Non-Black Fillers For Rubber

THE BIG 3

Calcium Carbonate

Kaolin Clay

Precipitated Silica

The non-black fillers for rubber are calcium carbonate, kaolin clay, precipitated silica, talc, barite, wollastonite, mica, precipitated silicates, fumed silica and diatomite. Of these, the three most widely used, by volume and by functionality, are calcium carbonate, kaolin clay and precipitated silica. These will be the subject of this presentation.

Non-Black Fillers For Rubber

FILLER BASICS

A rubber compound contains, on average, less than 5 lbs. of chemical additives per 100 lbs. of elastomer, while filler loading is typically 10-15 times higher. Of the ingredients used to modify the properties of rubber products, the filler often plays a significant role. Most of the rubber fillers used today offer some functional benefit that contributes to the processability or utility of the rubber product. Styrene-butadiene rubber, for example, has virtually no commercial use as an unfilled compound.

The Effects of Fillers Depend On:

Particle Size
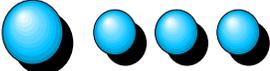
Particle Surface Area
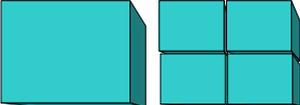
Particle Shape

Particle Surface Activity
**(Compatibility With/Adhesion To Matrix)**
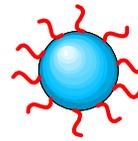
The characteristics which determine the properties a filler will impart to a rubber compound are particle size, particle surface area, particle surface activity and particle shape. Surface activity relates to the compatibility of the filler with a specific elastomer and the ability of the elastomer to adhere to the filler.

Functional fillers transfer applied stress from the rubber matrix to the strong and stiff mineral.

It seems reasonable then that this stress transfer will be better effected if the mineral particles are smaller, because greater surface is thereby exposed for a given mineral concentration. And if these particles are needle-like, fibrous or platy in shape, they will better intercept the stress propagation through the matrix.

A compound's physical/mechanical properties can be strongly influenced by the surface activity of the filler, which is the ability of the filler's surface to bond with the matrix. For instance, an air gap between a filler particle and the matrix represents a point of zero strength.

Particle Size

Smaller **is Better**

>10,000 nm (10μm): Degradants
1000-10,000 nm (1-10μm): Diluents
10-1000 nm (0.1-1μm): Semi-reinforcing
10-100 nm (0.01- 0.1μm): Reinforcing

nm

5000 — Non-Reinforcing

1000 —

500 — Semi-Reinforcing

100 —

50 —

Reinforcing

Barium Sulfate
Talc
Calcium Carbonate (dry ground)

Calcium Carbonate (wet ground)
Soft Clay

Hard Clay
Precipitated Calcium Carbonate

Precipitated Silica
Fumed Silica

N990
N765
N550
N330
N220

If the size of the filler particle greatly exceeds the polymer interchain distance, it introduces an area of localized stress. This can contribute to elastomer chain rupture on flexing or stretching. Fillers with particle size greater than 10,000 nm (10 μm) are therefore generally avoided because they can reduce performance rather than extend or reinforce. Fillers with particle between 1,000 and 10,000 nm (1 to 10 μm) are used primarily as diluents and usually have no significant effect, positive or negative, on rubber properties. Semi-reinforcing fillers range from 100 to 1000 nm (0.1 to 1μm). The truly reinforcing fillers, which range from 10 nm to 100 nm (0.01 to 01 μm), can significantly improve rubber properties.

Particle Size
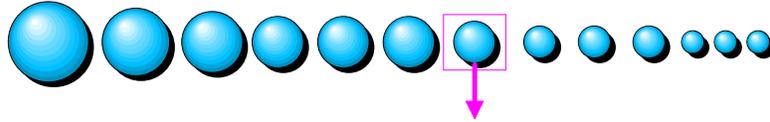
Median Particle Size = Half the particles are larger, half are smaller
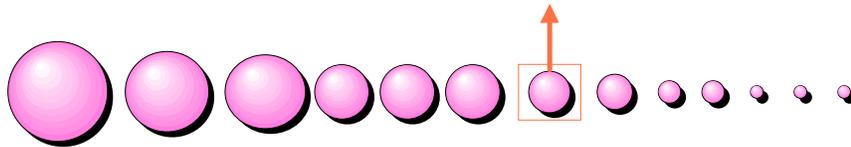
Size (top and bottom) Counts

The particle size of non-reinforcing and semi-reinforcing fillers are usually reported in terms of median size, with half the particles larger and half smaller. This can inaccurately represent particle size distribution, as suggested above. Both distributions have the same median size, but the lower one may, for example, have particles large enough to compromise compound properties.

Particle Size

What "size" is this particle?

450 nm

600 nm

0.72 nm
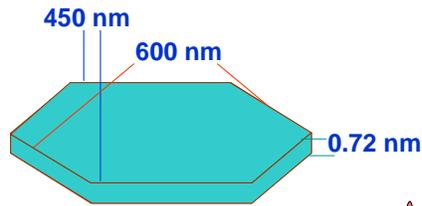
Equivalent Spherical Diameter
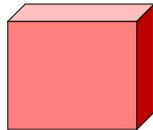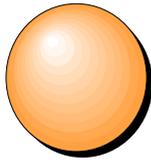
These are the same size!

In most cases, particle size is actually measured as equivalent spherical diameter rather than actual size or dimensions, since most automated particle sizing instrumentation will match the behavior of a particle to that of an idealized round particle of specific diameter. For round or block-shaped particles, such as natural calcium carbonate, there is no significant difference. For platy minerals, such as clay, talc and mica, or needle-like minerals, such as wollastonite, the equivalent spherical diameter will inaccurately represent actual particle dimensions.

Particle Size

Needle/Fiber Aspect Ratio:
Ratio of mean length to mean diameter

Plate Aspect Ratio:
Ratio of mean diameter of a circle of the same area as the face of the plate to the mean thickness of the plate
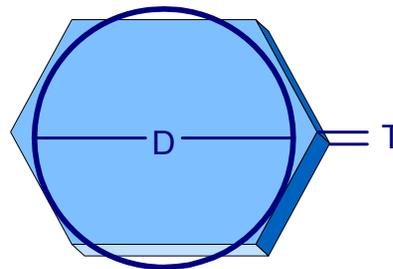
For platy and needle shaped fillers, the particle aspect ratio may be at least as useful as particle "size". For kaolin clay and other platy minerals, this is the ratio of the diameter of a circle with the same are as the face of the plate to the thickness of the plate. For needle- and fiber-shaped fillers, the aspect ratio is the ratio of length to diameter.

Particle Surface Area

Bigger Is Better
From smaller particle size
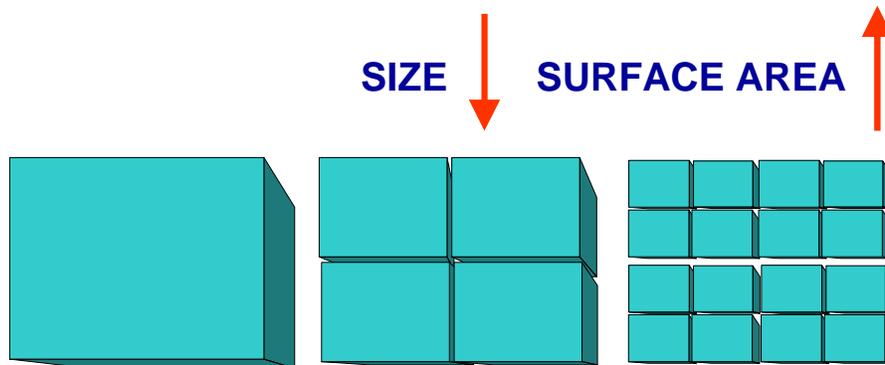
SIZE   SURFACE AREA

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

Particle Surface Area

	Median Size, μm	Surface Area, m²/g
Ground Calcium Carbonate	1-5	2-4
Precipitated Calcium Carbonate	0.7-1.0	8-10
Ultra-Fine Ppt Calcium Carbonate	0.07-0.09	19-28
Soft Clay	1.2-2.0	15-20
Hard Clay	0.2-0.5	20-26

The shape of the particle is also important. Particles with a planar shape have more surface available for contact with the rubber matrix than isotropic particles with an equivalent particle diameter. Among the calcium carbonates, for example, only the finest precipitated grades can expose a surface area equivalent to the surface area of hard clay.

Particle Shape

Broader (and Longer) is Better

Isometric: calcium carbonate

Platy: kaolin, talc, mica

Acicular: wollastonite

Fiber: glass fiber

**Cluster/Chain:** ppt silica, carbon black

Isometric fillers that are approximately round, cubic or blocky in shape, are considered low aspect ratio. Low, in this context, means less than about 5:1 aspect ratio. Platy, acicular (needle-shaped) and fibrous fillers are considered high aspect ratio.

Aspect ratio is not applied to carbon black and precipitated silica. The primary particles of these fillers are essentially spherical, but these spheres aggregate in such a way that the functional carbon black and precipitated silica filler "particles" are aggregated chains or bundles. The anisometry of these fillers is described in terms of "structure", which incorporates aggregate shape, density and size. The higher the structure, the greater the reinforcement potential.

Particle Surface Activity
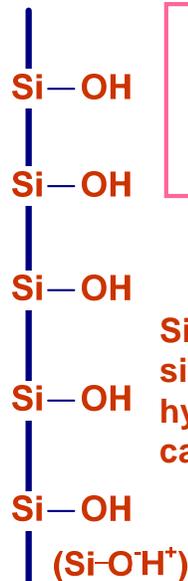
More is Better

Active sites on filler surface
Reactive surface treatments

Si—OH
Si—OH
Si—OH

Silanols on kaolin and silica surfaces can hydrogen bond, and they can react as acids.

Si—OH
Si—OH
(Si-O⁻H⁺)
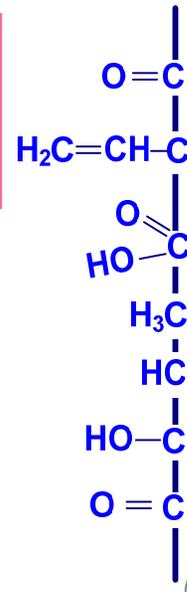
A filler can offer high surface area, high aspect ratio and small particle size, but still provide relatively poor reinforcement if it has low specific surface activity. In the simplest terms, this means the affinity for and ability to bond to the rubber matrix. Carbon black particles, for example, have carboxyl, lactone, quinone, and other organic functional groups which promote a high affinity of rubber to filler. This, together with the high surface area of the black, means that there will be intimate elastomer-black contact. The black also has a limited number of chemically active sites (less than 5% of total surface) which arise from broken carbon-carbon bonds because of the methods used to manufacture the black. The close contact of elastomer and carbon black will allow these active sites to chemically react with elastomer chains. The non-black fillers generally offer less affinity and less surface activity toward the common elastomers. Clay and silica surfaces are hydrophilic, but still react as acids and are capable of forming hydrogen bonds. The affinity and activity of non-black fillers in relation to elastomers can be improved by certain surface treatments.

Particle-Matrix Compatibility

Poor contact

Good contact — Matrix wetting

Bonded — Matrix adhesion
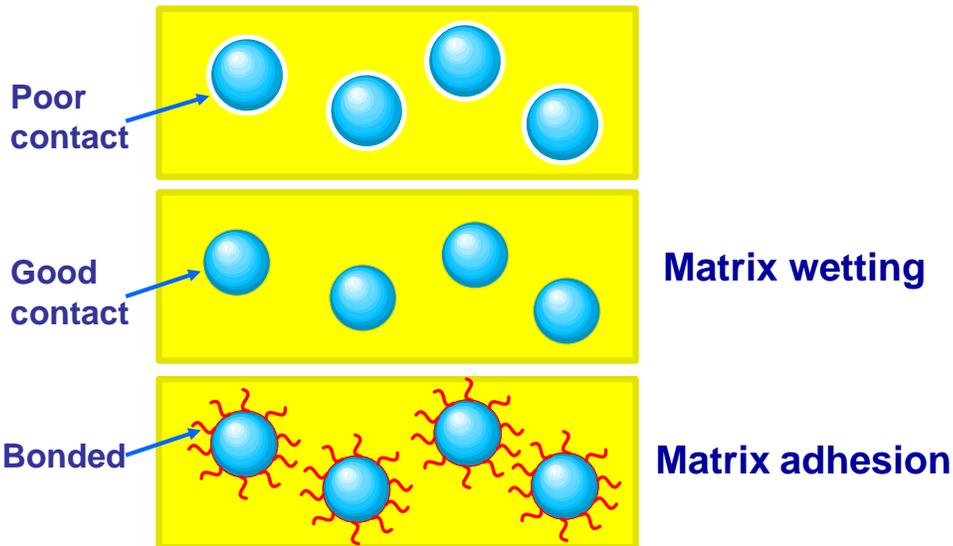
Regardless of filler size and shape, intimate contact between the matrix and mineral particles is essential, since air gaps represent points of permeability and zero strength. The surface chemistry of the filler will determine affinity for the matrix, or the ability of the rubber matrix to "wet" the filler surface. It is easier for most elastomers to "wet" the naturally hydrophobic carbon black surface, as compared to the naturally hydrophilic surfaces of most non-black fillers. This advantage of carbon black complements its reactivity. The hydrophobicity and the reactivity of most non-black fillers can be improved with suitable surface coatings.

Particle-Matrix Compatibility

For calcium carbonate:

Wettability is improved with stearic acid

**Adhesion is improved with maleated polybutadiene**
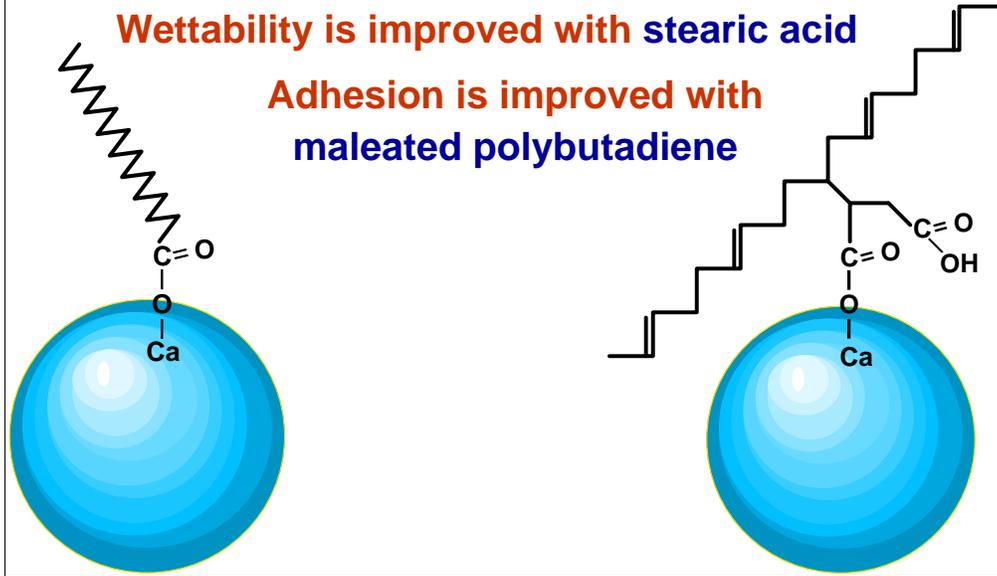
The conventional surface treatment for calcium carbonate is stearic acid, which improves the hydrophobicity and "wettability" of the filler, but does not provide for filler-matrix adhesion. Maleated polybutadiene (polybutadiene with grafted maleic anhydride functional groups) has been used as an *in situ* coupling agent to improve matrix adhesion to calcium carbonate fillers. Precipitated calcium carbonate is also available pre-treated with maleated polybutadiene.

Particle-Matrix Compatibility

Silica and silicate fillers have active surface silanols

ATH has active surface aluminols

KAOLIN has both

Legend: = O = Shared O = OH = Si = Al

Organosilanes are fond of hydroxyls
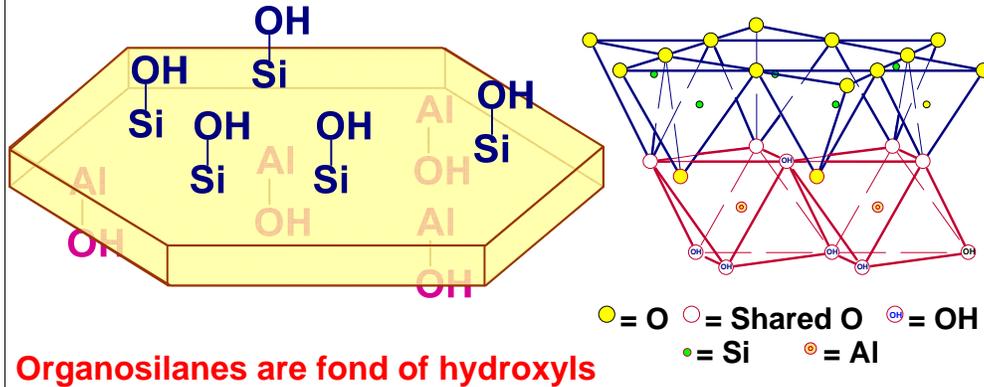
The surface hydroxyls on most non-black fillers allow for particle treatment with hydrophobizing and/or coupling grades of organosilanes.

Particle-Matrix Compatibility

Surface Treatments/Modifiers:
Silanes – RSiX$_3$

X is hydrolysable group (e.g., methoxy, ethoxy)

R is a organofunctional group (e.g., amino, mercapto, tetrasulfide, epoxy)

The general chemical structure of organosilanes is RSiX$_3$, where X is a hydrolysable group, such as methoxy or ethoxy, and R is a nonhydrolysable organofunctional group. The organo group may be reactive toward the rubber matrix, or it may be unreactive and serve as a hydrophobe or wetting agent.

Particle-Matrix Compatibility

Silane-Mineral Reaction:
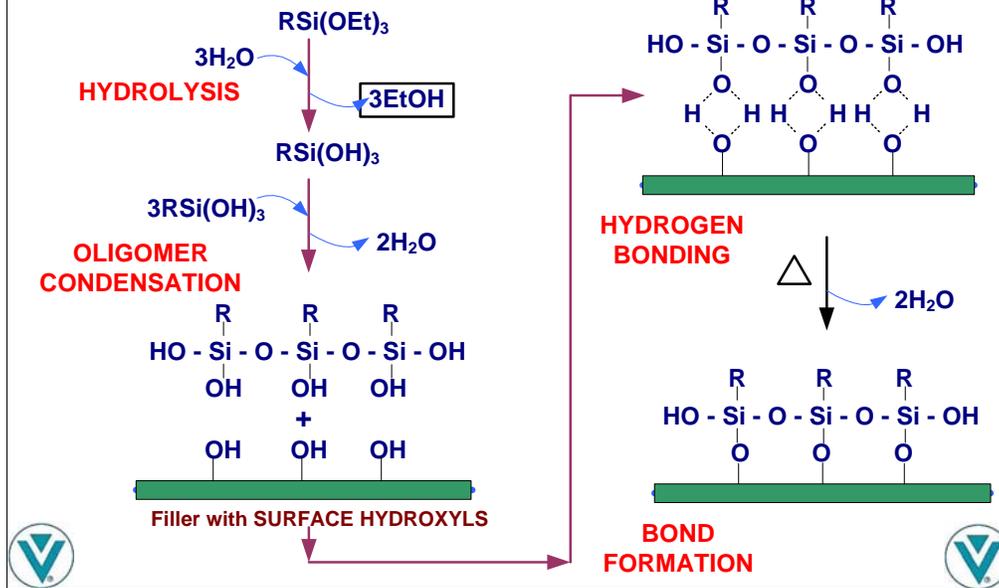
Modification with organosilane depends on the ability to form a bond with silanol groups, -Si-OH, and/or aluminol groups (-Al-OH) on the filler surface.

The hydrolysis of an alkoxysilane forms silanetriol and alcohol. The silanetriol slowly condenses to form oligomers and siloxane polymers. The -Si-OH groups of the hydrolyzed silane initially hydrogen bond with -OH groups on the filler surface. As the reaction proceeds, water is lost and a covalent bond is formed. The reaction of hydrolyzed silane with filler surface -OH can ultimately result in the condensation of siloxane polymer, encapsulating the filler particle if sufficient silane is used. Once the filler is reacted with the silane it exposes an organophilic or organofunctional surface for interaction with the rubber matrix. For pretreated fillers, silane treatment levels are typically 0.5 to 3.0% by weight.

SILANES

Sulfur Cure

$CH_3O-Si(CH_2)_2-SH$ with OCH_3 / OCH_3 groups — **Mercapto**

$EtO-Si(CH_2)_3-SCN$ with EtO / EtO groups — **Thiocyanate**
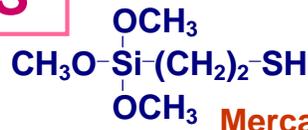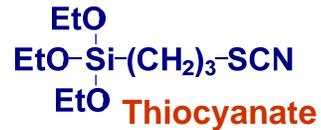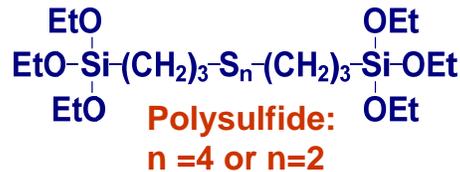
$EtO-Si(CH_2)_3-S_n-(CH_2)_3-Si-OEt$ with EtO/EtO and OEt/OEt groups — **Polysulfide: n = 4 or n = 2**

Non-Sulfur Cure

$EtO-Si(CH_2)_3-NH_2$ with EtO / EtO groups — **Amino**
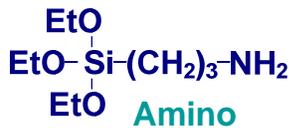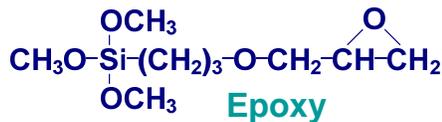
$CH_3O-Si(CH_2)_3-O-CH_2-CH-CH_2$ with OCH_3 / OCH_3 groups and epoxide O — **Epoxy**

Sulfur-functional silanes are usually used in sulfur-cured rubber compounds, in particular those with mercapto, polysulfide and thiocyanate active groups. The silanes typically used in non-sulfur-cured compounds have amino or epoxy functionality.

General Filler Effects

Increasing Surface Area
(Decreasing Particle Size)

Higher: Mooney viscosity, tensile strength, abrasion resistance, tear resistance, and hysteresis.

Lower: resilience
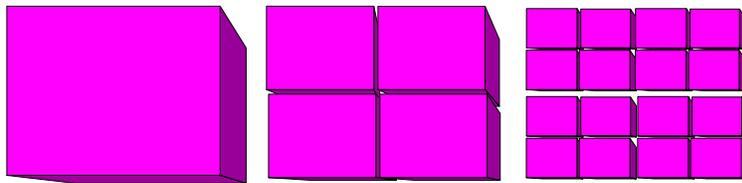
The principal characteristics of rubber fillers – particle size, shape, surface area and surface activity – are interdependent in improving rubber properties. In considering fillers of adequately small particle size to provide some level of reinforcement, the general influence of each of the other three filler characteristics on rubber properties can be generalized as follows:

Increasing surface area (decreasing particle size) gives: higher Mooney viscosity, tensile strength, abrasion resistance, tear resistance, and hysteresis; lower resilience.

General Filler Effects

Increasing Surface Activity
(Better Filler-Rubber Bond)

Higher: abrasion resistance, chemical adsorption or reaction, modulus, and hysteresis (except silated fillers).
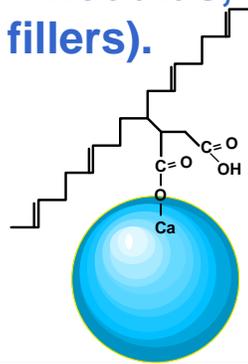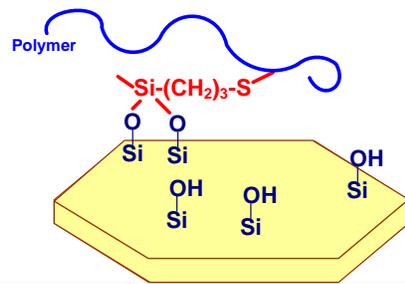
Increasing surface activity (including surface treatment) gives: higher abrasion resistance, chemical adsorption or reaction, modulus, and hysteresis (except for silane-treated fillers).

General Filler Effects

Increasing Aspect Ratio/Structure

Higher: Mooney viscosity, modulus, and hysteresis.

Lower: resilience and extrusion shrinkage; longer incorporation time.
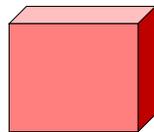
Increasing aspect ratio or structure gives: higher Mooney viscosity, modulus and hysteresis; lower resilience and extrusion shrinkage; longer incorporation time.

Modulus: Resistance to stretching

Resistance to Stretching

Stretching Force

300% Elongation

Uncompouded elastomer: disentangle polymer chains, break weak inter-chain bonds

Vulcanized, unfilled elastomer: break sulfur crosslinks

The force required to stretch a defined specimen of rubber to a given percent elongation is measured as modulus. Most often, modulus is reported at 300% elongation (four times the original length). This can be alternatively viewed as the resistance to a given elongating force. For an uncompounded elastomer, elongation is primarily a function of stretching and disentangling the randomly oriented polymer chains and breaking the weak chain-chain attractions. Vulcanized, but unfilled, elastomers, for example, more strongly resist elongation because the sulfur crosslinks must be stretched and broken to allow chain extension and separation.

Tensile Strength:
Resistance to stretching rupture

Break

Elongation at Break
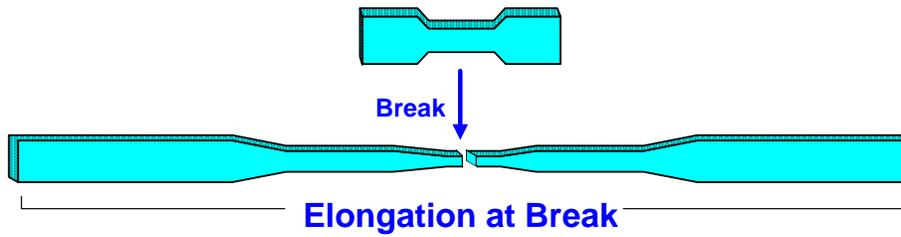
If stretching continues, rupture ultimately results.

Modulus/Tensile
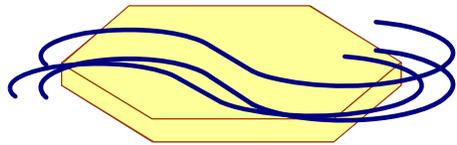
Viscous Drag

Low surface activity filler: Increases resistance to stretching via viscous drag.

High surface activity filler: Strongly resist stretching.
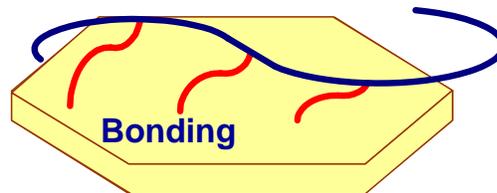
Bonding

The introduction of a filler into the vulcanizate provides additional resistance to elongation. A filler with low surface activity will increase resistance to elongation by the viscous drag its surface provides to the polymer trying to stretch and slide around it. Higher surface area, greater aspect ratio, and higher loading (the latter two effectively increasing the surface area exposed to the elastomer) will all increase the modulus. Fillers with strong chain attachments, through active sites or coupling agents, provide the most resistance to the chain extension and separation required for elongation.
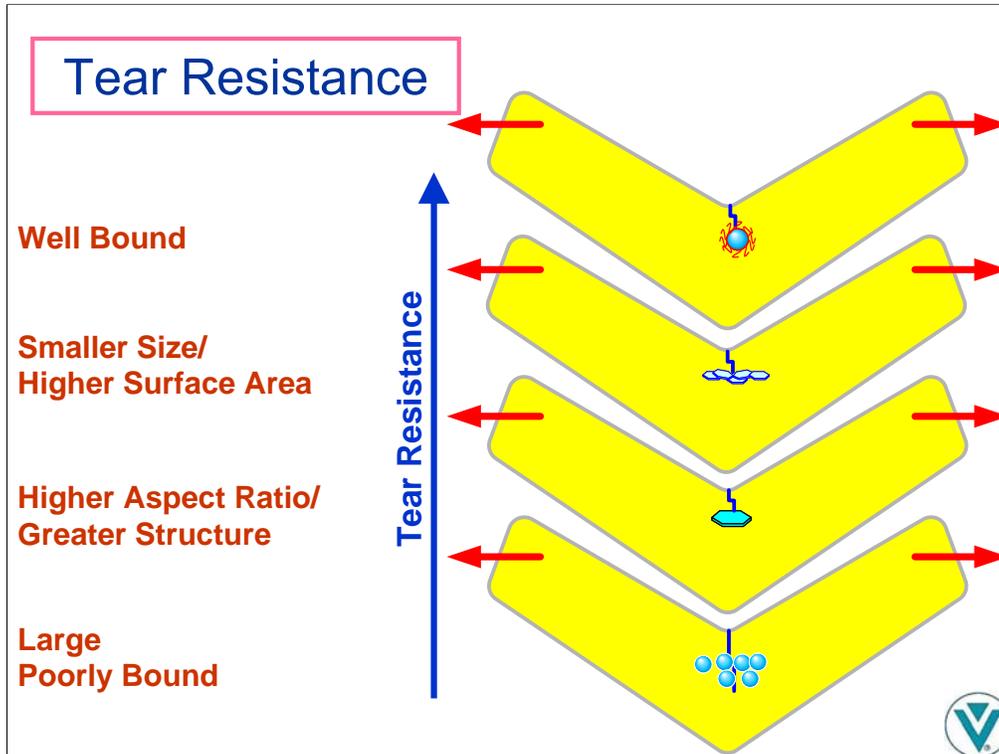
Tear resistance is essentially a measure of resistance to the propagation of a crack or slit under tension. Large or poorly bound fillers will act as flaws and initiate or propagate cracks under test conditions. Small particle size, high surface area, high surface activity and high aspect ratio allow the filler particles to act as barriers to the propagation of microcracks, in addition to providing the higher tensile strength required to resist failure.

Abrasion Resistance

Well Bound

Smaller Size/
Higher Surface Area

Higher Aspect Ratio/
Greater Structure

Large
Poorly Bound

Abrasion Resistance

Soft Edge of Depression
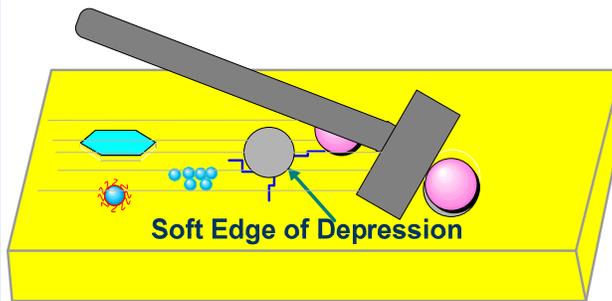
Filler particle are considerably harder than the surrounding matrix and can thus insulate the rubber against wear. Filler size, shape and matrix adhesion therefore also affect abrasion resistance. Loss of large or poorly bound filler particles by abrasion exposes the relatively soft surrounding elastomer matrix to wear. The effect is acute on the edge of the depression left by the dislodged particle. This is the area most susceptible to elongation, crack initiation and ultimate loss.

Resilience / Hysteresis (Heat Build-Up)

Filler Loading Reinforcement ↑ **Resilience** ↓

Except silated fillers

Resilience ↓ **Hysteresis** ↑
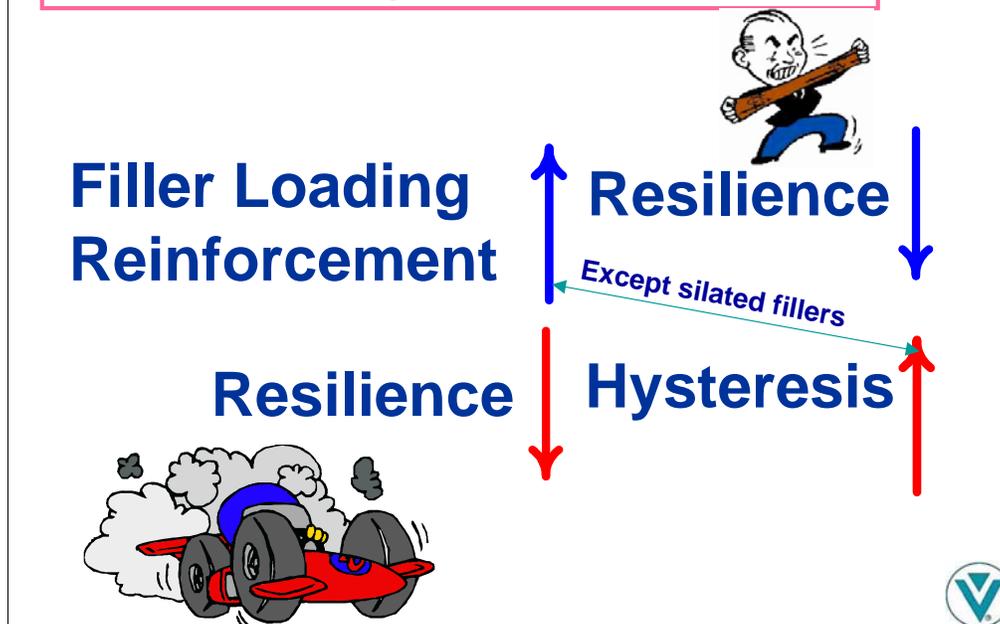
Resilience is essentially a measure of rubber elasticity – the ability to quickly return to the original shape following deformation. Unfilled elastomers are at their peak resilience because there is no obstacle to elastomer chain extension and contraction. The introduction of a filler creates such an obstacle in proportion to the strength of the particle-polymer interaction. A compound's resilience is therefore generally in inverse proportion to filler loading and reinforcement.

Resilience can be considered the ratio of energy release on recovery to the energy impressed on deformation. Hysteresis can be considered as the amount of impressed energy that is converted to heat instead of to mechanical energy as elastic rebound. In unfilled rubber the conversion to heat energy is related to the friction of elastomer chains sliding past each other. Fillers increase hysteresis from polymer-filler friction and the dislodging of polymer segments from filler surfaces. Reinforcing fillers, which adhere more strongly to the elastomer chains, usually provide the greatest increase in hysteresis. Notable exceptions are silane-treated kaolin and precipitated silica.
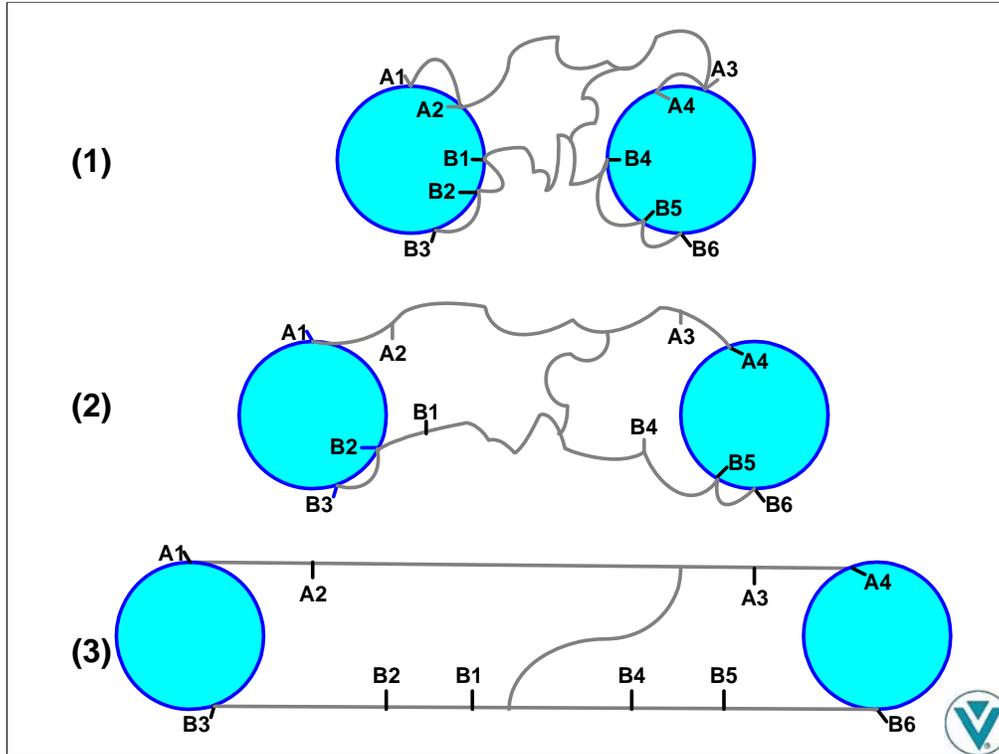
The effect of filler particles on the ability of the compound to stretch can be pictured as shown here. Before stretching, as in step 1, the elastomer chains are in random configuration. Chains A and B have multiple points of attachment to the filler particles, some loosely held by weak bonds, others strongly held by active sites. Under tension, resistance is the energy required to detach the chain segments from these active sites, as in steps 2 and 3.

The amount of energy required to attain maximum elongation, and then required to cleave chain-chain and chain-filler attachments, accounts for the tensile strength of a filled system of this type.
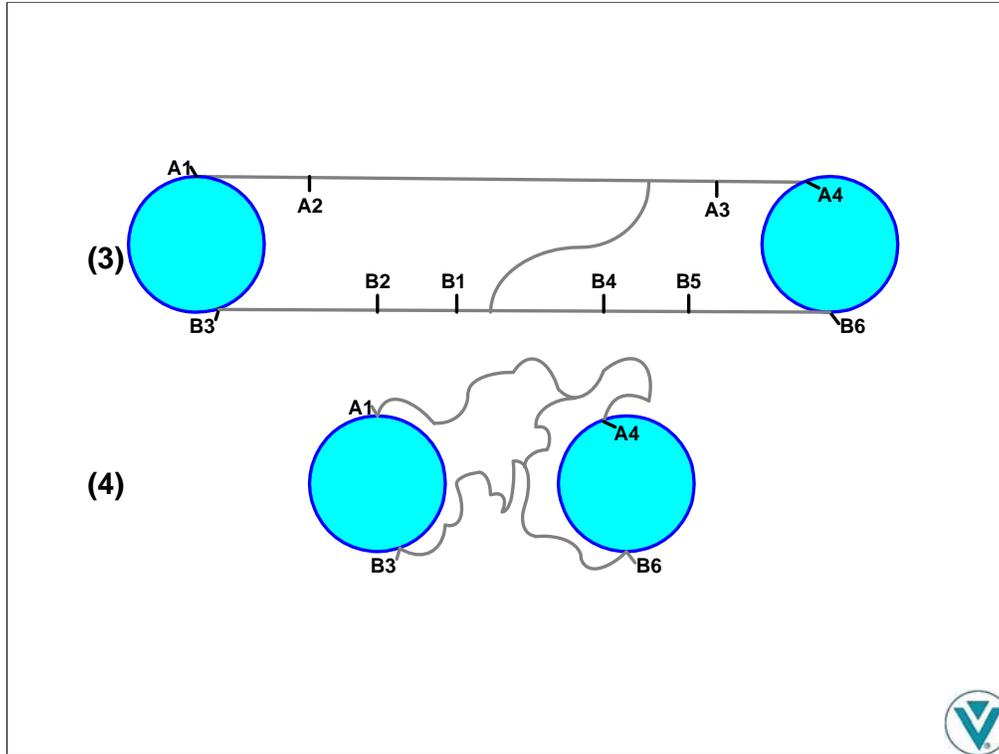
After the stretching force has been removed, the elastomer chains return to their preferred random orientation, as in step 4, except that now they have the minimum number of points of attachment to the filler as a consequence of having been extended in Step 3. Less force would now be required to return these chains to ultimate extension, because the intermediate points of attachment that existed in Steps 1 and 2 have been eliminated. This explains the phenomenon known as stress softening. With repeated stress-relaxation cycling, a decrease in modulus from the initial maximum is obtained. Stress softening is a temporary effect. After a period without strain, the rubber will recover most of its original modulus, as polymer segments reattach to the filler. A percentage of the original modulus can be permanently lost, however, due to irrecoverable chain and bond cleavage.

Non-Black Fillers For Rubber

THE BIG 3:
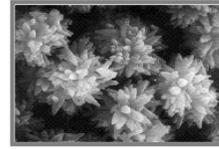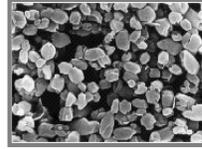
Calcium Carbonate

Kaolin Clay
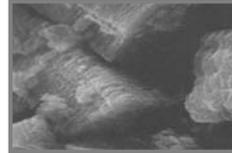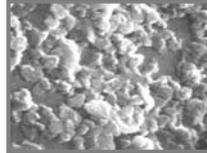
Precipitated Silica
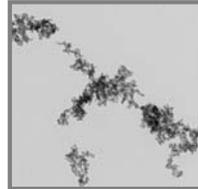
Calcium Carbonate

Ground calcium carbonate (GCC) – **Dry-ground: nominal 200 to 325 mesh. Wet-ground: FG; 3 to 12 μm median, 44 μm top, UFG; 0.7 to 2 μm median, 10 μm top.**

**LOW COST
HIGH LOADINGS**

**LOW ASPECT RATIO
LOW SURFACE AREA
LOW SURFACE ACTIVITY**

Photomicrograph: Minerals Technologies
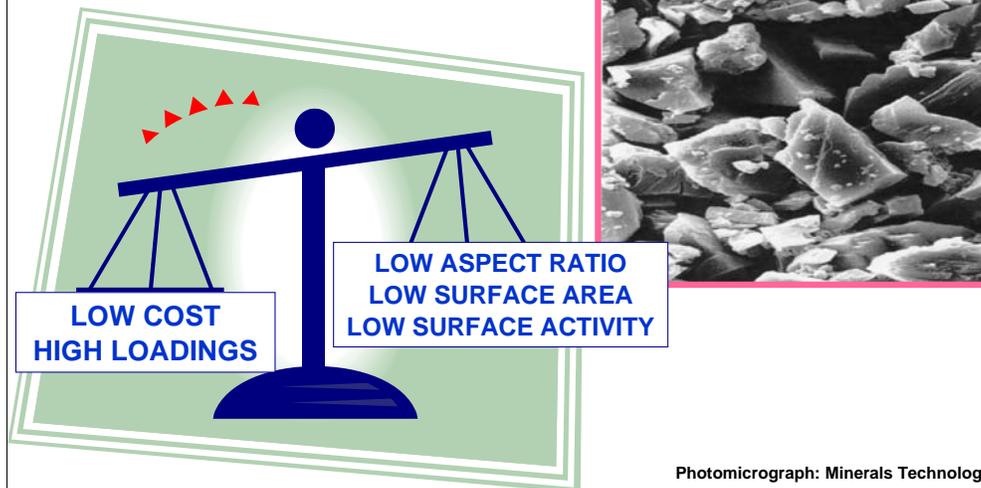
Calcium carbonates for rubber, often referred to as "whiting", fall into two general classifications. The first is wet or dry ground natural limestone, spanning average particle sizes of 5000 nm down to about 700 nm. The second is precipitated calcium carbonate (PCC) with fine and ultrafine products extending the average particle size range down to 40 nm.

The ground natural products used in rubber are low aspect ratio, low surface area and low in surface activity. They are widely used, nevertheless, because of their low cost, and because they can be used at very high loadings with little loss of compound softness, elongation or resilience. This follows from the relatively poor polymer-filler adhesion potential, as does poor abrasion and tear resistance. Dry-ground limestone is probably the least expensive compounding material available, and more can be loaded into rubber than any other filler. Water-ground limestone is somewhat more expensive, but offers better uniformity and finer particle size.

Calcium Carbonate

Precipitated calcium carbonate (PCC) − **Fine: 0.7 μm median; Ultrafine: 0.07 μm median.**

Precipitated calcite
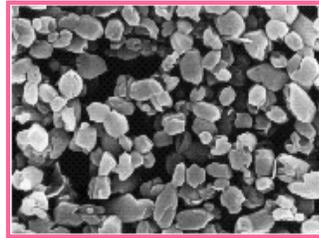
Prismatic
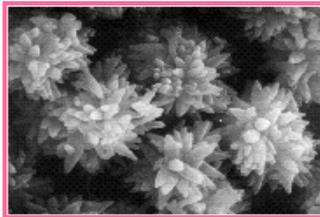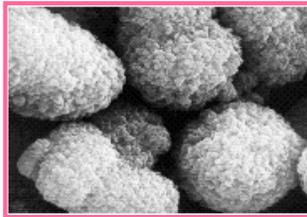
Scalenohedral   **Spherical**   **Clustered Aragonitic**
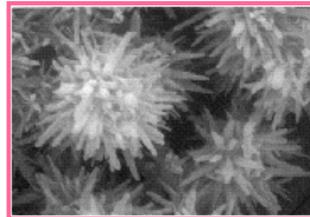
Photomicrographs: Minerals Technologies

The much smaller size of precipitated calcium carbonates provides a corresponding increase in surface area. The ultrafine PCC products (<100 nm) can provide surface areas equivalent to the hard clays. Manipulation of manufacturing conditions allows the production of precipitated calcium carbonates of several distinct particle shapes. Precipitated calcite, with isometric prismatic particles, is the form generally used in rubber compounding.

Calcium Carbonate

	GCC	PCC	UF-PCC
Avg. particle size, μm	3.0	0.7	0.07
BET surface area, m^2/g	4	8	19
Loading, phr	175	175	150
Hardness	70	75	70
M300, MPa	1.7	2.9	3.8
Tensile, MPa	4.5	7.2	13.0
Crescent Tear, ppi	45	125	200

SBR1502-100; ZnO-5; stearic acid-1; Cumar® MH 1½-15; sulfur-2.75; Methyl Tuads®-0.35; Altax®-1.5

Specialty Minerals

This table compares PCC products to a fine ground natural calcium carbonate. Tensile strength, tear strength, and modulus are all a function of particle size, while hardness is nearly unaffected.

Cumar is a registered trademark of Neville Chemical Company

Tuads and Altax are registered trademarks of R.T. Vanderbilt Company, Inc.

Kaolin Clay

A "platy" aluminum silicate

Plates tend to overlap ("books") with H bonding of octahedral layer OHs to tetrahedral layer Os. Separation into individual plates requires mechanical shear (delaminated clay).

0.72 nm

KAOLIN

Tetrahedral Silica Layer

Dioctahedral Alumina Layer

○ = O ○ = Shared O ◉ = OH
• = Si ◉ = Al
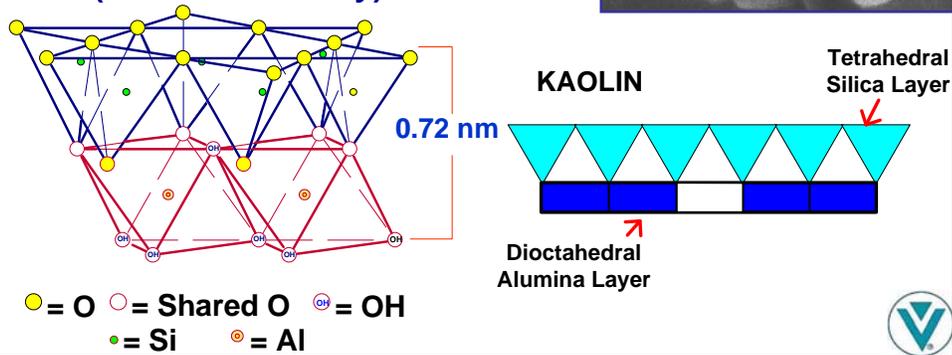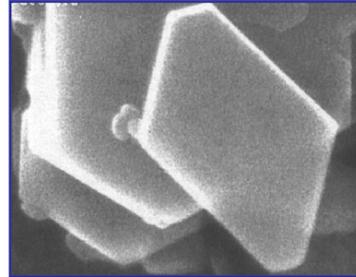
Kaolin clay is a platy aluminosilicate. Its continuous sheet structure produces thin particles which exist in nature as overlapping flakes. These can occur as "books" which under magnification resembling stacks of paper. Kaolin crystals are bound via hydrogen bonding of the octahedral layer hydroxyl face of one plate to the tetrahedral layer oxygen face of the adjacent plate. Separation into individual clay plates is therefore difficult, but can be accomplished by mechanical means to produce delaminated kaolin.

Kaolin Clay

Rubber Clays

Hard clay: 0.25-0.5 μm (250-500 nm)

Very fine-grained. Provides good tensile properties, stiffness and abrasion resistance. Improves properties of GCC compounds. Low cost substitute for portion of carbon black or ppt silica without loss of properties.

Soft clay: 1-2 μm (1000-2000 nm)

Larger flakes, low reinforcing effect. Higher loadings, quicker extrusions.

Rubber filler clays are classified as either "hard" or "soft" in relation to their particle size and stiffening affect in rubber. A 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 loadings (for economy) and faster extrusion rates are more important than strength.

Kaolin Clay

	Hard Clay	Soft Clay	GCC
Median particle size, μm	0.3	1.3	3.0
BET surface area, m^2/g	23	16	3
Hardness, Shore A	61	62	53
M300, MPa	3.2	2.8	1.2
Tensile, MPa	12.8	8.8	1.6
Die A Tear, kN/m	24.6	20.2	5.3

SBR1006-100; filler-100; Vanfre® AP2-2; ZnO-5; stearic acid-2; Agerite® Stalite® S-1.5; sulfur-2; Methyl Cumate®-0.1; Altax®-1.5

Vanderbilt

This comparison of hard clay, soft clay and ground calcium carbonate graphically illustrates the affects of particle size, surface area and shape on reinforcement of an SBR compound.

Agerite, Vanfre, Tuads and Altax are registered trademarks of R.T. Vanderbilt Company, Inc.

Stalite is a registered trademark of Emerald Polymer Additives, LLC

Kaolin Clay

N990 Black	100 phr		
Hard Clay		130 phr	104 phr
N650 Black			20 phr
Hardness	70	70	78
M300, MPa	5.3	1.9	7.0
Tensile, MPa	10.0	14.2	18.6
Die C Tear, kN/m	14	16	18
Abrasion Index	23	27	27

SBR1502-100; ZnO-5; stearic acid-1; TMTD-0.1; MBTS-1.5; sulfur-3; TEA-3 (clay cmpds only); filler-50 volumes

More hard clay than soft is used in rubber because of its semi-reinforcing effect and its utility as a low cost complement to other fillers. It is used to improve the tensile and modulus of ground calcium carbonate compounds and will substitute for a portion of the more expensive carbon black, as seen here, or precipitated silica in certain compounds, without sacrificing physical properties.

Kaolin Clay

150 m²/g Silica	45 phr	30 phr	30 phr
Hard Clay		23 phr	
GCC			23 phr
Hardness	**66**	**65**	**65**
M300, MPa	**3.6**	**3.1**	**3.1**
Tensile, MPa	**20.5**	**20.9**	**20.4**
Trouser Tear, kN/m	**27**	**25**	**8**
Abrasion Index	**68**	**67**	**48**

SBR1502-100; DEG-3; stearic acid-1; Zn carbonate-1; sulfur-2; MBTS-0.7; MBT-0.4; TMTM-0.3; DPG-0.1

PPG

This equal filler volume study demonstrates the advantage of hard clay, as opposed to ground calcium carbonate, in replacing a portion of the precipitated silica without significantly compromising compound properties.

Kaolin Clay

Airfloat clay: Dry-ground kaolin that has been air separated to minimize impurities and control particle size distribution.

About 80% of the kaolin used in rubber is airfloat hard clay.
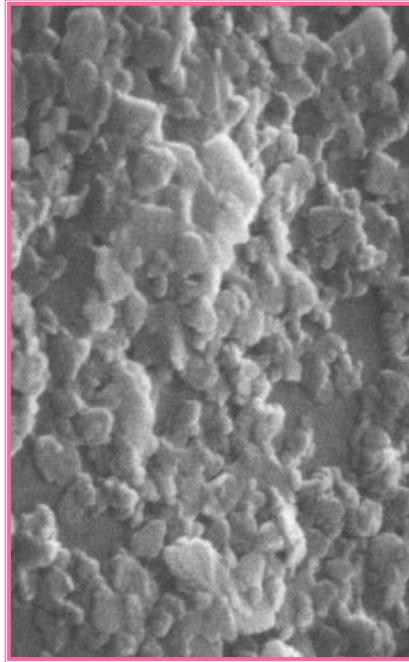
In addition to the designation "hard" vs "soft", which describes their general performance profile in rubber, kaolin clays are also classified according to to how they have been processed.

Airfloat clay is dry-ground kaolin that has been air-separated to minimize impurities, such as quartz, mica and bentonite, and control the particle size distribution. About 80% of the kaolin used in the rubber industry is airfloat hard clay.

Kaolin Clay

Water-washed clay: Soft clay that has been slurried in water and centrifuged or hydrocycloned to remove impurities and produce specific particle size fractions. Often bleached or magnetically separated for brightness.
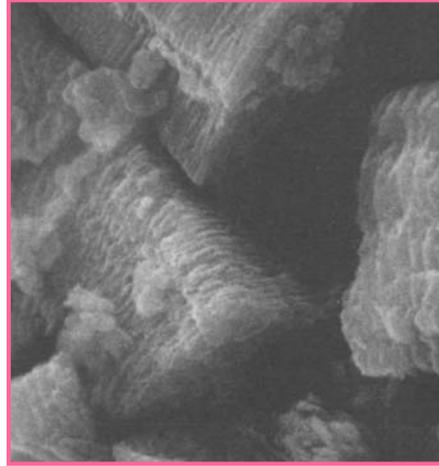
Water-washed clay, usually soft clay, has been slurried in water and centrifuged or hydrocycloned to remove impurities and produce specific particle size fractions. To improve brightness, these clays are often chemically bleached and/or subjected to high intensity magnetic separation to remove dark impurities.

Kaolin Clay

Delaminated clay: Coarse clay fraction from water-washing is milled to reduce the kaolinite stacks into thin, wide individual plates.
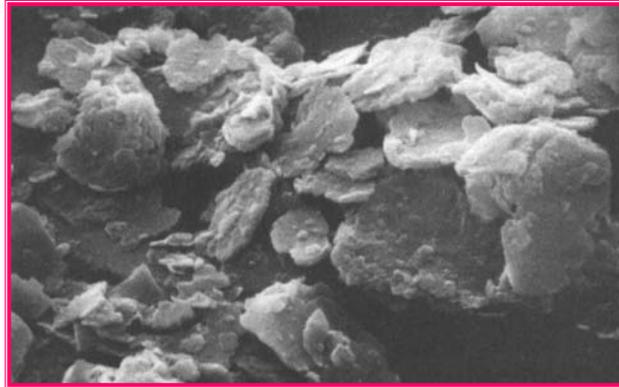
To produce delaminated clay, the coarse clay fraction from water-washing is attrition-milled to break down the clay stacks into thin, wide individual plates.

Kaolin Clay

	Delaminated Clay	Hard Clay
Hardness	74	70
M300, MPa	16.5	15.2
Tensile, MPa	21.2	20.7
Olsen Stiffness	27	17
Die Swell	100	150

NR (smoked sheets)-100; clay-156; ZnO-5; stearic acid-4; Cumar® MH 2½-7.5; sulfur-3; MBT-1

Huber

Delaminated clay is the most planar or anisometric form of kaolin clay available and is preferred when high stiffness and low die swell are needed, as shown in this comparison of delaminated clay to hard clay.

Cumar is a registered trademark of Neville Chemical Company

Kaolin Clay

Calcined clay: The kaolin is heated to partially remove surface hydroxyls. Used in wire and cable coverings for excellent dielectric and water resistance properties.
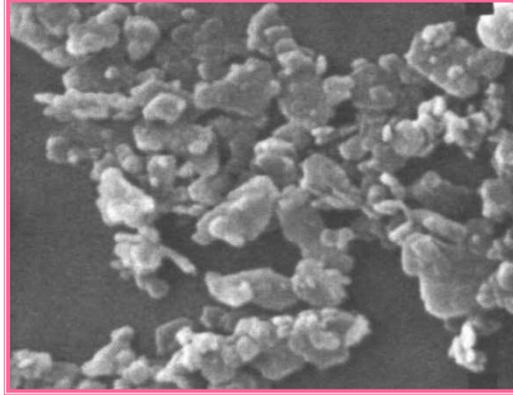

To produce calcined clay for filler uses, the kaolin, usually water-washed, is heated to partially remove surface hydroxyl groups. The partial or complete removal of surface hydroxyls provides a corresponding decrease in surface activity, and thus reinforcement, but calcined clay is commonly used in wire and cable coverings because it provides excellent dielectric and water resistance properties.

Kaolin Clay

Surface-treated clay: Surface modified to improve compatibility with other compound ingredients and to improve reinforcement.

Polymer

Si-(CH$_2$)$_3$-S
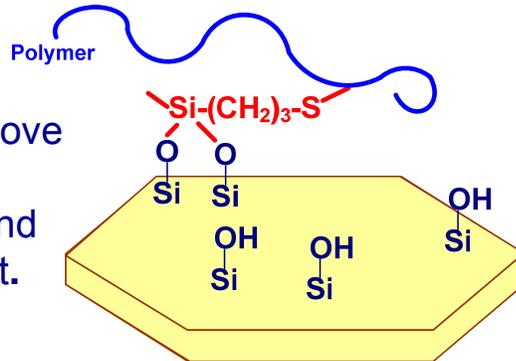
Surface-treated clays have had their surface chemistry modified, usually with organosilanes, to improve their compatibility with other compounding ingredients and to provide greater reinforcement.

Kaolin Clay

$$\begin{array}{ccc} OH & & O^-H^+ \\ | & = & | \\ Si & & Si \end{array}$$
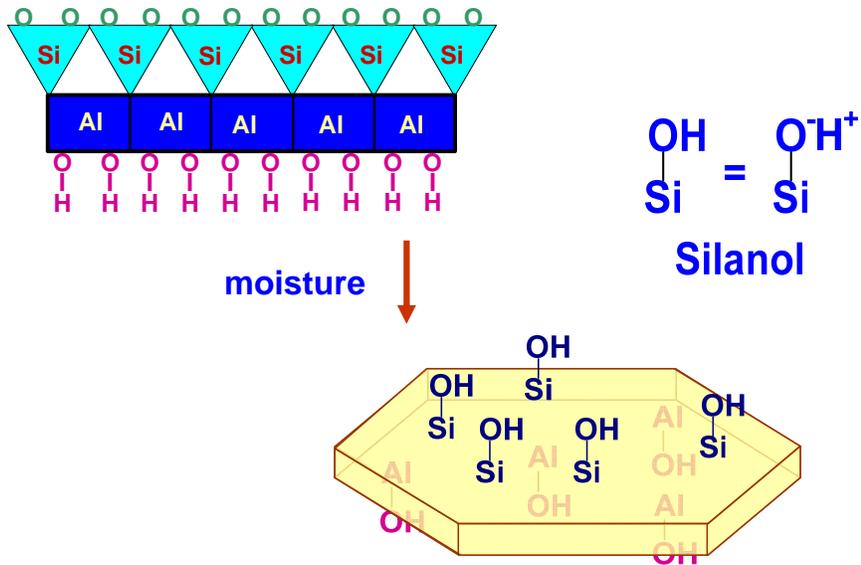
Silanol

moisture

Kaolin's surface silica (SiO_2) groups readily hydrolyze to silanols (-SiOH) in the presence of moisture. These silanol groups behave as acids (-SiO-H$^+$) and are chemically active. While this would normally be considered an advantage for a rubber filler, it can cause problems with other compounding ingredients.

Kaolin Clay
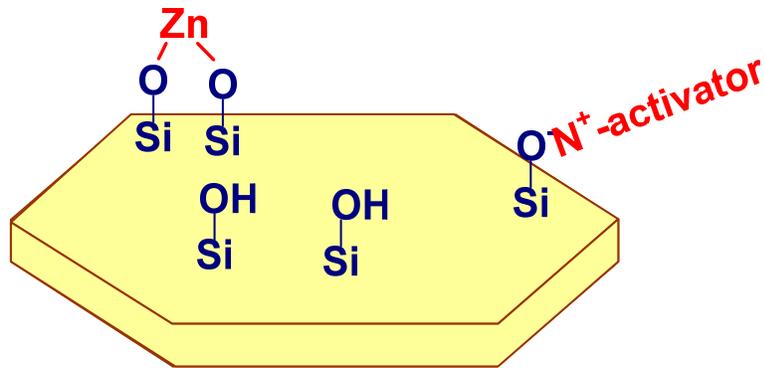
Silanols can interfere with sulfur cures:

The adsorption or reaction of accelerators by hard clay usually requires about a 15-25% increase in acceleration.

Silanols show similarities to carboxylic acid groups in their reactions with amines, alcohols, and metal ions. Some of the reactions with silanols can have a significant effect on the properties of the rubber compound, especially where the chemical involved is an important part of the cure system. Most of the accelerators used in sulfur cure systems contain an amine group. Strong adsorption or reaction with filler particles can decrease the amount of accelerator available for vulcanization reactions. This can give slower cure rates and a reduced state of cure. Similar effects can result from the reaction of soluble zinc ions with kaolin particles. The adsorption or reaction of accelerators by hard clay usually requires about a 15-25% increase in acceleration.

Kaolin Clay

TEA
DEG
PEG
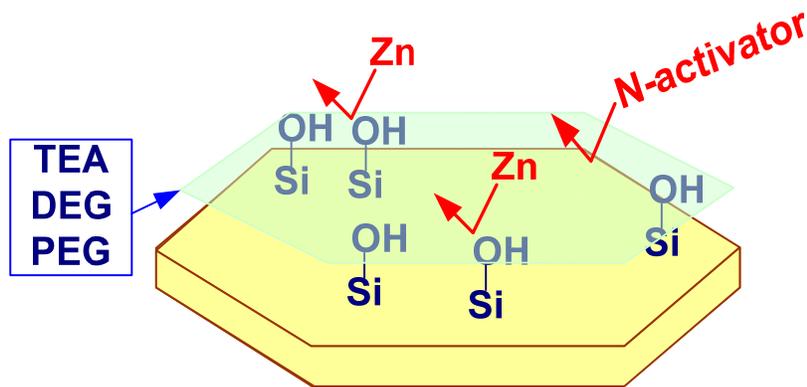
But their activity can be controlled

These negative effects on the cure system can be reduced or completely avoided, however, by adding other chemicals that will tie up the silanol groups and reduce their activity. Triethanolamine (TEA), diethylene glycol (DEG) and high molecular weight polyethylene glycol (PEG) typically serve this function. These are mixed into the compound prior to the addition of the accelerators.

Kaolin Clay

Silanes =
Rubber Reactivity

Polymer

Si-(CH$_2$)$_3$-S

O O

Si Si

OH

OH OH Si

Si Si

Accelerator
Reactivity

**Modulus
Tensile Strength
Abrasion Resistance
and Low Hysteresis**

Reactivity with accelerators is effectively avoided, and reactivity with the rubber matrix is promoted, by silane treatment of the kaolin. Silane-treated hard clays provide better reinforcement than untreated clay, and in some applications can rival furnace blacks. The combination of platy shape and chemical reactivity enable the silane-treated kaolins to impart a unique blend of properties to elastomers. These include high modulus, low hysteresis, good abrasion resistance, low viscosity, low set, and resistance to heat and oxidative aging. The unusual combination of high modulus and low hysteresis, in particular, allows silane-treated kaolins to be used alone or as a partial carbon black replacement in products requiring good dynamic properties, such as transmission and V belts, and non-tread tire components.

Kaolin Clay

Pretreatment	None	Mercaptosilane
Hardness, Shore A	60	65
M300, MPa	5.3	12.2
Tensile, MPa	21.2	22.3
Die C Tear, ppi	155	235
Compression Set	29.6	14.0

polyisoprene-100; hard clay-75; ZnO-5; stearic acid-2; Agerite® White-1; sulfur-2.75; Amax®-1.25; Methyl Tuads®-0.2

Huber

Hard clays pretreated with organosilanes are readily available. This table demonstrates the significant improvement in reinforcement provided by mercaptosilane treatment.

AGERITE, AMAX and TUADS are registered trademarks of R.T. Vanderbilt Holding Company, Inc. and/or its respective wholly owned subsidiaries.

Precipitated Silica

Precipitated silica: From the reaction of sodium silicate and acid.

Unlike carbon black, which has similarly small primary particles, silica's "structure" is not permanent.
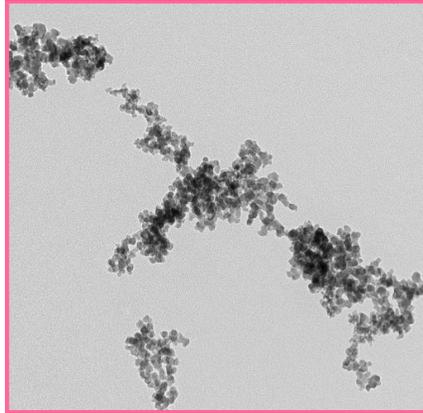
Precipitated Silica

Photomicrographs: Degussa

Precipitated silica is produced by the controlled neutralization of sodium silicate solution by either concentrated sulfuric, hydrochloric or carbonic acids. Reaction conditions are manipulated according to the particle size required.

Unlike carbon black, which has similarly small primary particles, silica's "structure" is not permanent. Hydrogen bonding among particles will form clusters or aggregates, and these aggregates may loosely bond as agglomerates. Compounding, however, disrupts agglomerates and even, to a certain extent, aggregates. So, for example, a compound with a 20 nm average particle size silica can contain primary particles plus aggregates as large as 100 nm.

Precipitated Silica

	Range
BET Surface Area, m^2/g	
Reinforcing	**125-250** (10-40 nm)
Semi-reinforcing	**35-100** (>40 nm)
Free Water, %@105°C	**3-9**
Bound Water, % (silanols)	**2.5-3.5**
pH	
Reinforcing	**5-7**
Semi-reinforcing	**6-9**
Salt Content, %	**0.5-2.5**
Specific Gravity in Rubber	**1.95-2.05**

The reinforcing properties of precipitated silica can usually be related to particle size; 10-40 nm particles are reinforcing, while 40+ nm particles are semi-reinforcing. Because of the difficulty in measuring the size of particles this small, as with carbon black, surface area, rather than particle size, is usually used for classifying various grades. For example, silica in the range of 125-250 m^2/g is generally reinforcing, while products in the range of 35-100 m^2/g are semi-reinforcing.

Precipitated Silica

Silica Surface Area, m^2/g	60	150	185	220
Hardness	58	66	67	68
M300, MPa	4.0	3.6	3.0	3.1
Tensile, MPa	6.9	20.5	19.9	18.6
Trouser Tear, kN/m	3	27	36	49
Elongation, %	450	735	750	750
Abrasion Index	25	68	70	78

SBR1502-100; ppt silica-45; DEG-3; stearic acid-1; Zn carbonate-1; sulfur-2; MBTS-0.7; MBT-0.4; TMTM-0.3; DPG-0.1

PPG

This is an illustration of the difference between semi-reinforcing and fully reinforcing silica, particularly the influence of particle size (surface area) on tear strength and abrasion resistance.

Precipitated Silica

Free Water

Silica Particle

Zn

Water is a:
Barrier to soluble Zn, accelerators
Hindrance to rubber bonding

polymer
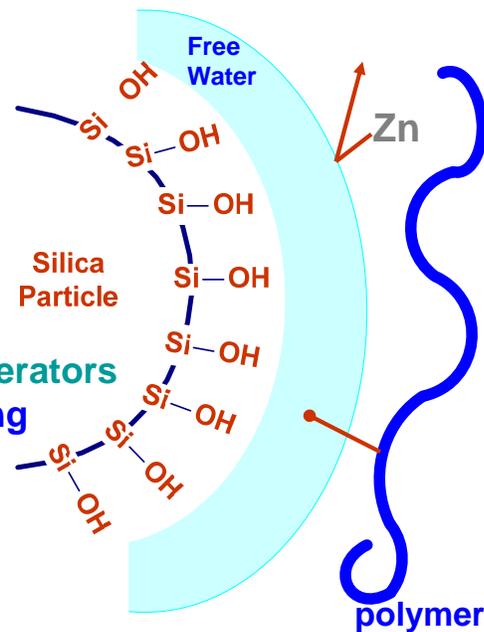
Precipitated silica is usually sold with about 6% adsorbed free water and a surface essentially saturated with silanol groups. Although it seems counter-intuitive for a rubber reinforcement, this significant free water content does offer some benefits, although it can be a double-edged sword. While the water insures that the silica particle is saturated with active silanols, it inhibits the reaction of accelerators and soluble zinc with those silanols. It also inhibits the bonding of the rubber matrix to the silica particle.

Precipitated Silica

Silica Free Water, %	3.8	0.7
MDR, 159°C, T_{90} min.	17	30
Mooney Viscosity	57	112
Durometer	61	64
M300, MPa	2.3	3.0
Compression Set	69	77
PICO Abrasion Index	45	68

SBR1502-100; 180 m^2/g silica-50; CI resin-10; oil-5; ZnO-3; stearic acid-2; ODPA-1; PEG 3350-2; sulfur-2; MBS-2; TMTM-0.6

PPG

Reducing free water-
Zn reaction: slower cure, more S_n xlinks, higher hardness & set
Better rubber bonding: higher modulus, abrasion resistance
Smaller aggregates: higher visc, modulus, abrasion resistance

Reducing the free water facilitates silanol-zinc reaction and silica-rubber bonding. Reduced Zn activation = cure retardation; increased polysulfide crosslinks = higher hardness, set . Better silica-rubber bonding = higher modulus, greater abrasion resistance. Less water = less plasticization, smaller aggregates = higher viscosity. Smaller aggregates = higher modulus, greater abrasion resistance.

Precipitated Silica

So why isn't low water silica commonly used?

It's expensive to make it that way.

It doesn't want to stay that way (except in the desert).

So why do we care about low water silica?

If compounding water loss is variable, compound properties can be inconsistent batch-to-batch.

If water loss is great enough, compound properties may be much different than expected.

Producing low moisture precipitated silica, however, is generally impractical due to the high cost of drying the silica during manufacture and its natural tendency to absorb (or lose) moisture to maintain equilibrium with the relative humidity of its environment. The contrast between the reinforcing properties of silica with normal vs low free water content is, nevertheless, a practical consideration because variations in water lost during compounding can lead to inconsistent or unexpected results.

Precipitated Silica

Glycol is a more dependable buffer than water

PEG 3350, phr	0	2	4
ODR, 144°C, T_{90} min	34	19	16
Viscosity, $ML_4$100	51	41	39
Hardness	59	66	60
Flexometer HBU, °C	32	29	22

NR-100; 150 m²/g silica-30; 35 m²/g silica-45; sulfur-2.8; MBS-1.5; DPG-0.3; ZnO-5; stearic acid-3
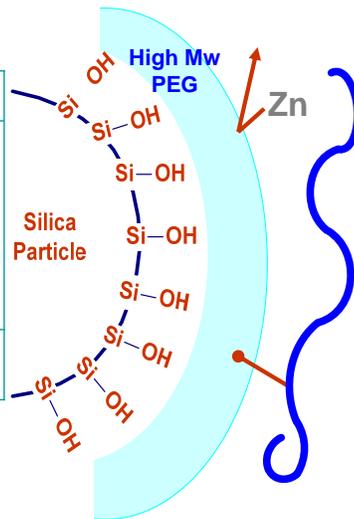
The variations in compound properties that result from variations in water content can be avoided by addition of certain glycols and amines. High molecular weight polyethylene glycol is usually used because of its low volatility, but diethylene glycol, glycerine and triethanolamine are used as well. As with kaolin, the glycol or amine insulates the surface of the silica particle from reaction with accelerators and soluble zinc.

Precipitated Silica	**Organosilane = Silica-Rubber Bond**	
Mercaptosilane, phr	**0**	**1.2**
150°C, T_{90} min.	**40**	**25**
Mooney Viscosity	**103**	**77**
Hardness	**71**	**68**
M300, MPa	**4.9**	**13**
Tensile, MPa	**18**	**28**
Flexometer HBU, °C	**47**	**27**
Tire Road Wear Index	**79**	**114**

SBR1502-100; 150 m²/g silica-60; aromatic oil-10; stearic acid-2; HPPD-2; ZnO-4; sulfur-2.8; MBTS-1.5; DOTG-1.5

PPG

In situ **treatment:**
Add organosilane before other silanol-loving additives

As with kaolin, the key to effective rubber-to-silica bonding is through treatment of the silica particle surface with an organosilane. Mercaptosilane is usually the most cost-effective choice and the treatment is typically *in situ*, with the silane added to the mill after the silica and before other additives that can interfere with the silica-silane reaction.

As noted earlier, there is a generally proportional relationship between filler-rubber bonding, reinforcement and hysteresis. A strong filler-rubber bond provides better reinforcement, but also greater hysteresis due to polymer-filler friction and the dislodging of polymer segments from filler surfaces. Silane-treated silica, however, provides reinforcement, but with decreased hysteresis due, at least in part, to the strength of the silica-rubber bond such that it is much more difficult to break and therefore consumes less of the energy of deformation overall.

Precipitated Silica	But MPTS stinks: TESPT or-	
	Untreated	**Pretreated***
Silica, phr	50	51.5
150°C, T_{90} min.	15	9
Mooney Viscosity	95	65
Durometer	73	70
M300, MPa	3.1	8.3
Tensile, MPa	18.6	23.4
PICO Abrasion Index	60	85
Flexometer HBU, °C	45	25

*3% mercaptosilane

SBR1502-100; HPPD-2; stearic acid-2; aromatic resin-10; HA oil-3; ZnO-3; PEG-1.5; sulfur-2; MOR-1.5; TMTM-0.6   *PPG*

As useful as mercaptosilane may be, its odor is generally objectionable. The effective, but less efficient (requires about twice the loading), testrasulfide is the usual alternative, although it requires a certain minimum compounding temperature to unblock the active mercapto group and a maximum temperature restriction to avoid scorching because of its free sulfur content. Pretreated silica is available that provides the benefits of mercaptosilane, as seen here, but without the smell.

Non-Black Fillers For Rubber

THE BIG 3

Calcium Carbonate

Kaolin Clay

Precipitated Silica