2-Compounding:
None of the elastomers discussed in the previous section have useful properties until they have been properly formulated. Although some of the science of compounding is understood, much art still remains in preparing technical rubber compositions. In this section, the science and technology of the various ingredients used in rubber are discussed.

2.1 Vulcanization and Curing:
An elastomer, as synthesized, is basically a high molecular weight liquid with low elasticity and strength. Although the molecules are entangled, they can readily disentangle upon stressing, leading to viscous flow. Vulcanization or curing is the process in which the chains are chemically linked together to form a network, thereby transforming the material from a viscous liquid to a tough elastic solid. Strength and modulus increase, while set and hysteresis decrease. Various curing systems are used to vulcanize different types of elastomers, but complete coverage is beyond the scope of this chapter. Rather, discussion here is primarily on the curing of general purpose diene elastomers with sulfur, with only brief mention of other cure systems.

2.1.1 Sulfur Curing:
The most widely used vulcanizing agent is sulfur. For sulfur to effectively crosslink a rubber, an elastomer must contain double bonds with allylic hydrogens. General purpose diene elastomers such as BR, SBR, NR, and IR meet this basic requirement.

Two forms of sulfur are used in vulcanization: soluble (rhombic crystals of S8 rings) and insoluble (amorphous, polymeric sulfur). Sometimes, in compounds containing high levels of sulfur, insoluble sulfur is used to prevent sulfur blooming, a process by which the sulfur migrates to the surface of a compound and crystallizes there. Blooming can occur when large amounts of soluble sulfur are used, because at high mixing temperatures, the solubility of S8 is high, enabling large amounts to dissolve, but upon cooling the solubility decreases. When the solubility limit is reached, excess sulfur blooms to the surface. Sulfur bloom reduces the "tack" of a rubber compound, a necessary property if layers of rubber are to be plied up to make a composite structure, such as a tire. Insoluble sulfur does not bloom because it disperses in rubber as discrete particles, which cannot readily diffuse through the rubber. However, above 120 °C, insoluble sulfur transforms into soluble sulfur. Thus, mixing temperatures must be kept below 120 °C to take advantage of the bloom resistance of insoluble sulfur.

Crosslinking with sulfur alone is quite inefficient and requires curing times of several hours. For every crosslink, 40 to 55 sulfur atoms are
combined with the rubber. The structure contains polysulfide linkages, dangling sulfur fragments, and cyclic sulfides. Much of the sulfur is not involved in crosslinks between chains. Moreover, such networks are unstable and have poor aging resistance.

To increase the rate and efficiency of sulfur crosslinking, accelerators are normally added. These are organic bases and can be divided into five major categories: guanidines, thiazoles, dithiocarbamates, xanthates, and thiurams. Of these, the guanidine-type accelerators, such as diphenyl guanidine (DPG), give the lowest rate of vulcanization as well as a relatively slow onset of vulcanization. Delayed onset of vulcanization is a desirable feature of rubber compounds. It allows shaping processes to be carried out before vulcanization starts and the material becomes set in its final shape. Premature vulcanization is known as "scorch."

Guanidines are seldom used alone, but rather are combined with another type of accelerator. The accelerators that increase the rate of curing the most are the xanthate types. These ultra-accelerators cause crosslinking so readily that they are seldom used in solid rubber because curing would be initiated just from the heat generated while mixing. Rather, xanthates are used mainly for crosslinking rubber as a latex.

The accelerators with the widest application are the thiazoles, a subcategory of which is the delayed-action sulfenamides. Compounds containing sulfenamides may be sheared for long times without premature vulcanization (scorch). This is particularly important in the tire industry, where a compound may be mixed, repeatedly milled, and then calendered or extruded before being fabricated into a tire.

Thiurams and dithiocarbamates are considered ultra-accelerators, although they are not as active as the xanthates. Because these accelerators have a short scorch time, care must be taken to keep processing temperatures low. Some compounds with ultra-accelerators may begin curing within one day at room temperature, so they must be processed soon after mixing. Crosslinking is efficient when ultra-accelerators are used, and especially when the ratio of accelerator to sulfur is high, so that only low levels of sulfur are required for proper vulcanization.

Often, a combination of accelerators is used to obtain the desired scorch resistance and cure rate. Generally, if two accelerators of the same type are combined, then cure characteristics are approximately the average of those for each accelerator alone. However, there is no general rule when combining accelerators of different types. Moreover, the type of accelerator is much more important than the level of accelerator in controlling scorch time. Although increased levels of
accelerator increase the degree of crosslinking attained, generally accelerator concentration has only a small effect on scorch time. Accelerated sulfur curing is more efficient when the activators zinc oxide and stearic acid are added. It is thought that these additives combine to create soluble zinc ions that activate intermediate reactions involved in crosslink formation.

One instrument used to determine the kinetics of crosslinking is the oscillating disc rheometer (ODR). An oscillating rotor is surrounded by a test compound, which is enclosed in a heated chamber. The torque required to oscillate the rotor is monitored as a function of time. Another instrument to follow curing is the rotor-less moving-die rheometer (MDR), which uses thinner samples, and hence, has faster thermal response than the ODR. Examples of cure meter responses are shown in Fig. 2.1.

Initially, there is a sudden increase in torque as the chamber is closed. Then, as the rubber is heated, its viscosity decreases, causing a decrease in torque. Eventually, the rubber compound begins to vulcanize and transform into an elastic solid, and the torque rises. Molecular chain scission also may be occurring; however, an increasing torque indicates that crosslinking is dominant. If the torque reaches a plateau, this indicates completion of curing and the formation of a stable network. If chain scission and/or crosslink breakage become dominant during prolonged heating, the torque passes through a maximum and then decreases, a phenomenon termed reversion. Some NR compounds, particularly at high curing temperatures, exhibit reversion. On the other hand, some compounds show a slowly increasing torque at long cure times, or "creeping cure." This behavior often occurs in compounds that initially form many polysulfidic linkages. With extended cure times, these linkages may break down and reform into new crosslinks of lower sulfur rank, thereby increasing the total number of crosslinks.
2.1.2 Determination of Crosslink Density:

The crosslink density of an elastomer can be determined from swelling or mechanical measurements. An elastomer crosslinked above its gel point absorbs solvent and swells, sometimes highly, but does not dissolve. Swelling continues until the retractive forces in the extended molecular strands in the network balance the forces tending to swell the network. For unfilled elastomers, the Flory-Rehner equation is widely used to relate the amount of swelling to the crosslink density:

\[
N' = \frac{1}{2V_s} \frac{\ln(1 - v_r) + v_r + x v_r^2}{v_r^{1/3} - v_r/2}
\]  

(2.1)

where \( N' \) is the number of moles of crosslinks per unit volume, \( V_s \) is the molar volume of the swelling solvent, \( v_r \) is the volume fraction of rubber in the swollen gel, and \( x \) is the polymer-solvent interaction parameter.

For vulcanizates containing reinforcing fillers such as carbon black, \( v_r \) for use in the Flory-Rehner equation may be obtained from the following expression derived by Kraus:

\[
\frac{v_r}{v_{rf}} = 1 - \left\{ 3r \left[ 1 - v_r^{1/3} \right] + v_r - 1 \right\} \frac{\phi}{1 - \phi}
\]  

(2.2)

where \( v_{rf} \) is the volume fraction of filled rubber in the swollen gel, \( \phi \) is the volume fraction of filler in the unswollen filled rubber, and \( r \) is the filler-rubber interaction parameter.

Crosslink densities of unfilled rubbers have also been determined from equilibrium stress-strain measurements using the Mooney-Rivlin equation:

\[
\frac{\sigma}{2(\lambda - \lambda^{-2})} = C_1 + \frac{C_2}{\lambda}
\]  

(2.3)

where \( \sigma \) is the engineering stress, \( X \) is the extension ratio, and \( C_1, C_2 \) are elastic constants. On plotting \( \sigma/2(\lambda - \lambda^{-2}) \), vs. \( 1/\lambda \) and extrapolating to \( 1/\lambda = C_1 \) a value of \( C_1 \) can be obtained from the intercept. From the theory of rubber elasticity, \( C_f = N'RT \), where \( N' \) is the crosslink density, \( R \) is the gas constant, and \( T \) is the absolute temperature. To assure near equilibrium response, stress-strain measurements should be carried out at a low strain rate.

2.1.3 Influence of Crosslink Density:

Mechanical properties of an elastomer depend strongly on crosslink density. Modulus and hardness increase monotonically with increasing crosslink density, and the material becomes more elastic, or stated
alternatively, less hysteretic. Fracture properties, such as tear and tensile strength, pass through a maximum as crosslinking is increased. To understand this behavior, it is helpful first to consider fracture in an uncrosslinked elastomer, and then to discuss changes in the mechanism of fracture as crosslinks are introduced.

When an uncrosslinked elastomer is stressed, chains may readily slide past one another and disentangle. At slow rates, fracture occurs at low stresses by viscous flow without breaking chemical bonds. The effect of a few crosslinks is to increase the molecular weight, creating branched molecules and a broader molecular weight distribution. It is more difficult for these branched molecules to disentangle and hence, strength increases. As crosslinking is increased further, the gel point is eventually reached when a three-dimensional network forms. Some chains may not be attached to the network (soluble sol phase), but the whole composition no longer dissolves in a solvent. A gel cannot be fractured without breaking chemical bonds. Thus, strength is higher at the gel point, because chemical bonds must be ruptured to create fracture surface. However, strength does not increase indefinitely with more crosslinking.

When an elastomer is deformed by an external force, part of the input energy is stored elastically in the chains and is available (released upon crack growth) as a driving force for fracture. The remainder of the energy is dissipated through molecular motions into heat, and in this manner, is made unavailable to break chains. At high crosslink levels, chain motions become restricted, and the "tight" network is incapable of dissipating much energy. This results in relatively easy, brittle fracture at low elongation. Elastomers have an optimum crosslink density range for practical use. Crosslink levels must be high enough to prevent failure by viscous flow, but low enough to avoid brittle failure.

Both the level and type of crosslinking are important. When curing with sulfur, the type of crosslinks depends on (1) sulfur level (2) accelerator type (3) accelerator/sulfur ratio and (4) cure time. Generally, high accelerator/sulfur ratio and longer cure time increase the number of monosulfidic linkages at the expense of polysulfidic ones. Vulcanizates containing predominately monosulfidic crosslinks have better heat stability, set resistance, and reversion resistance than those with polysulfidic links. This is attributed to greater stability of C-S bonds compared to S-S bonds. On the other hand, compounds containing a high proportion of polysulfidic crosslinks possess greater tensile strength and fatigue cracking resistance compared to compositions with monosulfidic links. This is thought to be due to the ability of S-S bonds in polysulfidic linkages to break reversibly, thereby relieving locally high stresses that could initiate failure.
2. 1.4 Other Cure Systems:

Peroxides are another type of curing agent for elastomers. Unlike sulfur vulcanization, carbon-carbon double bonds are not required for peroxide curing and thus, peroxides may be used to crosslink saturated elastomers, e.g., ethylene-propylene copolymers, chlorinated polyethylene, chlorosulfonated polyethylene, and silicone rubber. In addition, peroxides readily crosslink diene elastomers. Peroxide curing takes place via a free-radical mechanism and leads to carbon-carbon crosslinks, which are quite stable. The crosslinked materials show good aging resistance and low compression set.

Some elastomers, particularly polychloroprene, can be crosslinked with the metal oxides ZnO and MgO. It has been proposed that the crosslinking occurs via allylic chlorines on the polymer molecules. Generally, mixtures of ZnO and MgO are used because ZnO by itself is too scorchy and MgO alone is inefficient.

Butyl rubber cannot be cured with peroxides and sulfur vulcanization is often inefficient. Instead, polymethylol phenolic resins with metallic chlorides are often used. They give crosslinked materials with excellent resistance to high temperatures.

2. 2 Reinforcement:

Particulate fillers can increase the strength of an amorphous rubber more than 10-fold. For a filler to cause significant reinforcement, it must possess high specific surface area, i.e., the particles must be small, less than 1 gm in size. Small particles have large surface area to interact with the rubber and close particle-to-particle spacing in the compound. Two types of fillers that are most effective for reinforcing rubber are carbon black and silica. They can be produced with a primary particle size as small as 100 Å, corresponding to a surface area of a few hundred m² per gram of filler.

Two other important characteristics of fillers are structure and surface chemistry. Structure relates to irregularity in shape of filler aggregates (Fig. 2.2), determined by the extent and manner of clustering of primary particles. A filler aggregate with high structure has a large void volume within the space it pervades, in which rubber molecules may become "occluded." The combination of occluded rubber and filler then becomes the reinforcing entity, so that the effective volume fraction of filler is increased (Aggregates are not broken down into primary particles upon mixing with rubber.). Generally, reinforcement is enhanced by high structure and strong bonding between filler and rubber. Silica fillers are often treated with silane coupling agents to bond them chemically to rubber, or the coupling agents may be added directly to the rubber compound.
During shear mixing, rubber and carbon black become chemically linked. This has been demonstrated by attempting to dissolve filled, uncrosslinked compounds in good solvents. Only a portion of the rubber dissolves, leaving a "carbon gel" containing all of the carbon black and the remainder of the rubber which is strongly bound to the filler, termed "bound rubber." The interactions between rubber and carbon black include a spectrum of strengths, with some chains chemically attached to the black and others with physical bonds of varying magnitude. The importance of bonding between rubber and carbon black is illustrated by exposing carbon black to extreme heating (graphitization) in an inert atmosphere before mixing it into rubber. Graphitization removes active functional sites on the black, decreases the amount of bound rubber, and reduces the reinforcing effect, as shown in Fig. 2.3. Compared to the vulcanizate reinforced with normal furnace black, the vulcanizate containing graphitized black has lower modulus, higher ultimate elongation, and reduced strength. However, the rubber filled with graphitized black is much stronger than a simple unfilled (gum) vulcanizate or one filled with an equal volume fraction of larger-sized particles (e.g., clay).

Before addition to rubber, carbon black aggregates are "clumped" together as so-called agglomerates. To provide the greatest reinforcement, these black agglomerates must be broken down into aggregates and thoroughly dispersed in the rubber. This requires mixing at high shear stress. The viscosity of the rubber must not be too low, or the shear stresses will be insufficient to break apart the filler agglomerates. Thus, when oil is to be added to a stock, it should be added toward the end of the mixing cycle, after the carbon black has been well dispersed.

Besides enhancing strength, carbon black also improves processability by greatly reducing melt elasticity. This allows shaping operations, such as extrusion and calendering, to occur with less shrinkage and melt distortion.

Carbon black is most effective for strengthening non-crystallizing elastomers such as SBR. Strain-crystallizing elastomers such as NR already have a self-reinforcing mechanism. Indeed, unfilled and black-filled NR vulcanizates have comparable tensile strengths, although the latter have improved resistance to tearing and abrasion.
2.3 Anti-Degradants:

Oxygen and ozone can react with elastomers and alter network structure by causing chain scission and/or crosslinking. Antioxidants and antiozonants, which can function chemically or physically, have been developed to inhibit the action of these reactive components of air.

Chemical protectants are capable of reacting with the degradant or interfering with the chain of reactions that otherwise would culminate in degradation of the rubber. The most common types are aromatic amines, phenolics, and phosphites. The first type is staining, while the other two are not. Physical protectants function by migrating, i.e., blooming, to the rubber surface and providing a barrier to attack by degradants. Microcrystalline waxes, which are mixtures of alkanes, isoalkanes, and cyclo-aliphatic hydrocarbons, are commonly used. The rate and extent of blooming are important and depend on the level of compatibility with the elastomer.

2.3.1 Ozone Attack:

Ozone, even when present in the atmosphere at only a few parts per hundred million, readily cleaves carbon-carbon double bonds in elastomers. As a result, an unsaturated rubber, exposed to ozone in the strained state, quickly develops surface cracks. The severity of cracking increases rapidly if the applied strain is above a small threshold level, of the order of 10%. Para-phenylenediamines (PPDs) are effective in reducing ozone cracking in diene rubbers and there is good evidence that they react directly with ozone, competing with the ozone-rubber reaction. However, there are no additives that enable unsaturated elastomers to resist ozone as well as saturated ones.
2. 3.2 Oxidation:

In general, the reaction of oxygen with elastomers causes both chain scission and crosslinking. If chain scission dominates during aging, the elastomer softens and eventually may become sticky. This is the usual behavior of unfilled NR and IIR vulcanizates. However, most technical elastomer compounds eventually harden and embrittle during oxidation, a consequence of the dominant crosslinking reactions. For some compounds, in the early stages of oxidation, there is a fortuitous equality in the extent of chain scission and crosslinking, such that modulus does not change. Nonetheless, the altered network now contains increased chain-end defects, and strength and elongation are reduced.

A concentration of only 1 to 2% of reacted oxygen is normally sufficient to cause severe deterioration in an elastomer. The principal mechanism of oxygen attack involves an autocatalytic, free radical reaction. The first step is the creation of macroradicals as a result of hydrogen abstraction from rubber chains by a proton acceptor. Oxidation continues by reaction of macroradicals with oxygen and the subsequent formation of peroxy radicals and hydroperoxides, which are readily detected by infrared spectroscopy. Oxidation is accelerated by heat, exposure to ultraviolet light, and the presence of some metals, notably copper, cobalt, and manganese. Also, stress hastens oxidation. For sulfur-cured vulcanizates, the oxidation rate increases as sulfur content increases. It is believed that the allylic crosslink site is particularly susceptible to oxidation.

Antioxidants are employed to slow oxidation. They fall into two classes, with different functions. The first type, called preventive antioxidants, react with hydroperoxides to form harmless, non-radical products. In the process, the antioxidant is oxidized. The second type, chain-breaking antioxidants, destroy peroxy-radicals that would otherwise propagate. Chain-breaking antioxidants are aromatic and contain labile protons, which are "donated" to the peroxy-radicals. This occurs readily because the resulting antioxidant radical is highly resonance-stabilized. A listing of some common amine antioxidants, which are quite effective in diene elastomers, is given in Table 2.1.

Usually, accelerated aging tests are used to determine the resistance of a vulcanizate to oxidation. However, caution should be used in attempting to infer long-term aging performance from short-term tests carried out at temperatures much higher than the service temperature. The reason is well illustrated in Fig. 2.4. A black-filled NR vulcanizate was oxidized at various temperatures, while the degree of oxidation was determined directly by the quantity of oxygen absorbed. Stress-strain measurements were carried out on the aged samples. Stiffness at room
temperature is plotted schematically against oxygen uptake at various temperatures. It is noteworthy that, when aged at 50 °C, the vulcanizate stiffened, while when it was aged at 110 °C, it softened. Clearly, in this case, relative rates of chain scission and crosslinking depend on aging temperature.

A convenient way to determine separately the extent of chain scission and crosslinking during aging is to carry out two types of stress relaxation test: continuous stress relaxation (CSR), and intermittent stress measurement (ISM). The procedures are as follows:

In CSR, a sample of the rubber to be aged is stretched to a given low extension ratio, \( k \). The stress is allowed to decay to an equilibrium value, \( \sigma(0) \). Then, while the extension is maintained, the sample is placed in an aging chamber and stress, \( \sigma_c(t) \), is monitored continuously as a function of aging time, \( t \). Newly formed network chains resulting from additional crosslinking are non-load bearing because they are introduced in the strained state. Only scission of the original network chains causes \( \sigma_c(t) \) to be reduced. In ISM testing, on the other hand, a sample is aged in the unstretched state; then periodically, the equilibrium stress, \( \sigma_f(t) \), required to impose the extension ratio, \( \lambda \), is determined. In this case, the measured stress depends on the net difference between crosslinking and chain scission.

<table>
<thead>
<tr>
<th>Table 2.1 Some Amine Antioxidants and Their Common Abbreviations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl-( \alpha )-naphthylamine (PAN)</td>
</tr>
<tr>
<td>N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD)</td>
</tr>
<tr>
<td>N-(1,3 dimethyl butyl)-N'-phenyl-p-phenylenediamine (6PPD)</td>
</tr>
<tr>
<td>N,N'-diphenyl-p-phenylenediamine (DPPD)</td>
</tr>
<tr>
<td>Poly-1,2-dihydro-2,2,4-trimethylquinoline (TMQ)</td>
</tr>
</tbody>
</table>

Figure 2.4 Stiffness of an NR vulcanizate determined at room temperature after oxidative aging at the temperatures indicated.
Now, based on rubber elasticity theory, it is assumed that the stress $\sigma(t)$ is directly proportional to network chain density, $N(t)$, thus

$$\frac{\sigma(t)}{\sigma(0)} = \frac{N(t)}{N(0)} \quad (2.4)$$

where $N(0)$ is the network chain density at the start of aging. Furthermore,

$$N_s(t) = N(0) - N_s(t) \quad (2.5)$$

and

$$N_c(t) = N(0) + N_s(t) - N_s(t) \quad (2.6)$$

where $N_c(t)$, $N_s(t)$ and $N_x(t)$ are, respectively, the number of molecular chains remaining after aging time $t$, the number of chain scissions that occurred and the number of new crosslinks introduced per unit volume. $N_c(t)$ is determined from Eq. (2.4) and the results of CSR, and $N_i(t)$ likewise from ISM. Thus, the number of chain scissions $N_s(t)$ is obtained directly from CSM, and the number of new crosslinks, $N_x(t)$, is obtained from $N_s(t)$ when combined with the results of ISM.

### 2.4 Process Aids:

Process aids are additives that lower viscosity and thus enable a rubber compound to be fabricated with less energy. They also increase melt stability so that the rate of processing can be increased. There are two general kinds of process aids: chemical peptizers and physical plasticizers. Chemical peptizers, typically added at 1 to 3 parts by weight per hundred parts of elastomer (phr), reduce molecular weight by increasing oxidative chain scission. Examples include sulfonic acids and pentachlorothiophenol, which are commonly used in NR. Excess peptizer must be avoided, because it results in reduced vulcanizate strength.

Physical plasticizers soften a compound by reducing entanglements and decreasing internal friction. An additional benefit of physical plasticization may be improvement in low temperature flexibility. Plasticizers should have good compatibility, which can become a problem at low temperatures, because a poorly compatible plasticizer may "bleed" from the compound. Common plasticizers include oils, fatty acids, esters, liquid polymers, and rosin.
2. 5 Extenders:

Extenders are added to rubber compositions to reduce cost. Usually, this results in a decrease in physical properties, which limits the amount of extender that can be used. Oil extension of rubber, especially in tire treads, is widely practiced. Oil levels of 30 to 40 phr are typical. Oil addition permits the use of elastomers with higher molecular weights and the addition of greater amounts of filler than would be possible otherwise. These two factors compensate for the dilution of network chains, so that good physical properties are obtainable even at rather high oil levels.

Other types of extenders are particulate solids with primary particle sizes greater than about 1 µm. These stiffen rubber compositions, but either have little effect on strength or diminish it. Examples include clay, calcium carbonate, and ground coal.

Resins are hard brittle solids which can dissolve in rubber at processing temperatures, but may separate out as another phase in the vulcanized material and stiffen it. Some are two-component systems, which react chemically at vulcanization temperatures. A phenolic resin that reacts with a formaldehyde donor is an example.

2. 6 Tackifiers:

Tack is the ability of two materials to resist separation after being in contact for a short time under light pressure. Tackifiers are a class of resins added to elastomers to improve tack. Several types are available:

1. Rosin derivatives that are chemical mixtures of abietic and related acids.
2. Aliphatic petroleum resins.
3. Alkyl modified phenol-formaldehyde resins.

Tackifiers generally have molecular weights in the 500 to 2000 range. Softening points vary from 50 to 150 °C and tackifiers often have limited compatibility with the elastomer to which they are added; they are less compatible than a plasticizer, but more compatible than a filler. The function of tackifiers, typically added in the range 1 to 10 phr, is two-fold: to increase initial tack and to prevent tack degradation that can occur after a stock has been processed.

A tackifier must be compatible with the rubber. This is dependent on chemical composition and molecular weight. For modified phenolics, the para-alkyl group must be large, t-butyl or greater, to improve compatibility with a non-polar hydrocarbon elastomer. When the alkyl group is t-octyl, the most effective tackifying action occurs at a molecular weight of about 2000.
3- Typical Rubber Compositions
This chapter concludes with a few typical rubber formulations and some physical properties of the vulcanizates obtained from them.

Table 2.2 An Unfilled Natural Rubber Formulation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount (phr*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>100</td>
</tr>
<tr>
<td>Process oil</td>
<td>2</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
</tr>
<tr>
<td>Antioxidant: 6PPD</td>
<td>1</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.75</td>
</tr>
<tr>
<td>Cure accelerator: benzothiazyl disulfide</td>
<td>1</td>
</tr>
<tr>
<td>Cure accelerator: tetramethyl thiuram disulfide</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*Parts by weight per 100 parts by weight of rubber

Cure: 10 minutes at 150°C
Shore A Hardness 39
Tensile Strength (MPa) 24
Breaking Elongation (%) 750

Table 2.3 Carbon Black-Filled Natural Rubber Formulations for General-Purpose Engineering Use

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount (phr*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>100</td>
</tr>
<tr>
<td>Process oil</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
</tr>
<tr>
<td>N-550 carbon black</td>
<td>25, 50, 75</td>
</tr>
<tr>
<td>Phenylamine antioxidant</td>
<td>1.5</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.5</td>
</tr>
<tr>
<td>Cure accelerator: benzothiazyl disulfide</td>
<td>1.0</td>
</tr>
<tr>
<td>Cure accelerator: tetramethyl thiuram disulfide</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*Parts by weight per 100 parts by weight of rubber

Cure: 20 minutes at 150°C

<table>
<thead>
<tr>
<th>N550 carbon black (phr)</th>
<th>25</th>
<th>50</th>
<th>75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore A Hardness</td>
<td>51</td>
<td>62</td>
<td>72</td>
</tr>
<tr>
<td>300% Modulus (MPa)</td>
<td>7</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>22</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>Breaking Elongation (%)</td>
<td>700</td>
<td>600</td>
<td>550</td>
</tr>
</tbody>
</table>