Science and Technology of Polymers

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Lecture - 21
Rubber Products (Contd.)

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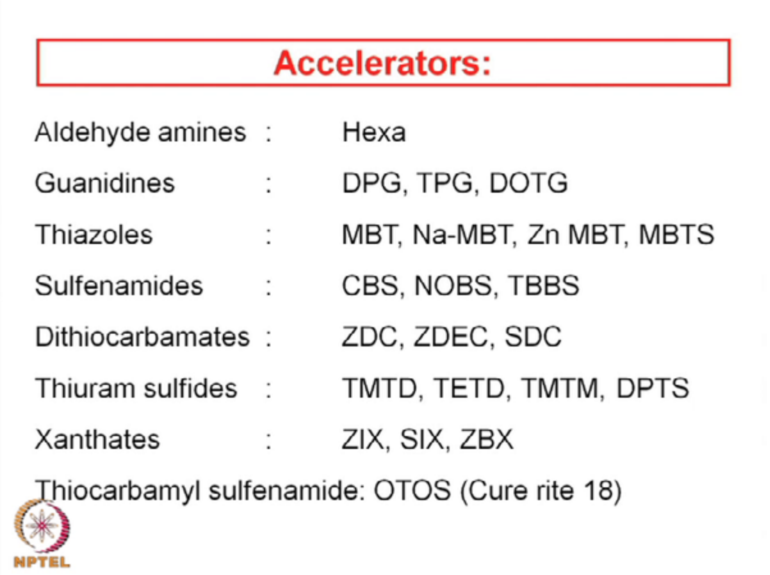

Accelerators:

Aldehyde amines : Hexa
Guanidines : DPG, TPG, DOTG
Thiazoles : MBT, Na-MBT, Zn MBT, MBTS
Sulfenamides : CBS, NOBS, TBBS
Dithiocarbamates : ZDC, ZDEC, SDC
Thiuram sulfides : TMTD, TETD, TMTM, DPTS
Xanthates : ZIX, SIX, ZBX
Thiocarbamyl sulfenamide: OTOS (Cure rite 18)

In the in the previous lecture of rubber products, I was discussing about the different types of accelerators used for the vulcanization or cross-linking of different rubbers - natural rubber or synthetic rubbers. There are large number of accelerators available for vulcanization of rubbersm, accelerators are used for the accelerating the reaction between sulfur and rubber; these are basically amine derivatives and there are different classes of accelerators, aldehyde amines guanidines, thiazoles, sulfonamides, dithiocarbamates, thiuram sulfides, xanthates, thiocarbamyl sulfonamides.

Now, there speed of reaction with sulfur, in order to form cross-link bounds sulfur cross-link bounds they differ depending on their chemical formula, chemical structures, etcetera, etcetera. And that is why there lies a proper selection of a suitable accelerator from this list of accelerators; that is necessary. Someone is very fast accelerator, someone is slow accelerator, someone is medium fast accelerator, etcetera.

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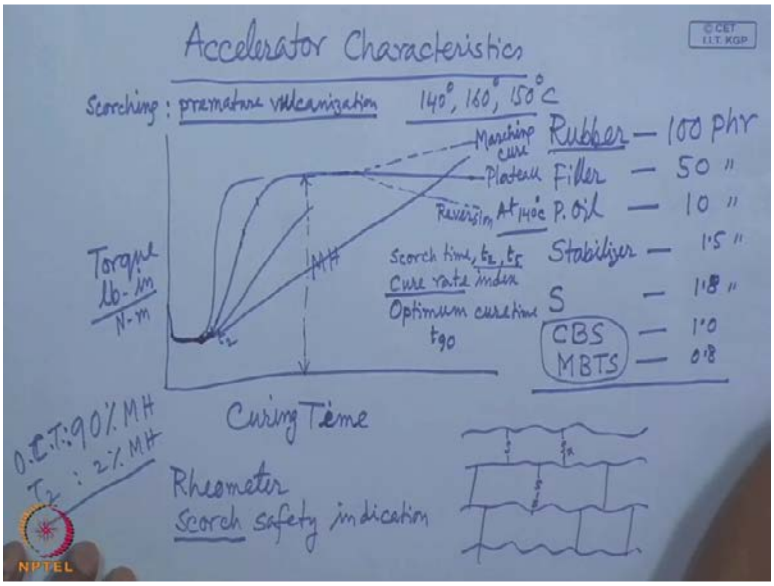

Now, to tell about the accelerators once again little bit, we must say about the accelerator characteristics, we must know about the accelerator characteristics. Accelerator characteristics can be explained with the help of a rheo meter trace, rheo meter trace which mix a plot of torque in pound inch or newton meter in any units verses temperature, sorry verses time curing time verses curing time, this is curing time.

Basically it is a torque time profile produced by one accelerator in a rubber compound; a rubber compound contains rubber say for example, 100 parts per 100 per PHR 100 PHR parts by weight. Then filler that may be 50 PHR, then process oil that may be 10 PHR then stabilizer anti-oxidant orantiozonant that may be 1.5 PHR cross-linking agent sulfur as the cross-linking agent that may be present as a 1.8 to 2 parts, parts by weight then along with sulfur as the cross-linking agent that can be accelerators say from that list I have shown CBS as well as MBTS combination or other combinations can also we used.

So, say it is 1 part, it is suppose 0.8 part or more than 0.8 part and some retarder can also be... So, this can be a fabulation using this accelerator or accelerator combination like this, and rubber can be natural rubber - a combination of natural rubber with synthetic rubber styrene butadinerubber or natural rubber polybutadiene rubber or SB rpolybutadiene rubber. So, that depends on the type of product which is (( )), anyway I am showing you a general composition or formulation of a rubber product, in which this sulfur and accelerators are present; if this acceletor is present that accelerator decomposes to form some intermediate chemical compounds which forms some complex with sulfur, that is known assulfuratingcomplex; thatsulfurating complex produces some sulfur atom from the a string of sulfur that sulfur atom reacts with the diene rubber to form a cross-link bond.

During such reaction what happens? There will be intermolecular linkage between the linierpolymer molecules through sulfur atoms like this, either disulphide or poly sulfide S X or disulfide linkage etcetera, so that forms a three dimensional linkage through sulfur like this. So, that cross-linking during that cross-linking formation, the mobility or the flexibility of the segments of in between two cross-links are gradually changed with the introduction of more and more sulfur cross-link bonds and that actually manifests to the deployment of torque in this that rheometer.

This this kind of rheogram is produced by a rheometer, rheometer which contains a roater which is connected to a motor ossolating disc motor ossolating rotationa ossolatering ossolatary rotation is provided by that motor, that rotate ossolates atone degree or othree degree arc and that rooter is placed in a cavity and over the rooter that rubber compound is placed, and two platens of that cavity are closed, and that platens are have some heating arrangement at different temperatures, it is a temperature controlled heating arrangement that temperature is maintained vulcanization temperature of 140 degree celsius or 160 degree celsius or even 150 degree celsius as per the requirement , and this temperature is maintained.

And as soon as the rubber is placed what happens? Rubber compound gets heated and slowly what happens that the viscosity or the torque decreases due to due to increase of temperature, then it becomes parallel to the time axis for sometime then it this torque starts rising, this torque increase rising torque that happens due to the introduction of this cross-link bonds in the in between the rubber molecules. And ultimately it gives this kind of profile torque profile with time at say for example, one at say 140 degree celsius temperature.

Now, there can be another kind of curve which leads to this type of torque raising instead of a becoming parallel to the x axis curing time axis or it can come down, this is the different cases can occur. This is a known as a cure profile or cross-linking profile, and this is the characteristic of accelerator. Now, this characteristic of accelerator basically these are scorch time and curing rate, cure rate index, optimum cure time, this is marchingcure, this is plateau plateaucure, this is a reversion.

And let us see what is scorch time? Now, when it is placed the viscousity of torque decreases due to the increase of temperature of the compound as soon as that compound sense this temperature of 140 degree, then it becomes parallel to the time axis, that means there is no chemical change till this point. Beyond this point, some chemical change as started to occur and then torque starts raising, means that compound is provided some restriction of mobility.

That means, it is a torque oscillated, rooter is oscillated. So, that rotor experiences some opposing force to its towards its oscillation, that opposing force towards oscillation is contributed by introduction of these bond this starts, here it is this introduction of such cross-link bond sulfur intermolecule linkage, bond formation starts at this point of time. Then slowly the number of this such bonds inter moleculer bond formation increases, and this torque goes raising this way.

That means the curing reaction or cross-link reaction started over here, and it is increasing at this rate, this is the this can be this this slope of this curve is the cure rate, this slope of the cure rate can be obtained from the slope of this torque verses time; these two parameters the ratio of these two parameter gives the cure rate index. Now, the time require, this is the maximum cure for this particular plateau effect, if you say this is the maximum torque, maximum torque.

So, time require to achieve 2 percent of the maximum torque say t 2 is known as scorch time t 2; t 2 is the scorch time time require to achieve 2 percent of the maximum torque, now there can be t 5 also there can be t 3 t 4, that means the time required to two percent of the torque maximum torque time require to achieve five percent of the maximum torque or three percent of the maximum torque or four percent of the maximum torque, that is known as the scorch time.

That scorch time information can be available from this cure curve; that means, rheometer profile or cure profile obtain from a rheometer. Now that information is necessary, because that scorch time gives a scorch safety indication. What is scorching? Scorching is pre mature, scorching is pre mature vulcanization. What is that pre mature vulcanization? Now, because this rubber compound is prepared by mixing with filler, stabilizer, (( )), other things, and sulfur acceletor, etcetera.

Now, during compounding the compound temperature arises to beyond 78 degree celsius. So, the compound should not start curing during such compounding not only that after compounding that rubber compounding, compound is used for fabrication of some some to give a shape of that productsay making a tire product or making a tube or making any profile.

So, that is that passes through some machineries say a schouten machine or curing mold, curing, etcetera. So, during that period the compound should not start any premature cross-linking. That means, the temperature raises, so it should remain on cross-links that at that temperature during possessing and fabrication, that is knownas scorch scorching. If that is reaction starts there during fabrication, that is known as scorching or pre mature vulcanization starts over there that should be prevented in orderto get that information.

This scorch time information is very much important; that means, at this high temperatureof 150 or 160, this T 2 value gives an indication that till 150 degree Celsius, only if even some reactions starts only 2 percent maccab this maximum torque can two percent of the cross-link can occuror, one percent of the cross-link can occur or no cross-link can occur.

So, this t 2, this say t 2 can be over here, and optimum cure time is known as t 90; that means, t time required to achieve 90 percent of maximum torque, 90 percent of maximum torque say MH. t 2 this optimum cure time, optimum optimum cure time OCT, and scorch time t 2. So, this is 90 percent of maximum torque, this is 2 percent of maximum torque MH, this is MH.

So, this is one parameter, this is one of the accelerator characteristic, and the curve can be, this curve can rise this way or this can also rise this way, this can also rise this way, this can also rise this way. So, these are known as the character. How heat actually this rubber compound starts curing or continuous curing, that is known as the that is the characteristic of the accelerator. That means, whether there is delayed accelerator, whether there is slow accelerator, whether there is fast accelerator, whether there is quasi accelerator; those things can be judge from this rheometer profile. If more informations required the reader is refered to some special books on rubber rubber technology or vacuolization or science of scienceand technology of rubber.

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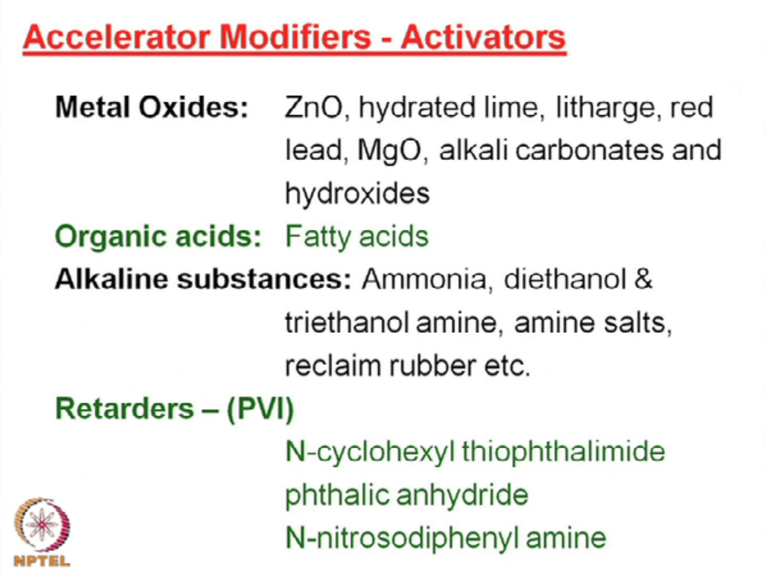

Accelerator Modifiers - Activators

Metal Oxides: ZnO, hydrated lime, litharge, red lead, MgO, alkali carbonates and hydroxides

Organic acids: Fatty acids

Alkaline substances: Ammonia, diethanol & triethanol amine, amine salts, reclaim rubber etc.

Retarders – (PVI)

N-cyclohexyl thiophthalimide

phthalic anhydride

N-nitrosodiphenyl amine

Then up to this accelerator, accelerators; accelerator modifiers are also required in order to help the reaction between accelerator and sulfur. Now, there can be that those are known as accelerator activators. What are these? Accelerator activators are a combination of chemical compounds of oxides inorganic oxides and organic acids. Ammonia organic oxides, there are zinc oxide is the most common in all rubber industries, in all rubber products, see in tyre products, the zinc oxide is common ingredientas metal oxide accelerator or in some cases hydrated lime can be used, litharge can be used, red lead can be used, magnesium oxide can be used or alkali carbonates can be used, and some metal hydroxides can also be used.

That means basically these are alkaline materials or neutral materials, neutral zinc oxide neutralas a neutral or alkaline materials. Along with these compounds, any of these compounds some organic acid has to be has to be used; that means, a combination of both metal oxide and organic acid constitute, this accelerator activator. What happens? this metaloxide and organic acid form a salt during the vocalization reaction with in the rubber product.

So, a combination of these two form a salt, and that salt interacts with the accelerator through select complex formation, then that complex interacts with the sulfur to form asulfurating complex, and that releases sulfur atoms for making activated sulfur atoms, energetic sulfur atoms; that produces cross-link between the rubber molecules. Other than metal oxides alkaline substances like ammonia, diethanol, diethanol or triethanol amine or amine salts or reclaim rubber can also be used.

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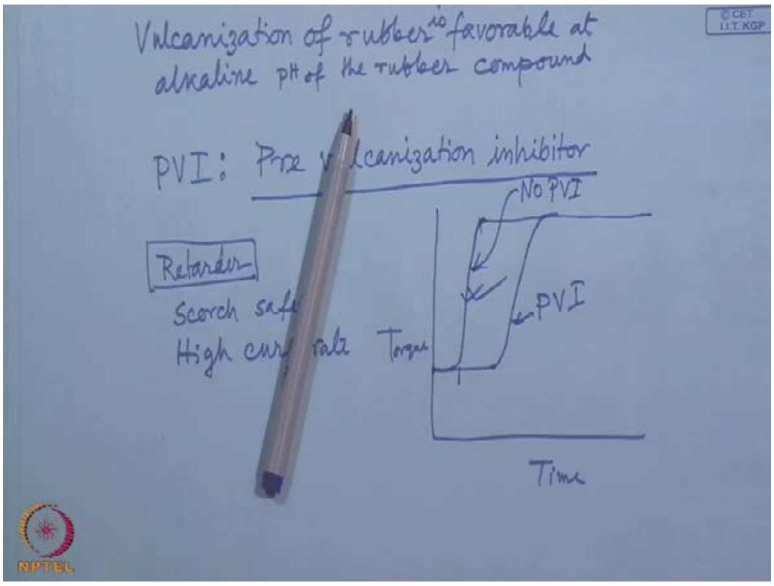

Vulcanization of rubber is favorable at alkaline pH of the rubber compound

PVI: Pre v lcanization inhibitor

Retarder

Scorch saf

High cur rate

One thing should be known from here at this point I must refer that is the vulcanization reaction favorably occurs or favorable is favorable at alkaline pH of the rubber compound. So, such alkaline pH is developed or maintained through the use of this alkaline substances, although organic acids are used; since that forms with forms salt with this things that does not cannot reduced, because that cannot ionized. So, these cannot decrease the pH. So, in order to increase the curing rate, vulcanization rate alkaline substances are preferable. So, ammonia diethanolor, triethanol amine or amine salts or even reclaim rubber which is alkaline, that can increase the curing reaction rate, vulcanization rate.

So, we have discussed about the accelerators, accelerator modifies, that means accelerator activators then there is another class of compound in the rubber product used which as known as retarders; retarders or they are sometimes told as PVI, PVI basically this PVI is pre vulcanization inhibitor. I was talking about this scorching reaction before final setting and vulcanization, this scorching or prematured vulcanization should not occur during rubber compound formation, as well as during fabrication and shapping.

Now, in order to increase the productivity of a rubber product, sometimes high speed accelerators are used means fast accelerators are used. Now, those fast accelerators what happens? They produce a cure profile torque time profile, torque and time profile like this very fast accelerator; that means, this this time is very small and this keeps stiff rise of this curing rate like this. This small time is required for high productive, that is vulcanization is complete over here, say vulcanization should be complete within five minutes in that case one should use very fast accelerator.

Now, if you fast accelerator is used, that fast accelerator should be compounded with proper care otherwise that will scorch the rubber compound during compound formation or during the processing or shapping operation during fabrication operation. But this is little difficult. So, use of fast accelerator is restricted there, but one can use provided if this region can be kept safe, even if this fast accelerator is used that is done by the use of a retarder.

That means, during compounding compound formation in a mixing mixture say internal baneberry mixture or open mill for proper mixing and dispersion of the ingredients, the the the accelerator and sulfur should not start reaction over there that can be kept dormant provided, some retarder is used by the use of some retarder retarder means that will retard the reaction a vulcanization reaction, that is calledor that will inivit the vulcanization reaction, that is called pre vulcanization inviter compounds liken-cyclohexyl thiophthalimide, N-cyclohexyl thiophthalimide or even phthalic an hydride accedic in nature I told you, that acidic compound acidic compound does not allow the cross-linking reaction or slows down the cross-linking or vulcanization reaction.

So, acidic compound or this thiopthalimide type of compound or nitrosodiphenyl amine these compounds are used as retarders along with very fast accelerator. So, even if fast accelerators is used, if this pvi compounds are present that will prevent this vulcanization reactionah to occur during the compounding or fabrication period. That means, that retarder will provide some scorch safety, maintaining the high cure rate high vulcanization rate; that means, this is maintained, but this can be delayed this way, so instead of this curve one can get this kind of curve, if some PVI is used. So, if PVI is there here is no PVI, in this case no PVI in this case, there is no PVI in this case there is PVI. So, this kind of characteristics can be available, if some pre vulcanization inviter is used.

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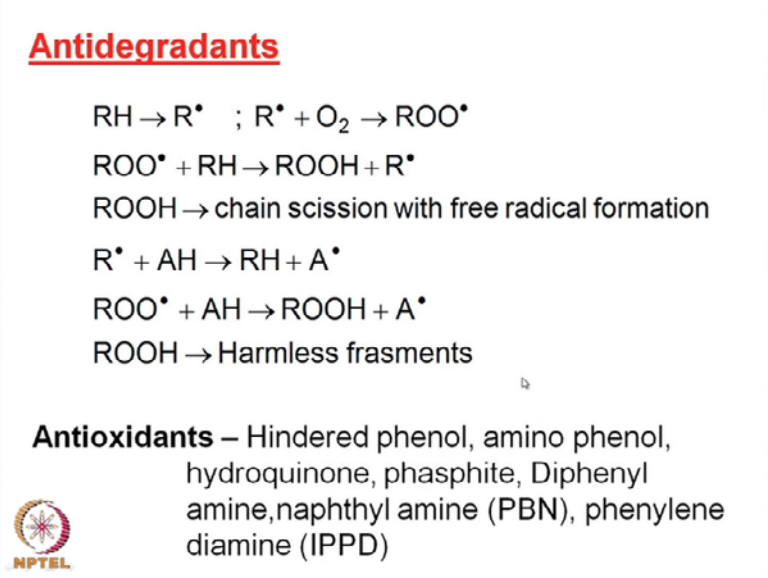

Antidegradants

$RH \rightarrow R^{\bullet}$; $R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$

$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$

$ROOH \rightarrow$ chain scission with free radical formation

$R^{\bullet} + AH \rightarrow RH + A^{\bullet}$

$ROO^{\bullet} + AH \rightarrow ROOH + A^{\bullet}$

$ROOH \rightarrow$ Harmless frasments

Antioxidants – Hindered phenol, amino phenol, hydroquinone, phasphite, Diphenyl amine,naphthyl amine (PBN), phenylene diamine (IPPD)

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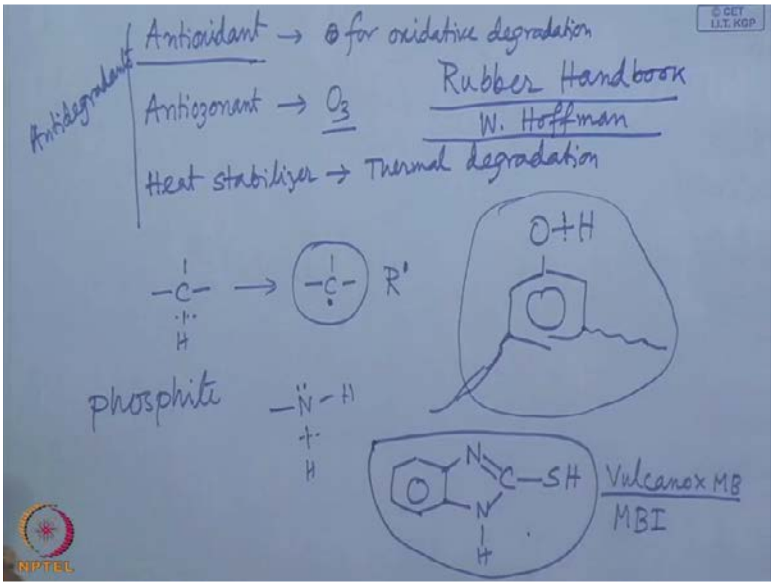

Antidegradant

Antioxidant → for oxidative degradation

Antiozonant → O_3

Heat stabilizer → Thermal degradation

Rubber Handbook

W. Hoffman

phosphite

Vulcanox MB

MBI

Anti degradants, now after this pre vulcanization inviter I mention that stabilizers are used, this stabilizers say that can be antioxidant. If the degrading agency is oxygen of oxidative degradation of rubber product, rubber products are exposed to air which contains oxygen. So, slowly oxygen will degrade the product. So, that degradation should be prevented by some by the presence of some compound. So, that the life of the rubber product is prolonged those are known as antioxidants.

Now, if the degrading agency is ozone, now there are certain regions on their on the out surface, atmosphere contains ozone higher ozone concentration to prevent the product rubber product from degradation by the presents of ozone in the air, in the atmosphere that compound is known as anti ozonant, anti ozonant. There can be thermal agency. So, heat stabilizer for thermal degradation. So, these are in order to prevent the degradation by different agencies, stabilizers are used or antidegradants are used these are in effect called antidegradants.

Now, let us have a very quick look into the degradation mechanism of rubber, now RH represents a rubber hydrocarbon containing carbon carbon linkage containing unsaturation bonds containing carbon-hydrogen bonds. So, that is that rubber represented by RH, now somehow if there is some agency which attacks the rubber that attack can produce some say rubber contains this carbon-hydrogen bonds, I am showing only one carbon-hydrogen bond, and that bond can be broken over here forming a free radical free radical, that is represented by here as R dot R dot this R dot is produced. Now, this R dot is very active, now if it case gets axis to oxygen from the atmosphere that forms a peroxyradical R O O radical. So, once this is initiated in a rubber product on the surface of a rubber product, that gets access to oxygen in the atmosphere that forms peroxyradical.

Now, this peroxyradical is form morea active than this R radical, now this peroxy radical then further abstracts one hydrogen, abstracts hydrogen from the other part of the rubber hydro carbon or from other rubber hydrocarbon molecules that form by abstraction of that hydrogen from rubber. This peroxyradical forms hydro peroxide, this is again more reactive, more harmful than this rradical or peroxy,radical. So what happens? It forms hydro peroxide as well as the generating one more free radical.

So, what happens? There is a chain of reaction which is initiated over here that gradually increase in rate, and increase in concentration of this radicals and that leads to breakage of chain, chain scission, chains breakage of polymer chain, rubber chain with free radical formation . If if this is, if this occurs then what happens? Altemetely in a short period of time, the properties or the mechanical propertiesor any other properties of the rubber product would be reduced or that product become use less.

Now, this is the basic very simple mechanistic view of degradation of rubber, in order to prevents such prevent that rubber product from such degradation, if some anti degradant of AH type antidigradants AH represents one antidegradant or it can be antioxidant or it can be anti ogonent, etcetera. So, that will that anti oxidant anti degradant will react with this free radical produced over here like this, R radical by supplying hydrogen from this from its back bone to this to stabilize this R radical; that means, it becomes R H that means R H has been regenerated.

So, even if some free radical is created, this antioxidant willconvert it will reward back to rubber hydrocarbon, creating a new radical. Now, these radical is not harmful this is harmless, because these this structure configuration and this formula of this compounds is such that electronic configuration of this, this radical is such that this free radical is stabilized; that means these stabilizedfree radicals is not that reactiveas the reactivity of R dot ROO dot or ROOH etcetera, so this is not harmful, this is harmless. What happens? In the other cases, so there are R dot, there are ROO dot peroxyradical that also be taken care of by this anti degradant forming, this peroxy hydroperoxide and A dot. And again hydroperoxide will be also we converted to other harmless fragments f r a g is wrong over here her harmless fragments.

Now, these are the… this is a basic mechanistic principle, mechanistic way, how this anti degradant functions? A nti oxydants examples of anti oxidants hindered phenols means phenol is this the formula of phenol is this, formula of phenol is this O H phenol. Now, if it can break over here forming free radical, that free radical will be stabilized with the aromatic phenolsring, so phenol is a good antioxidant or antidegradan ttype of thing.

Now, this is hindered, this is hindered means this is connected to some bulky groups, bulky organic groups. So, that kind of phenol derivative is known as hindered phenols or amino phenol; that means there can be some aminogroup, now having this amino group N H, N H having (( )). So, this can also prevent degradation by breaking of air and when it is connected to some such type of phenyl ring

So, that will create stabilized free radical. So, amino phenol hydroquinone phasphite, this is PHOSPHIT phosphate phosphate or diphenylamine or naphthyl amine or phenylenedaimine; many antioxidants are available in the market, commercial antioxidant sare available in the market; and these are commercially used for making commercial rubber products like tyres, tubes, oasis, belts different or condorbelts etcetera. These antioxidants any of these antioxidants are used.

Now, there is oneantioxidants made by bayer germany, that is mercmercap to benzimidazole; the formula of this mercmercap to benzimidazole is this, this is mercap, to this is very good antioxidant as well as antiozonant. Mark 2 MBI or vulcanox MB, this is in other way it is known as MBI mercap to benzimidazole or thecompanies name is vulcanox MB, chemical name is mercap to benzimidazole.

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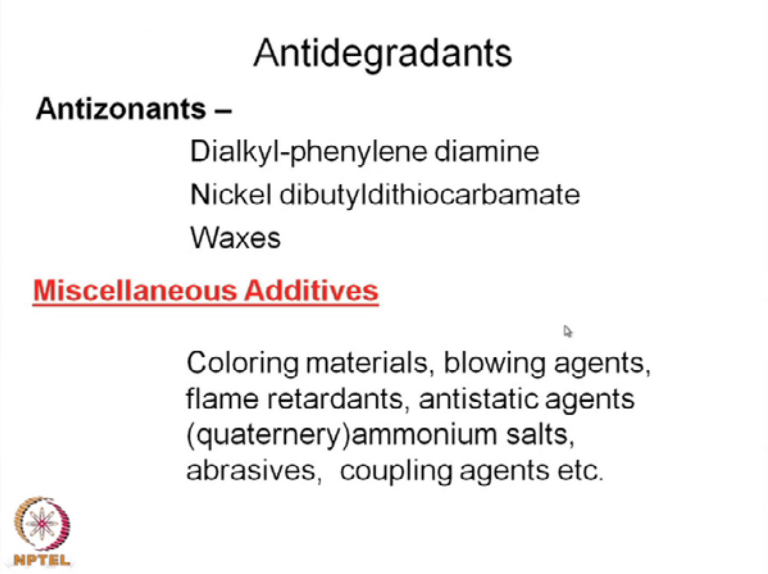

Antidegradants

Antizonants –

Dialkyl-phenylene diamine
Nickel dibutyldithiocarbamate
Waxes

Miscellaneous Additives

Coloring materials, blowing agents, flame retardants, antistatic agents (quaternery)ammonium salts, abrasives, coupling agents etc.

Examples of antiozonants and dialkyl-phenylene diamine. Here is no scope of detail description, if somebody wants to need to know details, he can he is refered to a book by rubber and book by W Hoffman, excellent book on polymer rubber additives. Chemistry is excellently described exastability described in this book. So, different types of examples apart from these examples, few examples mentioned over here. Dialkyl-phenylene demine, nickel dibutyl dithiocarbamate or waxes even say paraffine waxe microcrystal wax, these are also used asantiozonants, because if wax is used as an additive with a rubber compound, what happens? That is blended with rubber then slowly these wax molecule, these are basically hydrocarbon. So, that blooms or defuses to the surface and forms a very thin layer of coating over the rubber over the rubber product.

So, that that is saturated, so that saturated thin layer coating prevents the ozone entry to the rubber vulcanized rubber surface. So, that prevents degradation by the action of ozone. So, other than those additives say process in accelerators, cross-linking agents, accelerators, accelerator modifiers, and stabilizers; there are other miscellaneous additives which arealso used for making rubber products.

So, these are coloring materials, these are pigments or dyes mostly these are pigments to develop attractive color to bring aesthetic appeal to the rubber product, this can be yellow colored, this can be red colored, this can be brown colored, this can be green colored, this can be blue colored, whatever color is a required that can be take up by using coloring material.

Sometime cellular rubber products are use a rubbers sponge or soft rubber cellulars say cellular rubber products are used, that can be open cell sponge or close cell sponge these are made by using some blowing agents; the blowing agents can be either a gas or some gas generating chemical compound, flame retardant in order to impart some fire retardencyto the rubber product some flame retardant ingredients are used that can be fluorinated hydrocarbon that can be fluorinated rubber, that can be some say alumina trihydrate, alumina trihydrate or some antimoniya compounds or some phosphorous compounds or some boron compounds ; these are usedasflame retardants.

Some antistatic agents in order to prevent this static charge accumulation over a rubber product surface, some antistatic agents are used because if static charge is allowed to accumulate over a rubber product surface, what happens? That will attract dust from the air and a always a thick layer of dust will be deposited (( )) to prevent that dust accumulation through static charge development, if some antistatic compounds are like say quarternary ammonium salts are used; these are basically electrolyte type of compounds, that helps in the dispassion of static charge which is generate over accumulated over the rubber product. Then abrasives for grinding wheels etcetera grinding surfaces for abrading surface to some rubber products abrading rubber products are available, there some hard materials say carborundum powder etcetera; these are used as abrasive material additives.

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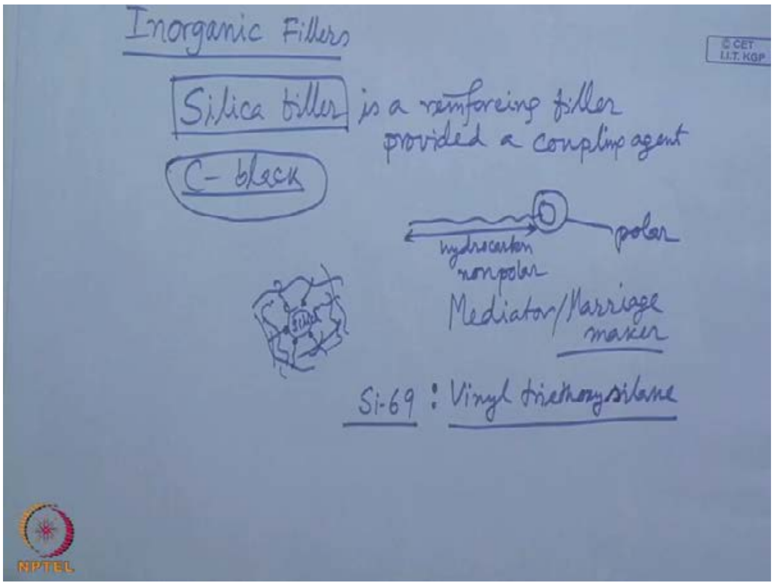

Inorganic Fillers

Silica filler is a reinforcing filler provided a coupling agent

C- black

Mediator/Marriage maker

Si-69 : Vinyl triethoxysilane

In coupling agents sometimes, sometimes, sometimes this your silica fillers are used or inorganic fillers are used, inorganic fillers are used. Now, this inorganic fillers, inorganic fillers say for examples silica, silica fillers; now this is not comfortable with hydrocarbon rubber. Whereas carbon black I discussed earlier, carbon black is very good miserable or comfortable with this hydrocarbon rubbers, now this carbon black can be easily accommodated by rubber, and that there can be this interaction between the carbon black particle and the rubber molecules. Whereas, silica filler cannot enter into interactive physical encourage or chemical encourage to the rubber polymer chain.

In order to use this silica filler as filler in silica filler is reinforcing filler provided a coupling agent is used, what is this coupling agent? Coupling agent will have two parts; one is organic part; that means, this your hydrocarbon part, and this is polar part, this is non-polar, this is polar. So, what will happen? This if such type of compound is used with or this this is used with along with silica filler, the silica particle will be will be covered by these molecules like this.

So, silica particle will be interacted with this polar group of the coupling agent, and this rest of the part of this your coupling agent will interact with the polymer chain. So, that way interaction between the silica filler, silica filler, silica filler will be developed through this coupling agent this is nothing but a mediator or marriage maker, this is known as coupling agent.

So, for example, for silica filler say Si 69, this is a basically vinyl triethoxysilane, this Si 69, the chemical name of 69 is vinyl triethoxysilane. This triethoxysilane is used along with this silica filler, then only this silica filler can act as a reinforcing filler in rubber product; these are something about miscellaneous additives.

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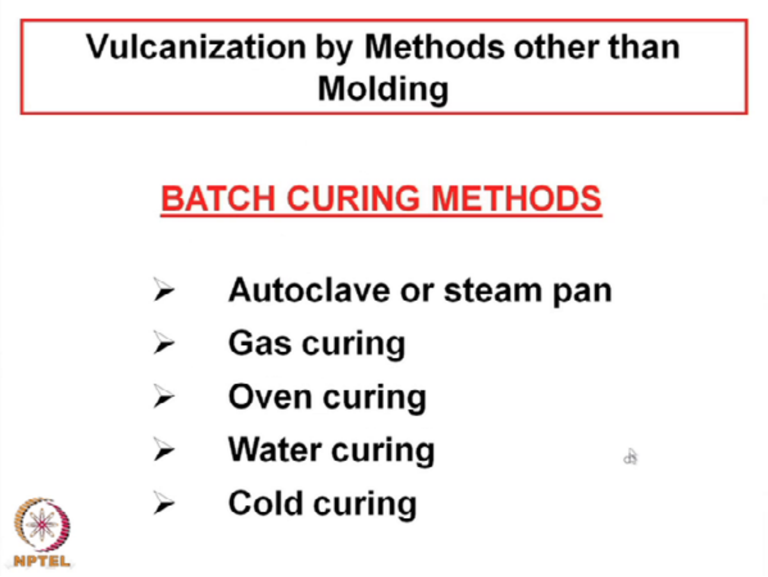

Vulcanization by Methods other than Molding

BATCH CURING METHODS

- Autoclave or steam pan
- Gas curing
- Oven curing
- Water curing
- Cold curing

Then let uslook into the… So, I have discussed till now up till now about the composition of a rubber product, and I have explained basic or fundamental rules of the ingredients or additives used in the rubber different types additives used in the rubber product. Now, next step comes after compounding of such additives with the rubber, next step comes the fabrication and after fabrication giving shape or shape of the item or manufacture or the formation of the product. Then it needs to vulcanized or cross-link the product is needs to a cross-linked which contains those additives along with the sulfur, etcetera, etcetera.

So, till now the vulcanization is not allowed. So, after only this complete shape is given, then that is vulcanized or allowed to cross-link. Now, there are various techniques available for vulcanization, the batch curing methods are involved autoclave or steam pan at which provides atemperature 140 to 160. Then gas curing hot gas is used for curing there can be a chamber which is known has oven, where the temperature is maintained, where the product can be introduced and slowly that will achieve the temperature of the oven and starts curing. Then hot water for curing or sometimes some cold curing is done by using some chemical compounds

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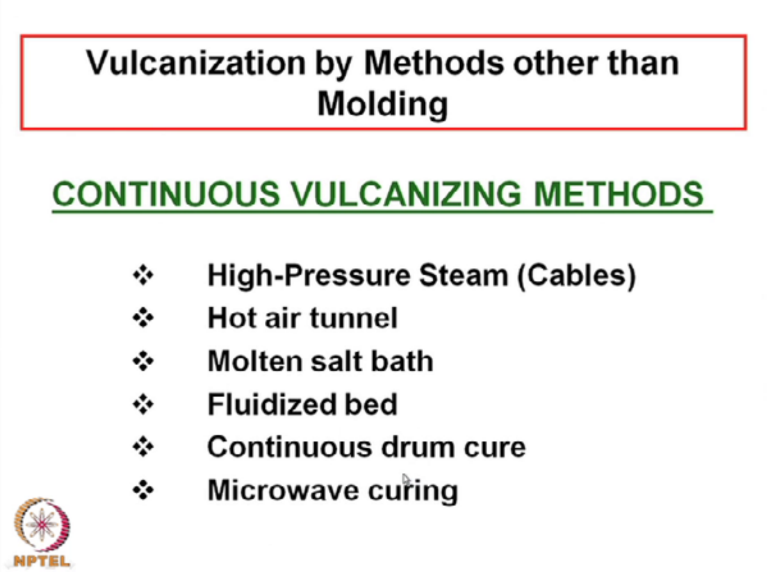

Vulcanization by Methods other than Molding

CONTINUOUS VULCANIZING METHODS

- High-Pressure Steam (Cables)
- Hot air tunnel
- Molten salt bath
- Fluidized bed
- Continuous drum cure
- Microwave curing

Then other then compression molding say continuous vulcanization methods can be done can be adopted; that means, product is being fabricated and contineously it enters into a system or device where the product is continually volculized. So, in case of cable cable is made throughah excution process and that passess through a high-pressure steam chamber, where the covering rubber covering of the cable gets cured while it enters in between the entering and going out of the that chamber heat chamber or steam chamber

So, continually it is entering and going out during the residence time of that cable within the chamber it starts curing, and completes curing then it ultimately goes out of the tunnel. Then there can be hot air tunnel there can be molten salt bath, there can be fluidized bed there can be continuous drum cure system, there can be also microwave curing. That means there can be some microwave chamber, if that product is introduced in that microwave chamber that will cause queering of vulcanization.

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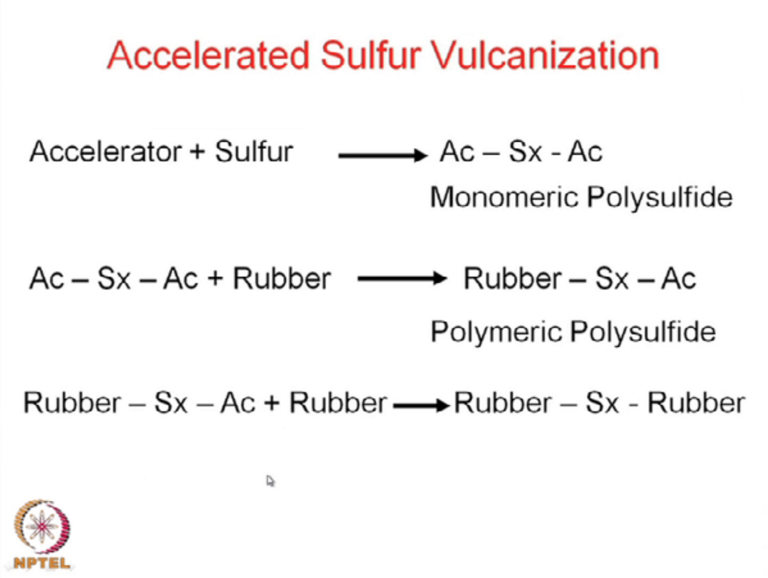

Accelerated Sulfur Vulcanization

Accelerator + Sulfur ⟶ Ac – Sx - Ac
Monomeric Polysulfide

Ac – Sx – Ac + Rubber ⟶ Rubber – Sx – Ac
Polymeric Polysulfide

Rubber – Sx – Ac + Rubber ⟶ Rubber – Sx - Rubber

Now, let us look in the mechanism of this vulcanization, brief mechanism of this vulcanization mechanism of vulcanization is very interesting.

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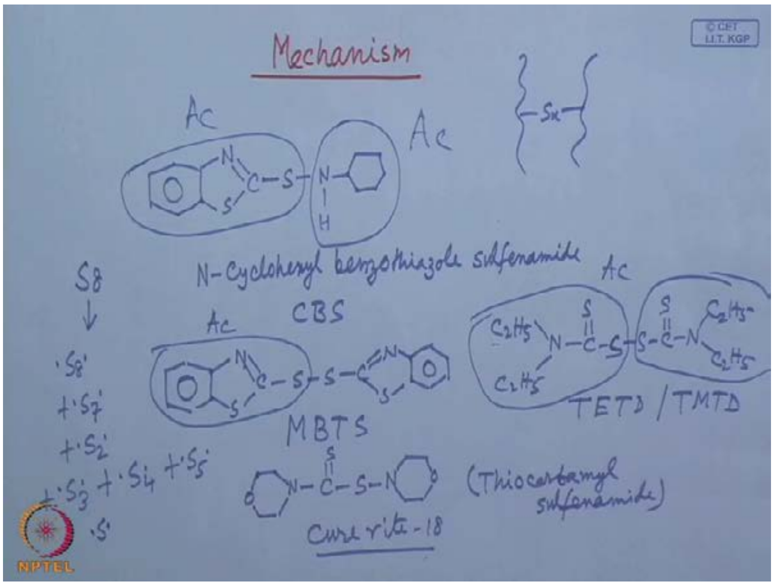

In this mechanism of vulcanization, you just have a look I described about the accelerators, accelerators I mean to say I can show you one representative formula, this is a formula of a cyclicexile ring, This is mercapto benzo thiozolering, this is the Si linkage sulfenamide linkage, this is known as n-cyclohexyl benzo thiazole sulfonamide, in brief it is known as CBS, there can be other accelaters, this is MBTS, there can be other accelerators, This is actually TETD or if the methyl ethyl groups are replaced by methyl group, there can be TMTD, there can be another very good accelerator, that is this is cure rite 18, this is thiocarbamyl sulfonamide. Now, let ushave a look into this mechanism, now accelerator here, this accelerator can be any of these compounds any of these compounds. Now, AC here it is written, AC AC represents a part of this structure AC, this can be AC or this can be AC, this can also be AC accelerator residue this can be a C, this part can also be AC.

So, this AC accelerator reacts with sulfurforming AC-SX-AC, this is known as mono mericpolysulfide, and this monomeric polysulfide reacts with rubber molecule forming; that means, this monomeric forming this sulfurated accelerated complex, it attaches to rubber forming a polymeric polysulfide. And when this polymeric polysulfide containing this sulfur, and accelerator fragment interacts with rubber that form a cross-link bond SX rubber to rubber. That means we can have rubber chain, rubber chain can have SX kind of linkage. Now, look at this thing, this is an accelerator say this type of this type of chemical compounds CBS type of chemical compound. So, that reacts with MBT, MBT structure is not shown very earlier I have shown.

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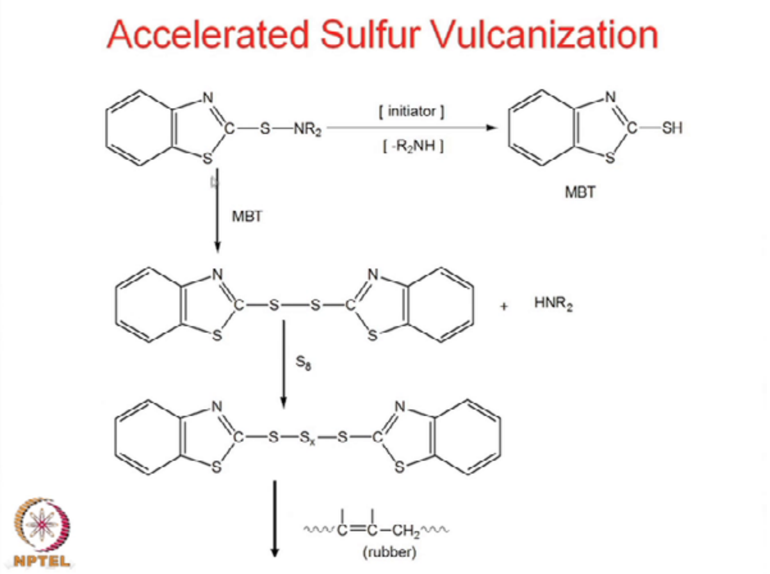

Accelerated Sulfur Vulcanization

So, that reacts with MBT after breaking over here, it forms MBTS and MBT is released over here either this can come over here to reform this MBTS.

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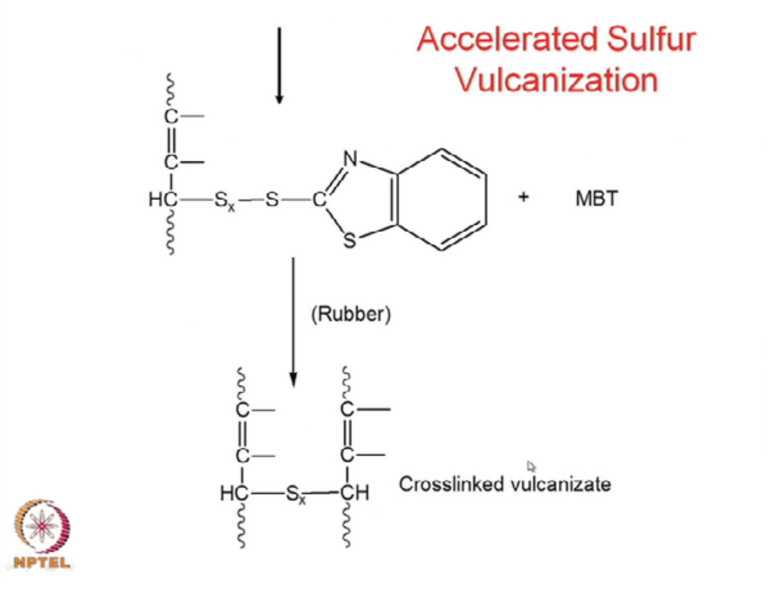

Accelerated Sulfur Vulcanization

This MBTS reacts with sulfur S 8 ring forming polysulfide, this polysulfide reacts with rubber to form this kind of linkage is acceleratormoiety this is sulfur linkage polysulfide linkage this is polymer chain and ultimately it reacts with another rubber molecule forming this type of cross-link this is rubber molecule this is rubber molecule these two rubber moleculesare linked with SX. So, this is a cross-linkedvulcanizate releasing this MBT.

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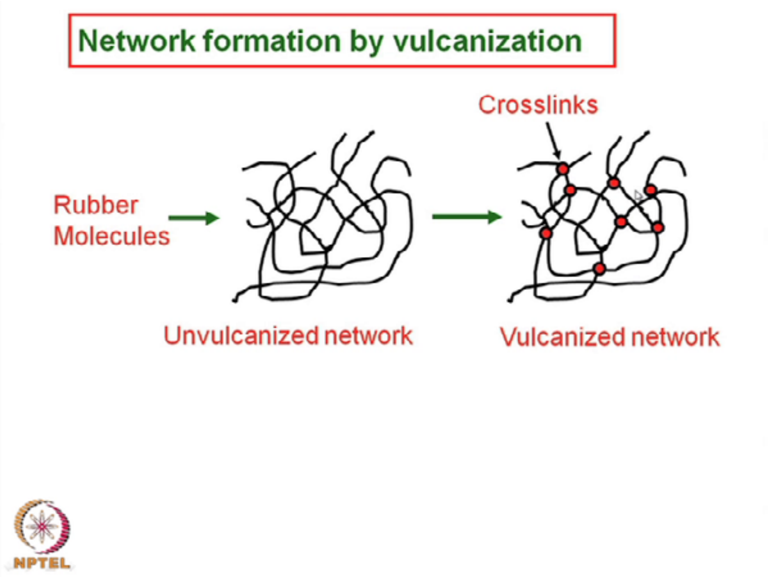

Network formation by vulcanization

Now, you just look into the network - three-dimensional network which is suppose to you form, now while before vulcanization before vulcanization rubber molecules can be viewed in this n tangled or quailed configuration. So, unvulcanized network you can say. Now, reaction with sulfur accelerator and accelerator activator all those things what happens? The rubber molecules are interlinked through sulfur as I showed in the mechanism in the previous two, three slides. So, this red dots red red dots are actually red dots are of the cross-link of vulcanization points or nodal points, where the sulfur has interlinked to rubber molecules. So, these are sulfur cross-link sides

So, now the mode is the number of the sides more will be the cross-link density, less the number of sides less will be the cross-link density; more is the cross-link density stiffer will be the rubber product, less the cross-link density softer will be the rubber product. So, this is basically known as vocalized network.

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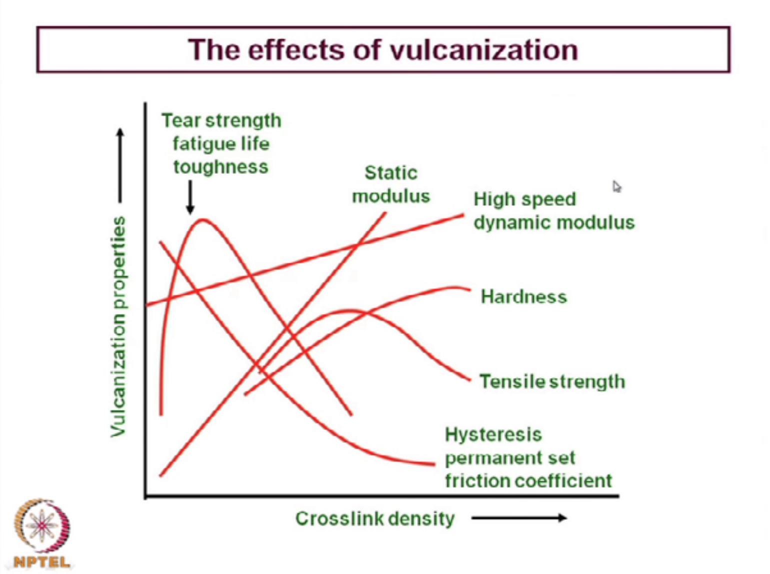

The effects of vulcanization

So, depending on the cross-link density, the mechanical properties of the valcunized network will be dependent. Having such information, let us look into this let us look into the effect of such vulcanization or introduction of cross-link bonds into the rubber products on the properties. Now, this shows a schematic variation of the vulcanization properties. So, those properties can be tensile strength, those properties can be hardness, those properties can be dynamic properties like fatigue properties that can be modules so and so with the change in cross-link density.

Now, you see this static modules this tensile strength and modulus all these things which are measured using a dumble specimen by applying tensile force; that is known as static test. Now, in this static state one can get static modules as well as tensile strength, as well as tear strength, etcetera and you see with the increase of cross-link density the static modules increases, hardness increases, tensile strength increases through a maxima; that means, after reaching a maxima then it decrease the if the there is more cross-link density goes beyond some cross-link density, maxima optimum cross-link density tensile strength decreases, whereas toughness also decreases at thiscross-link. So, if you look into the cross-link density this cross-link density can be taken as an indication of the properties are level of that particular product, which properties required that this kind of schematic diagram will help to make a proper formulation.

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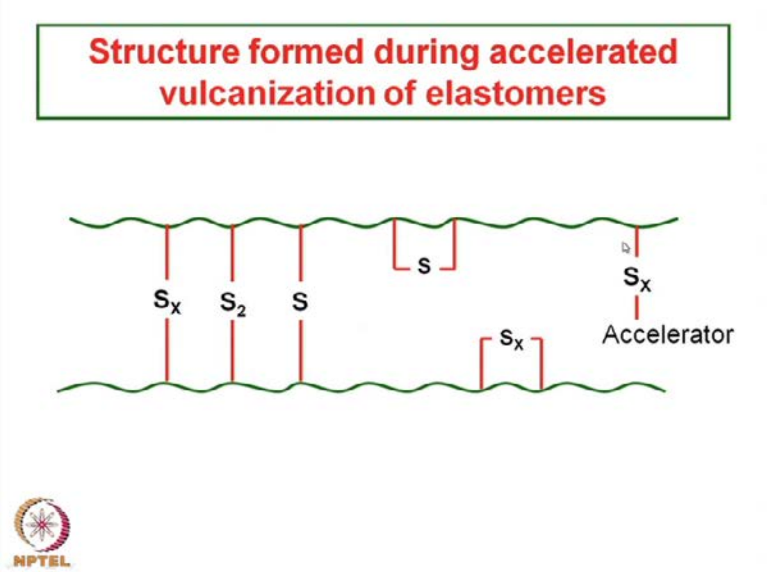

Structure formed during accelerated vulcanization of elastomers

Look at the ultimate vulcanized network of the rubber chains, as I mentioned when sulfur is used for vulcanization of diene rubber along with accelerator or accelerator activators there can be a various type of different type of linkages. Now, this sxrepresents polysulfide linkage, sulfur actually this your sulfur remains as S 8 ring, so that decomposes to S 8 this or S 7 or S 3 or S 3 or S 4 or S 5 like this. So, that can break into sulfur polysulfides or monosulfides or even sulfur radical or even sulfur radical like this, that leads to form polysulfide, disulfide, monosulfide, some cyclic sulfide, and cyclic mono sulfide, cyclic poly sulfide and some polysulfide accelerator complex.

So, this is the nature of the vulcanizate, nature of the cross-link cross-link in the rubber product. More is the concentration of this linkage more will be the tensile strength, but poorer will be the ageing characteristics; that means, this product will be if there is more concentration of S X, there will be the the life of the product will not be good, whereas less of S X more of S 2 and more of S and less of this sulfur S X, etcetera, so that will be the excellent or efficient of vulcanizations vulcanized network. Because this cyclic sulfide S X or S or this kind of linkage that goes for utilization of sulfur, this is unrequired, this if this is to be avoided. Whereas, these two presence of these two will be very efficient for making a stable as well as strong rubber product.

Thank you very much.