid use of raw materials containing volatile materials, test all raw materials for moisture content, allow the solvents or adhesives to dry up completely, check the volume and shape of the finished product, and increase curing pressure if feasible.

Debonding From Metal

It is often difficult to obtain satisfactory adhesion of rubbers of different compositions and types with metal. The amounts of sulfur and accelerators

of various types influence adhesion. These must be chosen so that there is no under- or overvulcanization. To attain proper rubber-to-fabric adhesion the fabric must be adequately dry and evenly coated with the adhesive. Defective adhesion occurs because of contamination by surface blooming of ingredients. Sulfur blooms can be eliminated by the use of insoluble sulfur. Waxy softeners that bloom at the surface should be avoided in compounding formulations.

Surface Scorching

Sometimes the surface of a rubber sheet might have been scorched or prevulcanized because of high processing temperatures and storage under improper storage conditions. To avoid this, modify the compound suitably. The preferred temperature of storing the in-process stock of rubber is 20–24°C.

References

- [1] H.L. Stephens, Associate Professor of Polymer Science University of Akron, Ohio, US, The compounding and vulcanization of rubber, in: M. Morton (Ed.), Rubber Technology, Van Nostrand Reinhold Company, NY, USA, 1973.
- [2] L.A. Mernagh, Practical vulcanization, in: W.J.S. Naunton (Ed.), The Applied Science of Rubber, Edward Arnold, London, UK, 1961, p. 1053.