LITERATURE REVIEW

1. Natural Rubber (NR)

1.1 Introduction of natural rubber

Morton (1987) Natural Rubber (NR) is the prototype of all elastomers. It is extracted from the bark of the *Hevea* tree. The rubber is collected from the latex in a series of steps involving preservation, concentration, coagulation, dewatering, drying, cleaning, and blending. Because of its natural derivation, it is sold in a variety of grades based on purity (color and presence of extraneous matter), viscosity stability, oxidation resistance, and rate of cure. The natural rubber polymer is nearly 100% cis-1,4 polyisoprene with MW ranging from 1 to 2.5×10^6 as shown in Figure 1. Due to its high structural regularity, natural rubber tends to crystallize spontaneously at low temperatures or when it is stretched. Low temperature crystallization causes stiffening, but is easily reversed by warming.

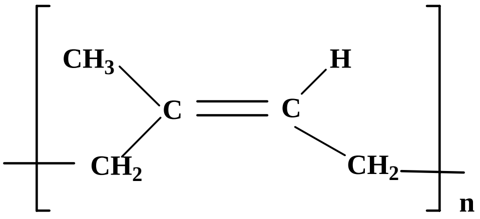


Figure 1 The structure of cis-1,4 polyisoprene

1.2 Properties of natural rubber

Strength

Natural rubber is well-known for the strength properties of its vulcanizates. The tensile strength of gum vulcanizates ranges from 17 to 24 MPa while those of black filled vulcanizates range from 24 to 32 MPa. Strength can also be characterized as tear resistance, in both of which natural rubber is excellent. This high strength of natural rubber is certainly due to its ability to undergo strain-induced crystallization. The strength drops rapidly with increase in temperature but is still better than in other elastomers.

Elongation at break

The ultimate elongation depends, naturally, very much on the nature and amount of fillers in the compound, and on the degree of vulcanization. In general, it is about 500 to 1000%, or even greater.

Abrasion and wear

Natural rubber has excellent abrasion resistance, especially under mild abrasive conditions. Below about 35 ^{o}C, natural rubber shows better wear than styrene butadiene rubber (SBR), while above 35 ^{o}C, SBR is better.

Dynamic properties

Natural rubber has high resilience, with values exceeding 90% in well-cured gum vulcanizates. At large strain, the fatigue life of natural rubber is superior to that of SBR, the reverse is true for small strains. Good resistance to flexing and fatigue together with high resilience makes natural rubber useful in applications where cyclic stressing is involved.

Compression set

Compression set and related processes, such as creep, are poorer in natural rubber than in synthetic polyisoprene. At ambient and slightly elevated temperature, the compression set of NR vulcanizates is relatively low. At lower temperatures the compression set appears to be poor. Heat resistance of the NR vulcanizate has a detrimental effect on the compression set.

Aging resistance

Natural rubber vulcanizates can be given adequate heat-aging resistance by a suitable choice of vulcanization system and by use of amine or phenolic antioxidants. The heat-aging resistance of NR vulcanizates is insufficient for many technical applications.

Weather and ozone resistance

Even after vulcanization, the NR has double bonds in the polymer chain. Therefore, it has an insufficient weather and ozone resistance, particularly in light-colored vulcanizates.

Solvents and Oils

Solvents will attack the rubber more rapidly with actual rates dependent on the types of solvent and rubber. Attack by contact with oils is usually restricted to a thin surface layer due to slow diffusion rate.

2. Vulcanization

Jame *et al.* (1994); Akiba and Hashim (1997) Vulcanization is generally applied to rubbery or elastomeric materials. These materials forcibly retract to their approximately original shape after a rather large mechanically imposed deformation. Vulcanization can be defined as a process which increases the retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force. Thus, vulcanization increases elasticity while it decreases plasticity. It is generally accomplished by the formation of a crosslinked molecular network.

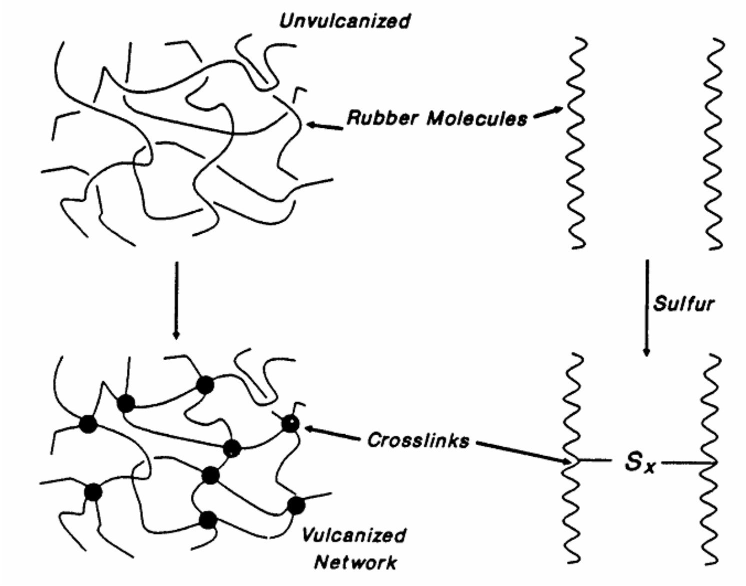


Figure 2 Network formation

After the rubber compound has been processed and formed, it is vulcanized. This process involves three stages: induction, curing, and reversion or overcure. The induction period is the time at vulcanization temperature during which no measurable crosslinking occurs. It determines the safety margin of the compound against “scorch” during the processing steps proceeding crosslinking. Scorch is premature vulcanization that can occur due to the effects of heat and time. Because these effects are cumulative, the time until scorch will slowly decrease with each processing step. Scorching results in a tough and unworkable batch, which must be scraped. The time to scorch is dictated by the processing and the additives used, so that a well designed compound will have a scorch time slightly longer than the equivalent of its maximum anticipated cumulative heat history. The amount of time the compound must be cured, the cure time, is determined in part by the “rate of cure”. This is the rate at which crosslinking and the consequent development of stiffness (modulus) occurs. Cure time is also a function of the desired “state of cure”. As vulcanization (crosslinking) proceeds, the various properties developed by vulcanization are not optimized simultaneously. At any given time during vulcanization, the state of cure is a measure of the development of these properties. Cure time is the time required for the compound to reach a state of cure where the desired balance of properties has been attained. When a compound is cured beyond the point where its balance of properties has been optimized it become overcured. For most elastomers, over cure means the compound becomes harder, weaker and less elastic. With other elastomers, particularly most natural rubber compounds, overcure results in reversion. The compound softens, becoming less elastic and more plastic.

2.1 Cure time

The oscillating disk rheometer (ODR) measures the complete curing characteristics of elastomer compound. The rubber is enclosed in a heated cavity (Figure 3).

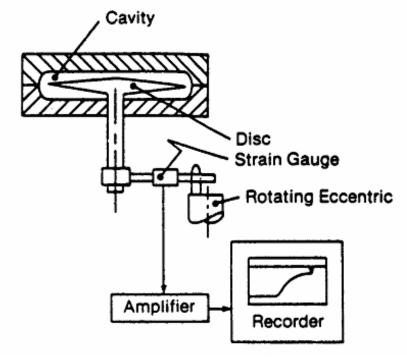


Figure 3 Oscillating disk rheometer

Embedded in the rubber is a metal disk which oscillates sinusoidally in it plane about its axis. Vulcanization is measured by the increase in the torque required to maintain given amplitude (e.g. degree of arc) of oscillation at a given temperature. The torque is proportional to a low-strain modulus of elasticity. Since this torque is measured at the elevated temperature of vulcanization, the portion of it due to viscous effects is minimal. Thus, it has been assumed that the increase in torque unit volume of rubber, while the torque is automatically plotted against time to give a so-called rheometer chart, rheograph, or cure curve as shown in Figure 4.

New versions of the curemeter have been introduced. The cavity is much smaller and there is no rotor. In this type of curemeter, one-half of the die (e.g., the upper half) is stationary and the other half oscillates. These instruments are called moving-die rheometers (MDR). The sample is much smaller and heat transfer is faster. Also, because there is no rotor, the temperature of the cavity and sample can be changed more rapidly.

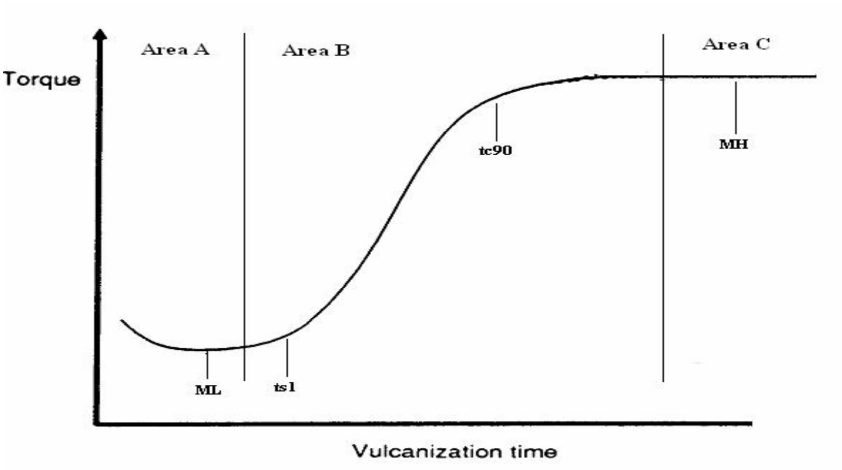


Figure 4 Rheometer cure curve

The measurements which can be made from this curve and the term used to describe them are:

Area A - This gives an indication of compound viscosity.

Area B - This indicates the rate of cure of the compound.

Area C - This indicates the state of cure of the vulcanizate.

M_L, Minimum torque - A measure of the viscosity of the uncured compound

M_H, Maximum torque - A measure of cure state, with some compound, maximum torque can be related to vulcanizate modulus and hardness.

t_{s1} - Time for torque to increase 1 dn.m (0.1 N.m) or 1 lb_f-in above M_L - a measure of scorch time or processing safety, some laboratories use t_{s2} (i.e., time for torque to increase 2 dN.m or 2 lb_f-in above M_L) instead of t_{s1}.

t_{c50}, t_{c90} - Time for torque to reach $M_L + 0.5\ (M_H\text{-}M_L)$ or $M_L + 0.9\ (M_H\text{-}M_L)$

2.2 Vulcanization systems

2.2.1 Sulfur vulcanization

Sulfur vulcanization is the most commonly used vulcanization agent for elastomers with chemically unsaturated polymer backbones, particularly the more common diene rubbers: natural rubber, SBR, polybutadiene, nitrile, polychloroprene, and polyisoprene. Other vulcanization agent can be used with unsaturated elastomers, but sulfur dominates because it is low in cost and toxicity, broadly compatible with other compounding additives, and able to predictably provide the desired vulcanization properties.

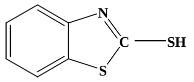
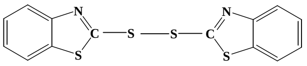
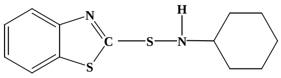
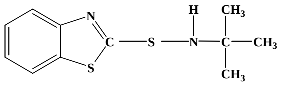
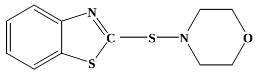
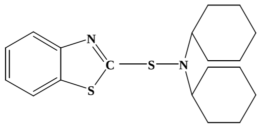
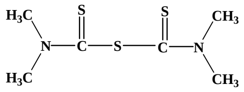
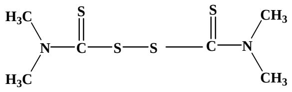
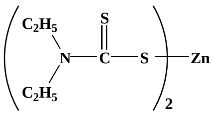
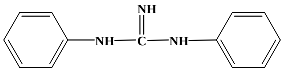
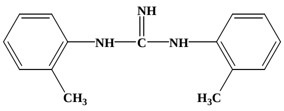
Sulfur is available to the compounder in two forms: amorphous and rhombic. The amorphous form, also known as insoluble sulfur is a metastable high polymer that is insoluble in rubber and most solvents. Rhombic sulfur, a ring of eight sulfur atoms, is soluble in rubber and the form normally used for vulcanization. About 1 to 3 phr of sulfur are used for most rubber products.

Diene rubbers and sulfur are mixed together. The mixture is heated; probably a free radical process is involved in which the eight-atom sulfur rings break down into free radicals:

$$S_8 \longrightarrow \bullet S_x \bullet$$

These free radicals unite with olefins, and rubber-sulfur-rubber crosslinks are formed. However, elastomer vulcanization by sulfur without accelerator is slow reaction. In addition it uses high sulfur level and high temperature. So addition of accelerators to a rubber/sulfur formulation greatly increased the rate of vulcanization and improved the final vulcanizate properties. Presently there are wide ranges of accelerator system available for elastomers, providing a range of cure rate, scorch times and final properties. The several common accelerators are shown in Table 1.

Table 1 Several common accelerators used in sulfur vulcanization

Compound	Abbreviation	Structure
Benzothiazoles		
2-Mercaptobenzothiazole	MBT	
2-2’-Dithiobisbenzothiazole	MBTS	
Benzothiazolesulfenamides		
N-Cyclohexylbenzothiazole-2-sulfenamide	CBS	
N-t-Butylbenzothiazole-2-sulfenamide	TBBS	
2-Morpholinothiobenzothiazole	MBS	
N-Dicyclohexabenzothiazole-2-sulfenamide	DCBS	
Dithiocarbamates		
Tetramethylthiuram monosulfide	TMTM	
Tetramethylthiuram disulfide	TMTD	
Zinc diethyldithiocarbamate	ZDEC	
Amines		
Diphenylguanidine	DPG	
Di-o-tolylguanidine	DOTG	

Source: Jame *et.al.* (1994)

Sulfur vulcanization is generally two categories such as unaccelerated- and accelerated-sulfur vulcanization. Unaccelerated sulfur formulations consist of rubber and sulfur, while accelerated sulfur systems contain rubber, accelerator and sulfur. In addition, zinc oxide and stearic acid are often included in both types of systems (in Figure 5). The reaction of sulfur vulcanization is shown in Figure 6.

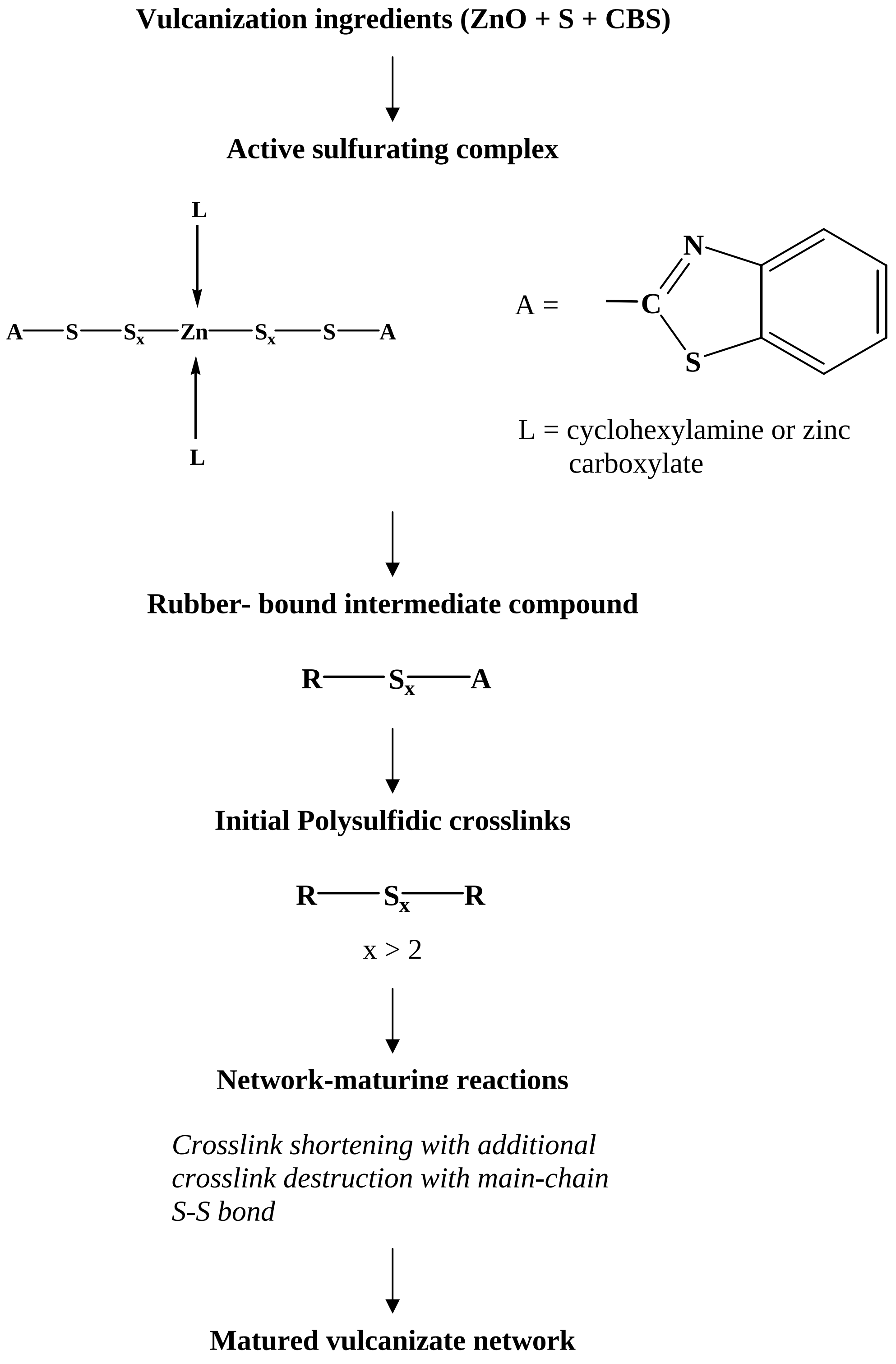


Figure 5 General reaction scheme for accelerated sulfur vulcanization

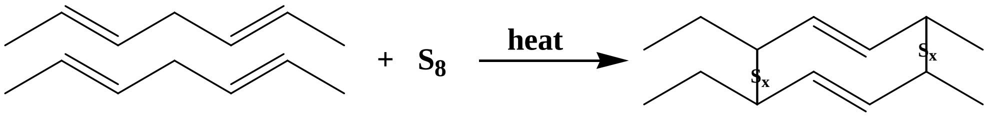


Figure 6 The reaction of sulfur vulcanization

In the sulfur vulcanization, various types of crosslinks is formed depending on the quantity and activity of the other additives, particularly accelerators. These crosslinks can be anything between monosulfidic to polysulfidic (Figure 7).

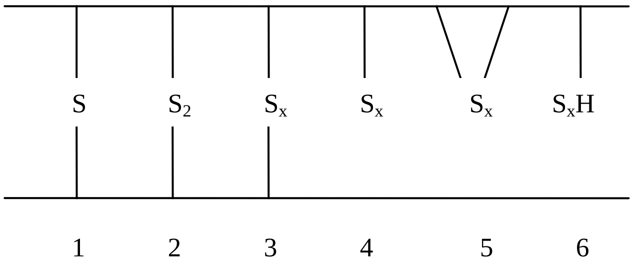


Figure 7 Different crosslink structures: (1) monosulfidic, (2) disulfidic, (3) polysulfidic, when $x \geq 3$, (4) sulfur chain, (5) cyclic sulfur structures, (6) thiol groups

The sulfur vulcanization system can be classified into three types.

Conventional vulcanization (CV)

Most frequently used systems, conventional cure systems which feature a high sulfur level and low accelerator concentration show poor heat and oxidation resistance because the polysulfidic crosslinks are thermally unstable and readily oxidized. But conventional system gives vulcanizates which poses excellent initial properties like strength, resilience and resistance to fatigue and abrasion.

Semi-efficient vulcanization (semi-EV)

Semi-EV cure systems, which are intermediate between EV and conventional systems, are comprised between resistance to oxidation and required product fatigue performance because of the presence of predominantly disulfidic crosslinks.

Efficient vulcanization (EV)

Efficient vulcanization systems which feature a low sulfur level, and a high acceleration level show good heat stability and oxidation resistance, however, have a poor resistance to fatigue because of the presence of predominantly monosulfidic and disulfidic crosslinks.

The level of sulfur and accelerator of such sulfur vulcanization systems are shown in Table 2.

Table 2 The level of sulfur and the ratio of accelerator to sulfur

Vulcanization system	Sulfur (S,phr)	Accelerator (A,phr)	A/S ratio
Conventional vulcanization (CV)	2.0-3.5	1.2-0.4	0.1-0.6
Semi-efficientvulcanization (semi-EV)	1.0-1.7	2.5-1.2	0.7-2.5
Efficient vulcanization (EV)	0.4-0.8	5.0-2.0	2.5-1.2

Source: Akiba and Hashim (1997)

For both CV and EV systems, the addition of reclaimed rubber (RR) into virgin NR increases the hardness and modulus but decreases the tensile strength, tear strength, abrasion resistance, and heat buildup resistance. Nevertheless, CV vulcanizates generally give higher mechanical properties than the EV vulcanizates. Tensile strength and tear strengthof the blends tend to be independent of curing system when RR content is high. EV vulcanizates exhibit greater heat aging resistance than CV vulcanizates, particularly when RR content is less than 50 phr, due to the greater thermal stability of mono- and di-sulfidic crosslinks compared to the polysulfidic ones. Although most of the properties of the blends are adversely affected by the addition of reclaimed rubber, the value of each property, especially when the ratio of NR/RR equals 80/20, may be suitable for some applications. Owing to the currently high price of the virgin rubbers and increasing environmental concerns, the utilization of reclaimed rubber as a cost-beneficial extender should be a good alternative for many rubber applications.

2.2.2 Peroxide vulcanization

Peroxide is vulcanizing agents for elastomers which contain no site attack by other types of vulcanizing agents. They are useful for ethylene-propylene rubber (EPR), ethylene-vinyl acetate copolymer (EAM), certain millable urethane, and silicone rubbers.

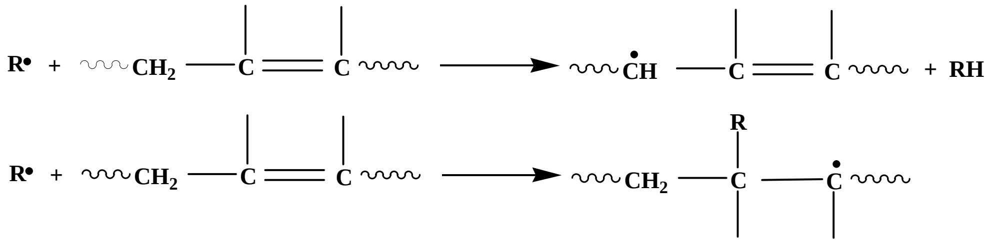
Elastomers derived from isoprene and butadiene are readily crosslinked by peroxides, but many of the vulcanizate properties are inferior to those of accelerated-sulfur vulcanizates; however, peroxide vulcanizates of these diene rubbers may be desirable in applications where improved thermal aging and compression set resistance are required.

Mechanisms of peroxide vulcanization of unsaturated hydrocarbon elastomers are divided into 3 steps. The initiation step in peroxide-induced vulcanization is the decomposition of the peroxide to give free radicals:

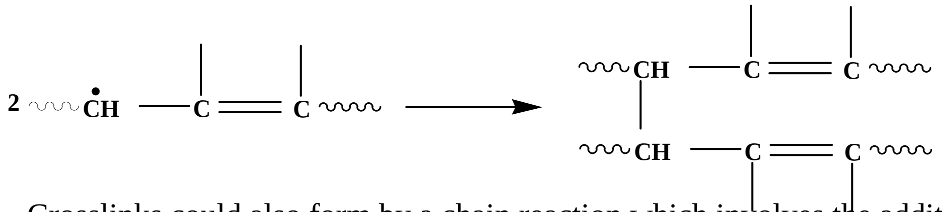
$$\text{Peroxide} \longrightarrow 2R\bullet$$

where R• is an alkoxyl, alkyl, or acyloxyl radical, depending on the type of peroxide used, e.g., dibenzoyl peroxide gives benzoyloxyl radicals but dicumyl peroxide gives cumyloxyl and methyl radicals.

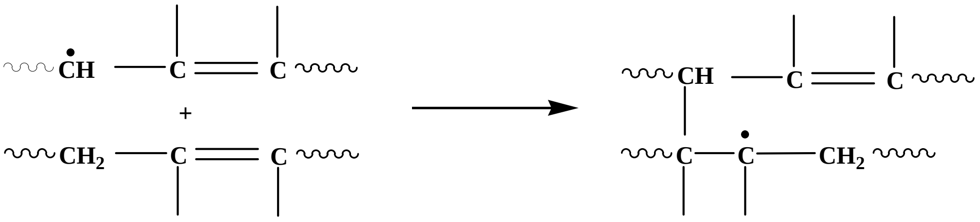
The next step is either the abstraction of a hydrogen atom from an allylic position on the polymer molecule or the addition of the peroxide-derived radical to a double bond of the polymer molecule:



Finally step, two polymeric free radicals combine to form a covalent crosslink, radical coupling:



Crosslinks could also form by a chain reaction which involves the addition of polymeric free radicals to double bonds:



In this case crosslinking occurs without the loss of a free radical, so that the process can be repeated until termination by radical coupling. Coupling can be between two polymeric radicals to form a crosslink or by unproductive processes.

3. Fillers

Hofmann (1989) Fillers are added to rubber formulations to improve rubber properties, to change the balance of properties, and to lower the cost. The fillers are classified as reinforcing filler and non-reinforcing or inert fillers, or are classified as carbon black and light-colored fillers.

3.1 Principle of reinforcement

Reinforcement is defined as the ability of fillers to increase the stiffness of unvulcanized compounds and to improve a variety of vulcanizate properties, e.g. tensile strength, abrasion resistance and tear resistance. At the same time the stress values and the hardness are generally increased and as a rule other properties such as elongation at break and rebound and other properties depending on these lowered. The reinforcement's effect of filler shows up especially in its ability to change the viscosity of a compound and also the vulcanizate properties with increase in the amount of filler loading. Those fillers which only lead to small increase in the viscosity of the compound and otherwise to a worsening of the mechanical properties of the vulcanizate, are not reinforcing; they are called non-reinforcing or inactive fillers such as talcum, calcium carbonate ($CaCO_3$), and clay. In contrast, reinforcing or also active fillers such as carbon black and silica lead to dramatic increases in viscosity of the compound as well as to maxima of the tensile and the tear strength and the abrasion resistance with increasing amounts of filler loading.

3.2 Effects between filler and elastomer

Efficiency of reinforced fillers depends on interaction forces between the elastomer and the fillers. These lead to conditions which range from weak van der Waal's force to chemical bonds. These adhesion forces are not distributed equally over the surface of the filler because the latter is energetically heterogeneous. The chemical composition of the filler's surface, its special structure on the other hand is of importance. The formed bond cause, of course, an increased deformation stiffness, because of less movability of the polymer chains. The reactivity of elastomer affects, of course, the filler-elastomer interaction as well. Because of this one should refer to active fillers with regard to certain elastomer.

3.3 Factors affecting filler reinforcement

The characteristics which determine the properties of filler and will impart to a rubber compound are particle size, surface area, structure, and surface activity.

Particle size

Fillers with particle size greater than 10,000 nm are generally avoided because they can reduce performance rather than reinforce or extend. Fillers with particle sizes between 1,000 and 10,000 nm are used primarily as diluents and usually have no significant effect, positive or negative, on rubber properties. Semi-reinforcing fillers, which range from 100 to 1,000 nm improve strength and modulus properties. The truly reinforcing fillers, which range from 10 nm to 100 nm significantly, improve rubber properties.

Surface area

Particle size is generally the inverse of surface area. Fillers must make intimate contact with the elastomer chains if it is going to contribute to reinforcement. Fillers that have a high surface area have more contact area available, and therefore have a higher potential to reinforce the rubber chains.

Structure

The shape of an individual particle of reinforcing filler (e.g. carbon black or precipitated silica) is of less importance than the filler’s effective shape once dispersed in elastomer. The blacks and precipitated inorganics used for reinforcement have generally round primary particles but function as anisometric acicular aggregates. The round particles clump together into chains or bundles that can be very dense or open and latticelike. These aggregate properties (shape, density, size) define their structure. High structure filler has aggregates favoring high particle count, with those particles jointed in chain-like clusters from which random branching of additional particle chains may occur. The more an aggregate deviates from a solid spherical shape and the larger its size, the higher is its structure. The higher its structure, in turn, the greater its reinforce potential. For reinforcing fillers which exist as aggregates rather than discreet particles, a certain amount of structure that existed at manufacture is lost after compounding. The high shear forces encountered in rubber milling will break down the weaker aggregates and agglomerates of aggregates. The structure that exists in the rubber compound, the persistent structure, is what affects processability and properties.

Surface activity

A filler can offer high surface area and high structure, but still provide relatively poor reinforcement if it has low specific surface activity. The specific activity of the filler surface per cm^2 of filler-elastomer interface is determined by the physical and chemical nature of the filler surface in relation to that of the elastomer. Nonpolar fillers are best suited to nonpolar; polar fillers work best in polar elastomer. Beyond this general chemical compatibility is the potential for reaction between the elastomer and active sites on the filler surfaces.

3.4 Filler effects

The principal characteristics of rubber fillers (particle size, surface area, structure, and surface activity) are inter dependent in improving rubber properties. In considering fillers of adequately small particle size, reinforcement potential can be qualitatively considered as the product of surface area, surface activity, and persistent structure or anisometry (planar or acicular nature). The general influence of each of these three filler characteristics above on rubber properties can be summarized as follows:

1. Increasing surface area (decreasing particle size) gives lower resilience and higher mooney viscosity, tensile strength, abrasion resistance, tear resistance, and hysteresis.
2. Increasing surface activity gives higher abrasion resistance, chemical adsorption or reaction, modulus (at elongation > 300%), and hysteresis.
3. Increasing persistent structure/anisometry gives higher mooney viscosity, modulus (at elongation < 300%), and hysteresis, lower extrusion shrinkage, tear resistance, and resilience, and longer incorporation time.

In general terms, the effect of filler on rubber physical properties can be related mainly to how many polymer chains are attached to the filler surface and how strongly they are attached. Filler surface area and activity are the main determinants, supplemented by structure. Since the filler particles can be considered crosslinks for the elastomer chains, the presence or absence of a coupling agent on the surface of non-black fillers is also important.

3.5 Filler Types

The use of fillers in rubber products is nearly as old as the use of rubber itself. Prior to the discovery of vulcanization, the tackiness of rubber goods was subject to correction by the traditional remedy for wet or sticky surface-sprinkling with talcum powder. The technological leap from talc on the outside to incorporation of talc on the inside of the rubber to serve the same properties is credible. Hancock’s masticator, and the rubber mixing machinery it spawned, facilitated the incorporation of all types of fine particulates, including ground limestone, clays, barite, zinc oxide, zinc sulfide, iron oxides, asbestos, mica, litharge (lead oxide) and kieselguhr (diatomite). Whether the original reason for adding these powders was reduction in tack, adjustment of color, or simply reducing the cost of the rubber compound, two conclusions were inevitably drawn. Some filler could be added in large amounts without detracting from desirable rubber properties, and others would actually improve rubber properties, usually by increasing hardness and durability.

3.5.1 Carbon black

Carbon black is essentially elemental carbon in the form of fine amorphous particles. Each particle is composed of randomly oriented microcrystalline layered arrays of condensed carbon rings. Because of their random orientation, many arrays expose open layer edges with unsatisfied carbon bonds at the particle surface. This in turn provides the sites for chemical activity (Figure 8).

As an empirical guide, an increase in a carbon black aggregate size or structure will result in an improvement in cut growth and fatigue resistance. A decrease in particle size results in an increase in abrasion resistance and tear strength, a drop in resilience, and an increase in hysteresis and heat buildup.

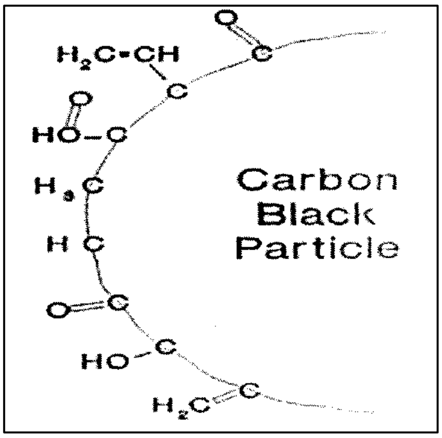


Figure 8 Chemical function on carbon black surface

3.5.2 Light colored fillers (Fred, 1993)

In classifying the dry fillers used in rubber to increase its usefulness or to make a cost-competitive product, it is convenient to speak of black and nonblack fillers. With few exceptions (such as color pigments) nonblack fillers are chosen over carbon blacks for one or more of three reasons:

- The product has to be white or light-colored.
- Certain unique properties are required like thermal conductivity by the use of zinc oxide.
- Cost-it is hard to get less costly materials than natural products in good supply like clay or ground limestone.

Silica

Fine particle silica gives the utmost in reinforcement in rubbers of the nonblack fillers. Use of silica rubber compounds offers two advantages such as reduction in heat buildup when used as a part for replacement of carbon black and improvement in tear strength. Silica can be made by pyrogenic or precipitation processes.

In the preparation of silica by pyrogenic process, Silicon tetrachloride is reacted at high temperatures with hydrogen and oxygen in combustion chamber. Silica produced by a thermal method is frequently called fumed silica. The reactions are:

$$2H_2 + O_2 \longrightarrow 2H_2O$$

$$2H_2O + SiCl_4 \longrightarrow SiO_2 + 4HCl$$

The reaction products are quenched immediately after coming out of the burner. For the normal types of rubber, pyrogenic silica is too active and too expensive.

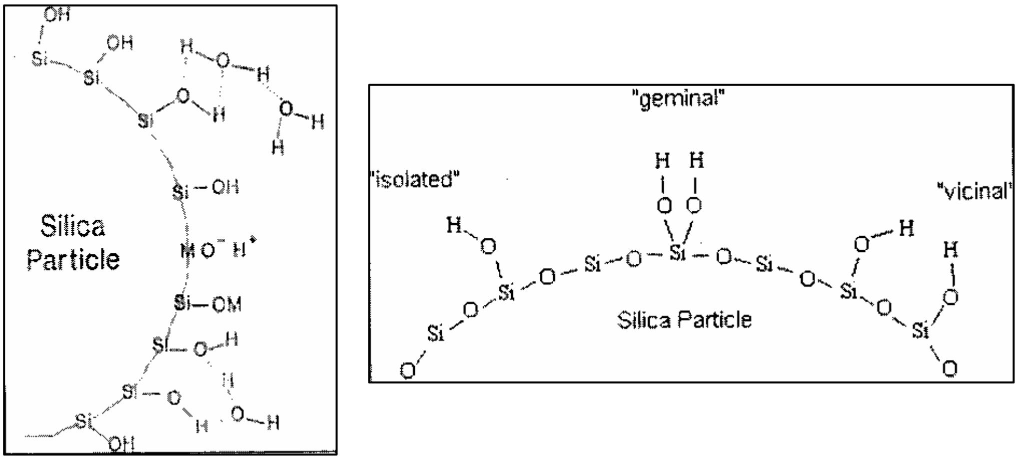
Precipitated silica is often used if highly reinforced tough or light-colored compounds are wanted. Precipitated silicas are made by the action of acids on water glass. The acid is usually sulfuric, the water glass an alkaline solution of sodium silicate, normally having a mole ratio of 2.1 to 3.5. The reaction is:

$$nSiO_2 \bullet Na_2O + H_2SO_4 \longrightarrow Na_2SO_4 + nSiO_2 \bullet H_2O$$

The hydrated precipitated silica is filtered out and washed to remove the sodium sulfate. It is then dried and ground.

The silica surface is highly polar and hydrophilic and contains adsorbed water as shown in Figure 9. The surface hydroxyl groups are acidic and tend to retard cure rate. The reactivity of the surface causes foreign substances to be adsorbed on the filler surfaces till they are saturated. The behavior of the filler and its effect on the rubber may be strongly influenced by that process.

All precipitated silica filler contains a certain amount of water from preparation. Since the water content can clearly influence processing and vulcanization properties, it is customary that a constant amount is present during packaging by controlling the production process. With increasing water content the dispersion time of colloidal silica into the rubbers is somewhat prolonged; the scorch time and vulcanization time with conventional sulfur-accelerator combination are prolonged.



(a) (b)

Figure 9 (a) chemical function on silica surface, and (b) type of silanol groups

The filler surface is capable not only to adsorb water but also compounds, particularly basic ones. If silica containing compounds are accelerated with basic products such as diphenylguanidine (DPG) or di-o-tolylguanidine (DOTG), a certain amount of accelerator is taken up by the filler and is not available as vulcanization accelerator.

Not only can silica fillers interact with water or accelerators, but also with polymers. Consequently with increasing filler content, respectively increasing filler activity the viscosity of the mixture increases and makes processing more difficult. To the extent that filler-polymer interaction is decreased, compound viscosity can be reduced. If materials are added to the mixtures that are adsorbed stronger on the filler than the rubber, softer mixtures are obtained that are processed more easily. Additives of this type are DPG or DOTG type accelerator, hydroxyl group containing compounds, like glycols, glycerol, etc. These additives act not only to improve processing but also to reduce accelerator absorption and to reduce their polarity.

Carbon black has reactive organics groups on the surface that furnish affinity to rubber. These reactive centers are missing in light-colored fillers. The use of additives to make the surface of precipitated silica less hydrophilic and more “rubberphilic” facilitates incorporation, dispersion, and more intimate filler-elastomer contact during compounding must be considered. This provides an improvement in rubber physical properties, as would be expected from a high surface area, high oil absorption filler. However, reinforcement comparable to that obtained with carbon black requires a polymer-filler bonding mechanism comparable to that provided at the carbon black active site. With precipitated silicas, this comes by way of a reactive silane. Common practice has been to use the functional silanes as separate compounding ingredients. This necessitates carefully control of addition sequence and procedures because the silane must react with the silica surface in preference to all other components in order to be optimally effective. Precipitated silicas pretreated with silane are now available to simplify compounding. The pretreatment also makes the silica less hydrophilic, for easier dispersion and lower viscosity.

Clay

Clay is one of the most widely used nonblack fillers for rubber. They owe this popularity to a combination of low cost, low-to-moderate reinforcement, and processing benefits. Kaolin clay, the type of clay used in rubber, has been derived from the weathering of aluminous minerals such as mica and feldspar. The closet approach to its chemical composition would probably be $Al_2O_3{\bullet}2SiO_2{\bullet}2H_2O$.

Rubber filler clays are classified as either “hard” or “soft” in relation to their particle size and stiffening affect in rubber. Hard clay will have a median particle size of approximately 250 to 500 nm, and will impart high modulus, high tensile strength, stiffness, and good abrasion resistance to rubber compounds. Soft clay has a median particle size of approximately 1000 to 2000 nm and is used where high loading and faster extrusion rates are more importance than strength.

The main factor to consider in adding clay to most formulations is its reduction of cure rate. Clay is an adsorptive material and can adsorb organic accelerator (similar silica) to such an extent that they do not function at high loading of clay. The adsorptive effects can be mitigated by using small amounts of triethanolamine or polyethylene glycols. These function by being preferentially adsorbed at the active sites on the silica layer of the clay. Not only must the slower curing rate of clays in general be considered, it also must be realized that hard clays are significantly slower curing than the soft clays.

Durometer hardness is the usual starting point for a guide in selecting clay loading. A role-of-thumb in many elastomers are to use 5-6 phr of hard clay and 7-8 phr of soft clay.

Calcium carbonate (Xanthos, 2005)

Calcium carbonate is the most common deposit formed in sedimentary rocks. Natural $CaCO_3$ used as filler in plastics is produced from chalk, limestone or marble found in the upper layers of the Earth's crust to a depth of about 15 km.

Calcium carbonate is abundant, largely inert, low cost, white filler with cubic, block-shaped or irregular particles of very low aspect ratio. Its use yields a cost reduction in a variety of thermoplastics and thermosets, and it can have moderate effects on mechanical properties. In terms of its primary function as a mechanical property improver, its advantages in thermoplastics are slightly increased modulus and often an increase in impact strength. These benefits are accompanied by shrinkage reduction and improved surface finish. In terms of secondary functions, calcium carbonate may act as a surface property modifier, as a processing aid, and as a stress concentrator by introducing porosity in stretched films. These functions may be enhanced or modified by the application of suitable surface treatment agents, such as stearates or titanates.

Calcium carbonate occurs in different crystalline forms. The most widespread is calcite, which has either a trigonal-rhombohedral or a trigonal-scalenohedral crystallattice. Another form is the orthorhombic aragonite, which is less stable and can be converted to calcite by heating. Vaterite, a third form, is unstable and over time will transform into the other two forms. Aragonite has a higher density (2.8-2.9 $g.cm^{-3}$), a higher single refractive index (1.7), and a somewhat higher Mohs hardness (3.5-4) than calcite. Its other properties are very similar. Both minerals are white and their refractive indices are not high enough to interfere with effective coloration.

Calcium carbonates for rubber, often referred to as “whiting”, fall into two general classifications. The first is wet or dry ground natural limestone, spanning average particle sizes of 5000 nm down to about 700 nm. The second is precipitated calcium carbonate (PCC), which are manufactured by the formation of calcium carbonate from milk of lime via the use of carbon dioxide. Particle sizes range down to 40 nm.

Calcium carbonate is one of the two most widely used nonblack fillers. The reason for this popularity is that very high loadings can be used to dilute rubber with little loss of softness, elongation, or resilience. The result is that cost is reduced without objectionable stiffening of the cured rubber product. Cured stocks loaded with whiting are soft and have reasonably good tensile strength, elongation, and a low modulus. Resilience to tear is only fair or poor, and to abrasion is poor.

4. Natural Zeolite

Zeolites are the most materials use in industry. They were used to pollutants removal, catalyst including the reactants for various reactions.

4.1 Definition of Zeolite

Zeolites are mainly compounds of naturally-occurring aluminosilicate minerals with symmetrically stacked alumina and silica tetrahedra which result in an open and stable three dimensional crystalline structure (similar to honey comb) with a negative charge. They have a three-dimensional framework structure bearing $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ coordination polyhedra linked by all their corners. Their frameworks generally are very open and contain channels and cavities in which are located water molecules and cations. Water molecules are readily lost and regained when the zeolites are heated and cations often have a high degree of mobility giving rise to easy ion exchange. In their channels and cavities they are able to selectively take up some molecules into porous structure. The negative charge within the pores is neutralized by positively charged ions (cations) such as sodium. Zeolites can be classified into two types such as natural and synthetic zeolite.

There are 39 kinds of natural zeolites and about 100 kinds of synthesized zeolites (Dyer, 1988). Natural zeolites are formed by hydrothermal transformation of basalt, volcanic ash, and pumice which can be found e.g. in basalt cavities and in large sedimentary deposits. The most important industrial natural zeolites are clinoptilolite, mordenite, chabazite, and erionite. Synthesized zeolites are synthesis of crystalline from an inhomogeneous gel, created from a silica sources and an alumina sources, combined with water under high pH conditions generated by hydroxyl ion concentrations. Control of the SiO_2:Al_2O_3 ratio in this gel qualifies the final framework composition of the product taken into the zeolite composition.

Synthetic zeolite is the zeolite A with a molecular ration of one silica to one alumina to one sodium cation. The zeolite A synthesis produces precisely duplicated sodalite units which have 47% open space, ion exchangeable sodium, water of hydration and electronically charged pores.

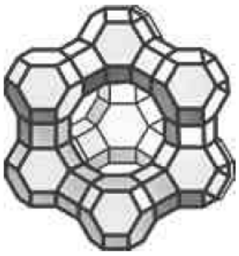


Figure 10 Structure of synthetic zeolite A

4.2 Structure of zeolites

Zeolites have framework structures constructed by joining $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ coordination polyhedra. These tetrahedra are assembled together so that the oxygen at each corner is shared with an identical tetrahedron, Si or Al, as shown in Figure 11.

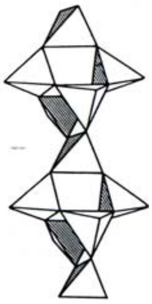


Figure 11 The tetrahedra linked together to create a three-dimensional structure

Source: Dyer (1988)

Composition of zeolite consist of Si, Al, and O positions in space relative to each other and excluding cations and water molecules sited within cavities and channels of framework.

Zeolites are a porous solid and as promoters in liquid-phase organic reactions provide some advantages:

1. Easy to separate products from solids by means of a sample procedure of filtration.
2. Adsorption or inclusion of reagent molecules into the small pores of solids with nanometer dimensions organizes the molecules in close proximity to lower the activation entropy of reaction.
3. The coexisting acid and base sites on solid surfaces accelerate organic reactions.
4. Pore structures of the solid discriminate between reactant molecules with respect to molecular dimensions.

4.3 Natural zeolite

In nature, the zeolites are often formed where volcanic rock of specific chemical composition is immersed in water so as to leach away some of the components. The composition and pore size depend upon what kinds of rock minerals are involved.

Natural zeolite formed, as a result of the chemical reaction between volcanic glass and saline water. Temperatures favoring the natural reaction range from 27°C to 55°C, and the pH is typically between 9 and 10. Nature requires 50 to 50,000 years to complete the reaction. Naturally occurring zeolites are rarely phase-pure and are contaminated to varying degrees by other minerals (e.g. Fe^{2+}, SO_4^-, quartz, other zeolites, and amorphous glass). For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.

The alumina and silica from the ash stack into a stable, open and three dimensional honey-comb structure. There are over forty other natural zeolite structures. For example, clinoptilolite (clino) has a silica to alumina ratio of 5 to 1, while chabazite has a ratio of 2 to 1.

All commercially useful zeolites owe their value to one or more of three properties: adsorption, ion exchange, and catalysis. But these properties must use synthetic zeolite.

Mordenite (MOR) is a kind of natural zeolite. Their structure type is MOR and based upon the 5-1 units in SBU's. The 5-1 units are linked into a series of chains joined together to form major channels, one restricted by 12 oxygen windows and one by 8 oxygen windows.

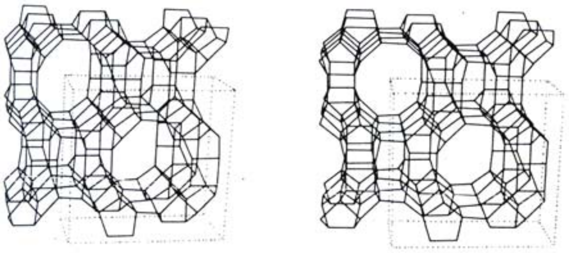


Figure 12 The structure of mordenite

Source: Dyer (1988)

Mordenite is found widespread in industrial applications as highly selective adsorbents, ion exchangers and, most importantly, catalysts of exceptionally high activity and selectivity in a wide range of reactions.

Researchers have studied the structure of mordenite. Korkuna *et al.* (2005) characterized mordenite using adsorption, AFM, FTIR, and TG–DTA methods. The initial natural mordenite has small specific surface area which increases significantly after their modification. The results of TG data show the presence of several types of water, and larger amounts of water desorbed from H-forms of mordenite up to 120ºC that can be caused by stronger changes in the mordenite structure

Over the past several years, there has been increasing interest in the use of thermoplastics as matrices for composite materials. Fillers such as $CaCO_3$, silica, clays, and silver have been used in composite preparations. Özmihçi *et.al.* (2001) investigated the preparation and characterization of natural zeolite–polypropylene composites proposing natural zeolite from Gördes region as alternative filler to $CaCO_3$. Efficient mixing of zeolite and PP with compounding extruders and then the film extrusion would give better distribution of fillers and voids around fillers. The crystallinity of the films with zeolite was higher than PP because zeolites act as nucleating agents. Although the start of the thermal degradation of PP was retarded by zeolite, PP with zeolite degraded at faster rate than pure PP once the degradation started.

Different types of zeolite minerals, either natural (e.g., clinoptilolite, mordenite, habazite) or synthetic (e.g., A type, X type, Y type), have been used as particulate fillers. Pehlivan *et.al.* (2006) studied the effect of pure and silver exchanged natural zeolite on the thermal degradation kinetics of polypropylene (PP). Clinotilolite, a natural zeolitic tuff, was used as the filler material composite. The thermal characterization studies showed that the addition of the zeolite increased the crystallinity of the structure acting as a nucleating agent in the PP crystallization as well as retarding the degradation temperature of PP. It was found that at low silver concentrations, the zeolite behaved as a decelerating agent in PP degradation, however at higher silver concentrations, the composites degraded at a faster rate than pure PP. As a result, PP is much more susceptible to the thermal decomposition in the presence of silver exchanged zeolite compared to the pure zeolite.

Since natural zeolites are abundant and low-cost materials and have silica composition. Because silicas are reinforced fillers of rubber, hence they could be also use as alternative filler in the rubber industry.