

## **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 S<sub>8</sub> 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 S<sub>8</sub> 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."