

# Vulcanization of Rubber

## How to Alter Molecular Structure and Influence Physical Properties

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The chemical modifications that occur during vulcanization of rubber and methods for controlling the process are discussed.

### Discovery

'Volcanising done here' or some variant of this is a common sign displayed on roadside sheds. We all know that some treatment is done to rubber to improve its properties. But what exactly is the chemical process that is carried out? How does it alter the structure of rubber at the molecular level? How can these changes be made in a controlled manner? Let us put on the glasses of a chemist and find the answers.

Natural rubber is obtained from latex, an emulsion which oozes out from the inner bark of many trees.<sup>1</sup> Coagulated rubber on separation and drying gives crude rubber. This is a polymer of isoprene (2-methyl-1,3-butadiene), with molecular weights in the range of 300,000. Synthetic rubber produced by polymerization of 1,3-butadiene, chloroprene, isobutene, etc., are also known today.

Rubber, at this stage, is soft, sticky and thermoplastic. It has low tensile strength and low elasticity. It is easy to understand the molecular structural origin for these properties. The substance is a mixture of polymeric chains with varying lengths. Most importantly, there is no crosslinking at all. As a result, the material, although known for several centuries, did not find any significant application.

The properties of rubber can be dramatically altered by cross linking the polymer chains. This process, carried out with sul-

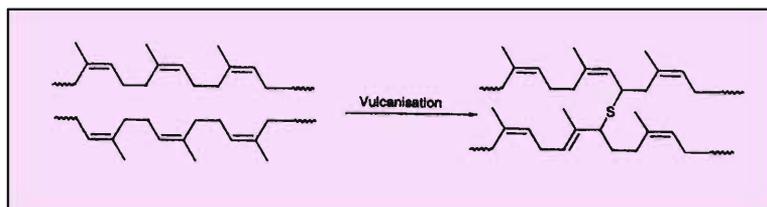
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<sup>1</sup> The scientific name for rubber tree is *caoutchouc*, which is derived from the word *caao-chu* meaning 'weeping tree'. Natural latex contains 30-35% rubber, 2-3% proteins and lipids, 0.3% resin and 1.5-4% glycosides.



**Figure 1** A schematic representation of the chemistry involved in vulcanisation. (Only one cross-link is shown. In reality multiple cross-links are formed in three dimensions).



<sup>2</sup> Vulcanization is derived from the word *Vulcan*, God of Fire in Greek mythology.

fur, is known as *Vulcanization*.<sup>2</sup> Charles Goodyear discovered the process of vulcanization in 1839, accidentally. While carrying out an experiment, he spilt a mixture of rubber and sulfur with other ingredients on a hot stove. Lo and behold, rubber had transformed into a tough and firm material. The key chemical modification is that sulfide bridges are created between adjacent chains (*Figure 1*). The crosslinking makes rubber non-sticky and improves its tensile strength. The material is no longer thermo-plastic. These attractive physical properties of vulcanized rubber have revolutionised its applications.

### Modern Improvements

The vulcanization process has undergone several modifications since its discovery. A typical process is shown in *Box 1*. It may be noted that many additives are included. These have been chosen to manipulate the property of rubber to suit specific requirements.

For the process of vulcanization to be useful and successful, it should be controlled. It should begin when required, accelerate when needed and must stop at the right time. In the jargon of rubber technologists, these are termed as *scorch resistance*, *acceleration* and *cure time*, respectively. Scorch resistance is the time elapsed before vulcanization starts. It is necessary to have suitable scorch resistance so that there is enough time for mixing, storing and moulding of the rubber mixture into the desired shape and size. Premature vulcanization results in the development of cracks in rubber, making the resulting products unusable. Once vulcanization begins, it should be completed as fast as possible in order to have practical batch cycle. Shorter

#### Box 1

##### A typical recipe for vulcanization

Temperature 140 - 180°C

Sulfur 2-3 parts per  
100 parts of rubber (phr)

Accelerator 0.5-1.0 phr

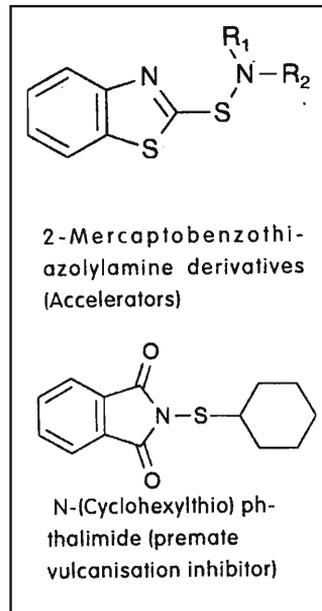
ZnO 3-5 phr

cure times are preferred. Thus, we need to control the way molecules interact with each other at different stages in order to achieve the desired physical property. Interesting organic molecules have been designed and synthesized to act as *molecular remote controls* (MRC's) of the vulcanization process. While some additives have been found to be effective on an empirical basis, optimum choices have been made from a sound knowledge of the reaction mechanisms (see *Box 2*).

There are several MRC's used in the vulcanization process. The mechanism of action of two of them, called *accelerator* and *premature vulcanization inhibitor* (PVI), are described in the following as illustrative examples (*Figure 2*).

### An Accelerator in Action

Sulfenamides have been found to have the unique ability to accelerate the vulcanization process. The mechanism of acceleration is shown in *Figure 3*. In the first step, the sulfenamide generates a sulfur containing radical which forms a polysulfide molecule by reacting with elemental sulfur. This molecule reacts with the polymer chain of rubber in an interesting fashion. Via the formation of a cyclic 6-membered transition state a sulfide unit is transferred to the polymer chain. This



**Figure 2** Molecular remote controls.

#### Box 2

The mechanism of vulcanization is fairly complex. It is strongly dependent on the components present, temperature and duration of the process. In general, during the initial period the structural fragments include polysulfide linkages and pendant polysulfide chains terminated by an accelerator fragment. During subsequent heat treatment or 'maturing' of the network these polysulfide crosslinks are converted to monosulfide crosslinks, (this process is facilitated by Zinc Oxide.) that are far more thermally stable. Some isomerizations of the double bonds are also believed to occur generally leading to the formation of conjugated diene and triene sequences.

Premature vulcanization results in the development of cracks in rubber, making the resulting products unusable.



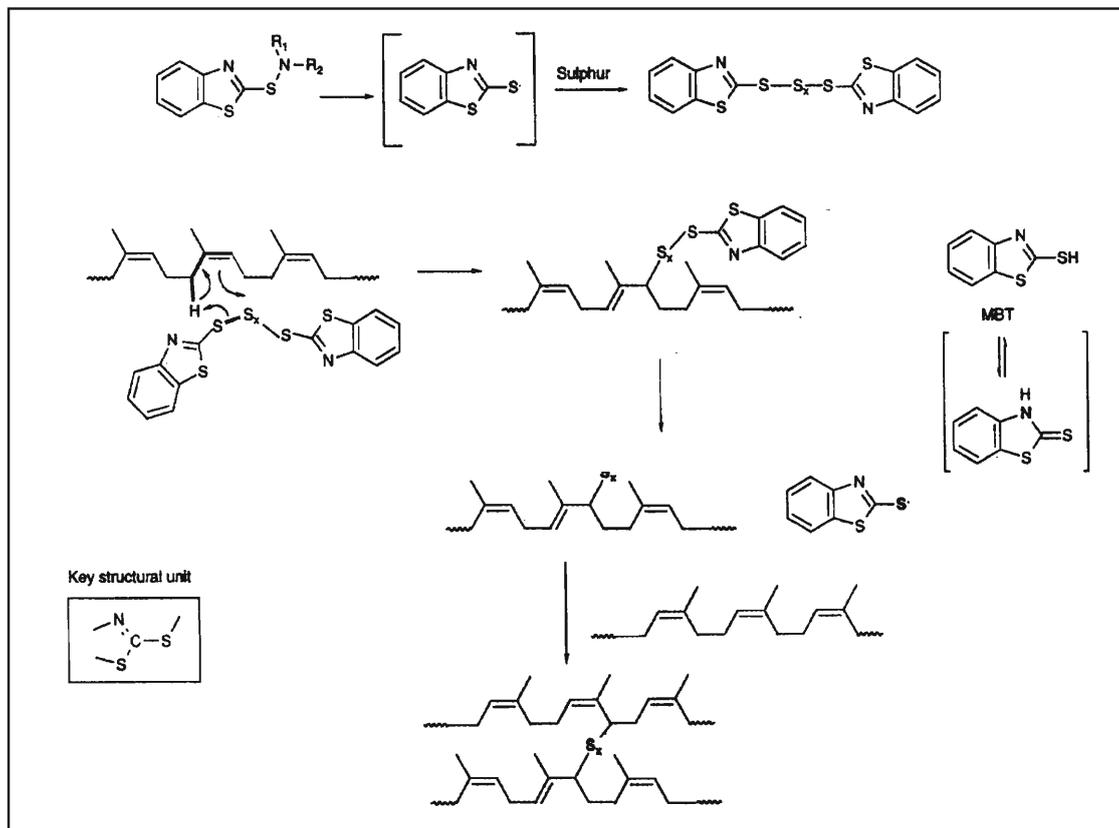


Figure 3

reaction is a heteroatomic analogue of the well known Alderene reaction (a thermally allowed process involving reorganization of 6-electrons over orbitals with Hückel topology). The polysulfide linkage undergoes fragmentation to yield another sulfur containing radical. This adds to a second polymer chain creating a crosslink.

Another important feature of this molecular remote control is its ability to delay the onset of vulcanization. This is because of autocatalytic disappearance of the accelerator with the formation of MBT (2-mercaptobenzothiazole). If MBT is removed as fast as it is formed, there will be a delay in acceleration. This results in high scorch resistance. As mentioned earlier, this delay time is an important factor in determining the physical properties of the rubber manufactured.

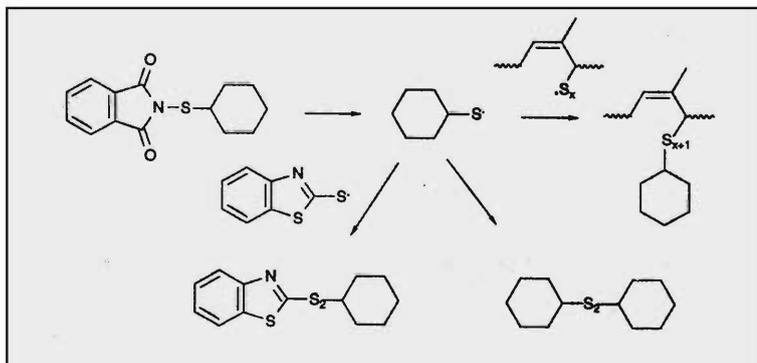


Figure 4

### Stopping When Needed

The second MRC we consider is N-(cyclohexylthio)phthalimide (CTP). This substance prevents premature vulcanization. That is, the onset of vulcanization is prevented till the rubber mixture is moulded into the required shape. How does CTP function? The molecule can react rapidly with MBT. As stated earlier, this results in the depletion of the accelerator, thereby stopping the vulcanization process. Further, reactive species generated from CTP can quench the crosslink precursor thiyl radicals (Figure 4). Hence CTP is effective in preventing premature vulcanization.

### Conclusion

Many MRC's are judiciously utilized in rubber industry for improving the quality of rubber for newer applications. Organic chemists have been playing a crucial role in the design and development of additives. Unravelling the mechanism of complex multiple reactions has proved to be important in controlling the overall vulcanization process.

### Suggested Reading

- ◆ F R Eirich. (Ed.) *Science and Technology of Rubber*. Academic Press. New York, 1978.
- ◆ J A Brydson. *Rubber Chemistry*. Applied Science Publishers Ltd. London, 1978.

### Box 3

Sulfenamides constitute a group of organic sulfur compounds containing both carbon-sulfur and sulfur-nitrogen bonds -  $\text{RSNR}_1\text{R}_2$ . They are also considered as amides derived from the corresponding sulfenic acids -  $\text{RSOH}$ . Since the beginning of the 1940's, sulfenamides have been used extensively in vulcanization of rubber. Recently, they have also been used as pesticides, fungicides and bactericides.

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