Rheology and Processing of Paints, Plastic and Elastomer based Composites
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Lecture 25
Importance of compounding and introduction to various compounding ingredients

Welcome to NPTEL online certification courses on Rheology and Processing of Paints, Plastic and Elastomer-based Composites. Today we are in week 5 and lecture number 1 that means 5.1. It is all about importance of compounding and introduction to various compounding ingredients in rubber specifically. So, concepts covered will be importance of compounding, vulcanization system, mostly we will be focusing on cure mechanism today, accelerators, polymer degradation, its mechanism, antioxidant and anti-ozonant and light stabilizers namely the UV stabilizers. Once again to for your self studies you can refer to these buzzwords, cross links, vulcanization or curing, filler, parts per 100 grams of rubber which is abbreviated as PHR, Mooney viscosity I already talked about, scotch time, cure time, cure system, accelerator, anti-degradant and reinforcement.

So, now as I mentioned you two earlier, the way rubber is defined it is a very weak baby. If you can recall their intermolecular forces of attraction is quite low and often for the elastomer classically they have a double bond. So, it does not have any crystalline, it is amorphous in nature, so it does not have the strength, it is very vulnerable to degradation by oxidative environment, ozones UV. And also strength wise it is very weak, its failure properties tear and wear it is very common in the pristine form.

So, it needs to be added with different ingredient, the purpose is to make your weak baby strong. So, a compound that way is defined is a mixture of different chemicals which are added together to combine their desired properties. As I mentioned rubbers on their own have limited uses and hardly any products where rubber can be used alone. Of course, certain examples like say certain adhesive formulation along with the solvent you can use say for example neoprene rubber, natural rubber etcetera. The desired properties can be improved through vulcanization or curing or cross linking, that is one of the way you just link up each molecules to one another so that it will not slip past, it will not show the liquid like character while application.

So, another way to improve the rubber properties is by adding different chemicals and ingredients includes fillers basically to rubber compound. So, the list of the ingredients is a conventionally means PHR, it is mentioned in PHR that is a unit parts per 100 gram that means with respect to 100 grams of rubber how much is that particular ingredient added.

Let us try to quickly examine what all ingredients, so this is what is the raw rubber. So, it can be any rubber, many rubber I mentioned already, but one of the important system is the cure system. So, in order to have effective cure system not only the curative say for example, sulfur along with that to make the process more efficient and more stable you may add certain other ingredients along with that.

So, activator, accelerator so that way your curing system becomes a package over which you can have the rubber cure, but remember one thing always when I mix it, this curatives are not active. So, you choose such a temperature is not active, it does not start flops linking up to the point when it close you want to give a desired shape and after that only you activate the cure system with the temperature and pressure and you cure it. So, that is very important one thing at this stage you must understand, rubber is a reactive system only like a plastic, fiber or anything else. So, it has to be added at the very initial stages then you have to deal it with until the point you are ready you are satisfied with the safe green safe of it and then you can activate the cure system. So, others as I mentioned it to you rubber as such if you use it however you cross link it also vulcanize it also it will be very susceptible to degradation like say in presence of ozone double bonds you have that will attack.

You have oxygen which can oxidize any you know aliphatic or hydrocarbon base backbone system which is normally common with the rubbers and UV stabilizer and in general it is called light stabilizers. So, other important part is reinforcement what is reinforcement? See rubber is not only the not only the you know hardness sometimes people misunderstand hardness or modulus with the reinforcement. Reinforcement means you add certain ingredient that will improve its failure properties tear abrasion so and so forth. So, that way your fillers can be three types reinforcing non-reinforcing semi-reinforcing. So, I am not going into that detail category will come back when as on when required.

So, filler is the one part. So, many a times in many rubber system you add excessive amount of fillers is something like you eat lot of puff rice. So, you would not be able to swallow it rubber cannot really take it unless you have water. So, in rubber case you have to add plasticizer or oil. So, automatically it invokes the possibility of another ingredients filler which make it tougher I mean harden mass plasticizer makes it soften.

So, you have to have a balance I mean unless it is soft you would not be able to make them flown properly surface irregularities will be there. So, at the same time you use lot of fillers some of the fillers like silica which is very much inorganic in nature that does not go in a non-polar system like rubber. So, you need to use certain additives which is called coupling agent I will try to have a effective bonding with the filler or with the rubber otherwise what will happen filler will try to stay together aggregated or agglomerated form. There will be I mean if you have agglomerate there will be flow of mind stress concentration there and failure will happen from there. So, these actually essentially teaches you a recipe like you cook in your kitchen you just you are trying to make a chicken you do not simply put the chicken boil it you get it no taste nothing no flavor.

So, you need to have a appropriate amount of water oil salt spices and you have to spend on some time of a cooking and then you get the optimum you know cooking done. So, essentially what I am depicting here not the cooking rather the recipe or formulation. So, at least here you can see you have 10-15 different types of ingredients some form or other are used for any rubber compound formulation for any practical use of it that is the bottom line. So, vulcanization name was coined by the after the name of Roman god Vulcans. So, it is actually accidentally invented.

So, somehow in a cold countries like in England people used to wear winter garments and that time during winter it rains also. So, now what happen if you have a warm cloths and go outside you get drenched and you feel cold. So, people invented sooner or later after Christopher Columbus went to you know Latin America and brought the latex. They figured out you dip it the your winter garments it become water repellent naturally because rubber coats on the surface makes a film, but in the summer time when the temperature goes it become tacky. So, somebody pours his you know raincoat just beside the fireplace and accidentally it falls on the fireplace it has a sulphur and wood with the heat and sulphur people figure out it is vulcanized that is how there are some myths that is how it is being discovered, but actually what happens molecular way you have a very gigantic chain molecules and you put sulphur and heat it will try to join this chain adjacent chains together and essentially what you have the polysulfur linkages you have a three dimensional network structure done and you call it cured.

Sometimes the vulcanization is otherwise called as curing as well. So, curing you know vulcanization cross linking is all the way same, but for rubber from the you know very very ancient time when it was coined it is called vulcanization. So, it is essentially formation of cross links. If you look it at two people are named after who discovered the vulcanization one from USA Charles Goodyear another one from England is Thomas Hancock. So, that time they invented you know you put white lead and sulphur into the rubber and try to heat it under pressure it will get vulcanized that was a revolution actually in world economy because that actually added the tire that has given mankind the tire for the movement it is a billion dollar business basically.

But however this cooking rubber or heating rubber with lead and sulphur is inefficient process is a quite slow process and not only that you know carbon-carbon double bond it actually links up if it is only sulphur and then each cross link requires 40 to you know 55 sulphur at a rate takes several hours about half a day or more. So, you can understand that when people try to look for certain amount of things which will accelerate the process of cross linking. And initially people figured out the ammonia does the job any basic material like ammonia does the job, but ammonia is a volatile essentially people figured out aniline does the job better and later on eventually people figure out instead of using aniline which is poisonous if you use aniline and aldehyde condenser product aniline and carbon disulphide condenser product it acts as a better acceleration and if it is efficiently within 30 minutes or even less time you will be able to finish the vulcanization which was apparently taking 12 odd hours. So, there are two types of accelerator one is called primary accelerator they are mostly thiazoles once again I will repeat all the structure what I am naming now are essentially a derivative based on aniline and carbon disulphide that is it and those type of compound includes thiazoles and sulphonamide those are called primary accelerator typically they are used 0.

5 to 1.5 PHR sometimes more sometimes two also I will define the cross linking system. Now some way or other using primary accelerator alone will not give me the essential characteristics I will explain you a rheograph what is essential. So, it may not be the process of cross linking may not be that fast it may not have that much of safety window basically. So, in order to get it often another compound is added alongside with the primary accelerator those are called secondary accelerator typically 10 to 40 percent doses of the primary accelerator is used those includes guanidine although guanidines are carcinogenic and bands these days thiorams dithiocarbonate etcetera and they are called secondary accelerators. So, this is the basics to start with.

Now if you just quickly want to see there are many types of accelerators see first one from the invention point of the primitive ones was aldehyde amine condenser product which is a slow type of an accelerator. Essentially mankind discovered DPG which is actually guanidine based then thiazole comes into picture MBT, MBTS I am not going into the structure structure looks little complicated you may get afraid as a beginner. Then you have a ZBDP then a CBS this is very important class of accelerator these are called fast but delayed action. What is fast and delayed action you may get confused. So, let me explain you with a appropriate figure of which you get it from either ODR or MDR that means torque versus time.

See ideally what you want is initially viscosity should be low and you should have a flat window, window is safety it should not get cross linked because by that time you have to mix it you have to mold it all process operation should be done. Then once you are ready say rubber get cross linked like a step it should get cross linked and then it should remain flat that is the ideal response which we always try to look for. But many a times this I will get it by the combination of such accelerator that is why the primary and secondary let me tell you. See if you use TM, TD and ZMC which are secondary accelerator they do not give you much of safety immediately it starts cross linking. While your TBBS which is a delayed action accelerator you have enough safety window before it gets cross linked.

Now if you add ZMT or TM, TD here see you see this is delayed this is slow build up is slow I can make it like this fast. So, that invokes the possibility of use of primary and secondary and at a particular combination you get a synergistic effect. So, based on its action speed of vulcanization we categorize it like I mentioned slow, slow, semi fast, ultra fast, delayed action and ultra fast. Supposing you would like to make a latex product like say balloons, globes. So, in that case in very thin section you may need very fast curing you once you put the mandrel into the oven.

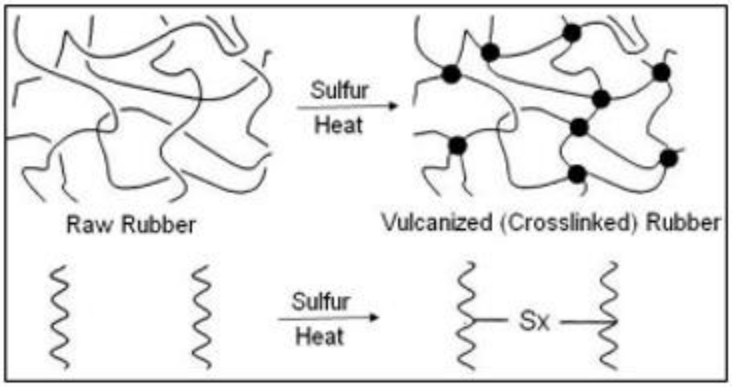
So, at that time you use the ultra fast accelerator. Suppose you want to make a thick section article you go for delayed action accelerator elsewhere this choice is yours depending on the thickness the combination. So, you can see in terms of three parameter once again I will tell you the first is the minimum viscosity. Actually this minimum minus maximum this viscosity of torque let us say its M minimum, M maximum and M max minus M min is the delta torque. Since this delta torque actually gives you how much property development will happen upon cross linking.

The minimum viscosity signifies how flowable your mass will be. This window this distance from this to 0 to say Ts this is your course safety and this slope of this curve is the cure rate you understand. So, this essentially tells you with this certain combination you will be able to achieve this is ideal one what I showed you and that you have to achieve. And upon cross linking as I mentioned it what happened many of the properties like tear strength, tensile strength they get increased although tear strength, fatigue strength, tensile strength they go for through a maxima which may not be the same. So, what it means not all property can be optimized at a particular cross link density.

So, what you are getting are actually you have a cross link density. So, as I mentioned it to you there is a critical cross link density that means in between two cross link there should be certain molecular weight and that I told you 6000 to 10000 and that is what ideally you are trying to achieve. Another thing also you are trying to achieve how equally they are poised because vulcanization is a solid state reaction it is a random process. You may have certain cross link very close by certain very distant place. So, that way the theoretical elasticity theoretical strength you will not be able to match it.

So, this is very very important and zinc the another part of it is zinc oxide and stearic acid combination it is called activator. So, what it does zinc and stearic acid it in situ forms zinc stearate and that makes it soluble in a rubber matrix and zinc actually forms a complex with the accelerator and accelerator and zinc form a complex that complex with you know sulphur that is the active sulphurating agent. So, if you compare vulcanizing with sulphur alone it always attacks the double bonds, but when you have the accelerator and zinc oxide it is always attacks the allylic carbon hydrogen bond that is the major difference. So, that after vulcanization also your double bond state remains same because double bond is important in the sense that is what gives you the elasticity because next to the double bond is susceptible for the free rotation. That is the basic physics of rubber elasticity and that you want to practice by judiciously selecting the ingredients here clear.

Again based on the again take primary plus secondary accelerator as accelerator sulphur as a concentration. So, sulphur by accelerator can be this concentration the ratio makes it different. See when you have a sulphur more than the accelerator total accelerator typically 2 is to 1 around you call it conventional system. If it is another extreme that means sulphur is less accelerator is almost double the amount or more you call it efficient system and if you have 50-50 that means sulphur accelerator similar concentration you call it semi-efficient system. So, what is difference? See if you have conventional system more most of the links are polysulphur in nature it will form majority of them while if you have a efficient system majority of them will be mono sulphur in nature.



See if it is polysulphur what will happen it has utmost flexibility. So, that way dynamic property tensile strength stress dissipation will be much efficient. However, if you have a mono sulphur link that happens in the efficient vulcanization system that will give you ageing resistance because carbon sulphur bond is more stable than that of polysulphur linkages that is the bottom line. So, I am not going into the details some of the formulations are given and you see polysulphur link concentration in a conventional semi-efficient that ratio you can see and that in turns going to give a difference in properties particularly this two properties I mentioned heat ageing properties which is often superior in case of you know efficient vulcanization system while for the conventional dynamic properties and tensile strength will be much superior. So, that is the bottom line you must remember.

So, this is how an accelerated system the efficiency in terms of cross linking how many sulphur molecules necessary to form a single cross links which was apparently as I said 40 to 45 and if you have a efficient vulcanization system because it is all mono sulphur link majority of mono and has disulphur link 4 to 5 per cross link because you may be wondering why not 1 the reason is what you have some polysulphur cross links 2. So, it averages out to 4 to 5 clear. So, now zinc oxide and stearic acid this package is called activator. So, initially people used to use 5 pH of zinc oxide now people use prefer to use 3 stearic acid they used to use 2 earlier now 1 that is a typical formulation. So, why less zinc oxide because zinc can interfere with the marine life it can leach out it is poisonous.

So, excess use of zinc is prohibited these days, but what zinc does in particular zinc actually enables you to have a more distribution of this cross link. So, type of cross link formation one cross link to the other distance. Second rank of sulphur it controls and it gives you some stability thermal stability because one thing I forgot to mention here is if you look at the Q curve see it looks like minimum viscosity then it goes here. So, after curing it depending on system you are using it can be reversion type it can be plateau type it can be marching type. So, if it is reversion type since you have excess zinc, zinc acts as a sink.

So, during the breaking of the cross link at higher temperature I mean at a constant temperature the rheometric experiment you have temperature is constant, but you are since you are allowing time the sulphur may come out from the polysulfur linkages and zinc will trap it. It will not allow it to participate in the cascade of reaction of degradation of the lava. So, it actually resist in that sense the chances of reversion of course. So, I believe I have talked about what activities done or does have already, but you can ask the question why not zinc stearate? Because it is kind of a nascent formation of zinc stearate, zinc oxide and stearate during mixing condition it forms a nascent zinc stearate that is more active than that of if you happen to have used zinc stearate.

Zinc stearate is also used as such. So, this is the mechanism as I mentioned accelerator plus zinc oxide one complex will form that complex reacts with S8, lumbic sulphur here and then this is the complex and that adds to two rubber chains and forms this link. Of course, whole gamut of byproducts also form byproduct means if you have a chain it can give you frustrated cross links it does not approach to the next chain. It can form a clays like thing look so likewise they will actually burden the rubber because remember rubber elasticity is the ease of rotation. So, that kind of a product we always try to omit it. So, efficiently remember this is a solid state reaction and you try to control the reaction it is not easy job and still today even though there are a very good books also Werner Hobman's book is a classic book mechanism of vulcanization.

But still it is solid proof it is not there because it is a solid state reaction and remember you do it in a very very you know messy system you have many different ingredients in presence of that you try to react it is not a single you know in a solvent you are trying to two molecules you are trying to do the reaction and monitor. Even if you do monitor with the solid state NMR also that is a tall task ESR also that is going to be a tall task. So, overall the mechanism is highlighted here any standard book you will get it how the vulcanization is being achieved. So, I am not going into that details any Morissian Moton's book you can refer to as a beginner and there are many books standard rubber books. So, another vulcanization system of course of peroxide cure system where Taq is used as an activator.

So, quickly for sulfur vulcanization it can be retarded also see sulfur vulcanization is a base catalyzed reaction. If you have use any organic acid to that like silysialic acid or any acid it will definitely reduce the rate of the reaction, but what happen the if you if you retard the reaction also that means cost safety you are getting it, but at the same time cure rate will diminish. So, you all have one thing called post vulcanization pre vulcanization inhibitors which is CTP is a classic example that you have you additional cost safety, but cure time will remain indifferent normally it is with the you know with the delayed action accelerated system. So, what happens you are trying to push the cost safety this direction at the same time you do not want to reduce the cure rate.

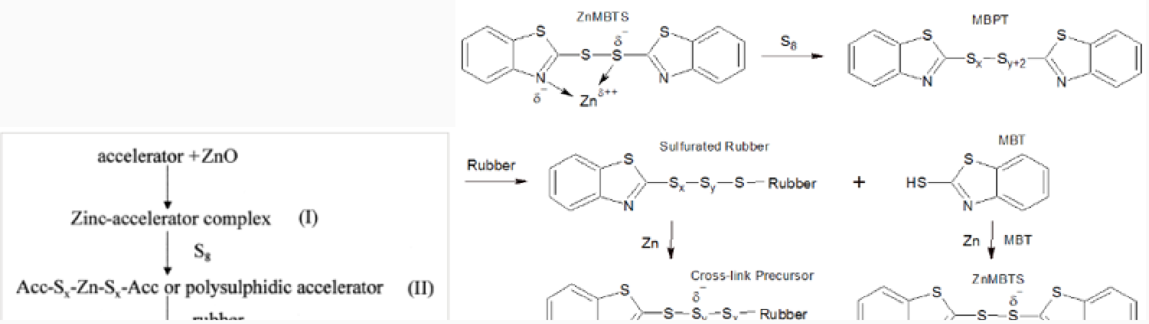
So, that is what how you actually try to use. So, retard that if you use the cure rate will try to flatten out. So, this is a exaggerated version of a Q-COP and you see before you finish the vulcanization start the vulcanization you have to do all these operation milling extrusion you know then building and what not. So, for that reason all these cost safety is at most important. So, this is about the mechanism where from you can see from the allylic hydrogen bond how the cross linking is happening between the two chains. So, I am not going into the details of it in the present context.

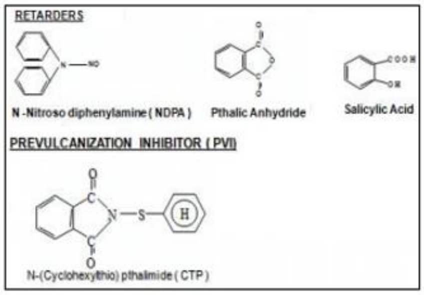
There are definitely different non sulphur vulcanization system available like say quinone based, but they are rarely practiced for butyl rubber case it is practiced this is the mechanism actually quinone is gets oxidized to nitroxide and that actually reacts basically. Similarly phenol formaldehyde resin it is used for again butyl rubber curing it is used in a tire curing bladder also because it has a more you know heat stability than the sulphur vulcanized ones. I am not again going into the details of resin Q-O system you have a organic peroxide Q-O system which actually competes with the sulphur vulcanization, but of course for dynamic application sulphur vulcanized system does not have any alternative for any other application semi static static sort of application peroxide vulcanizations are mostly practiced and that too for a comparatively saturated system like say EPM or EPDM sort of a system. Again peroxide means is a free radical initiated reaction. So, if you have a peroxide it will try to split it into two peroxide radicals and that will initiate initiation propagation termination and following that cross links will form.

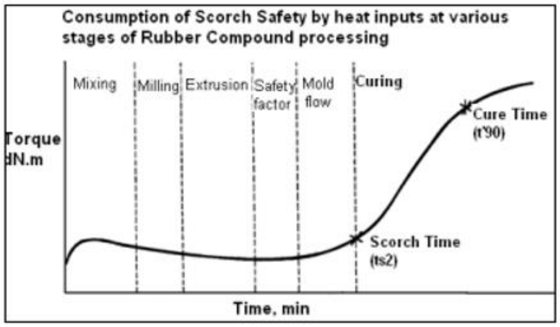
So, many of the rubber side related with the rate you can see those are actually practice for industrial uses vulcanization, but it is not practice for butyl rubber because butyl rubber if you want to do peroxide vulcanization it will try to session under negotiation rather than cross linking. So, there are few exceptions are also highlighted here, but many a times sulphur peroxide vulcanization cannot be accelerated. Rather some activator can be used to increase the radical yield like TAC I mentioned you triallyl cyanoylate or acrylates. So, if you compare vice versa from the heat stability point of view again monosulphuric I was talking about carbon carbon peroxide gives carbon carbon direct bonds. So, it is more stable actually than that of sulphur vulcanized system.

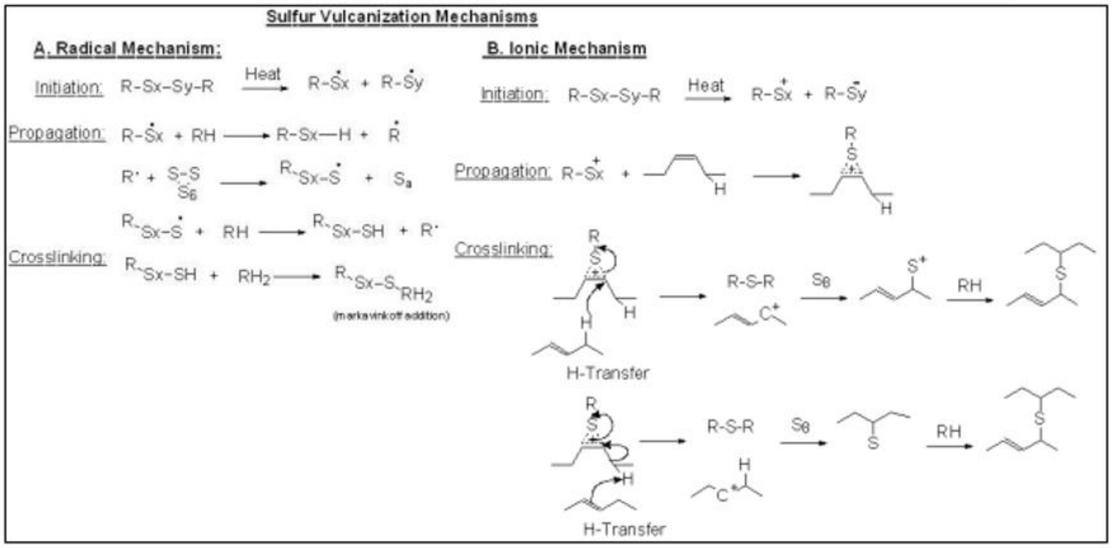
So, it will give you increase heat stability at the cost of flexibility because carbon carbon is more rigid than that of even monosulphuric carbon sulphur. So, other than that you can read it out I will share with you, but I am not going into the details for I am not neither I am going to ask you write a short note here. So, there are other alternative vulcanization

The mechanism of zinc catalyzed sulfur vulcanization



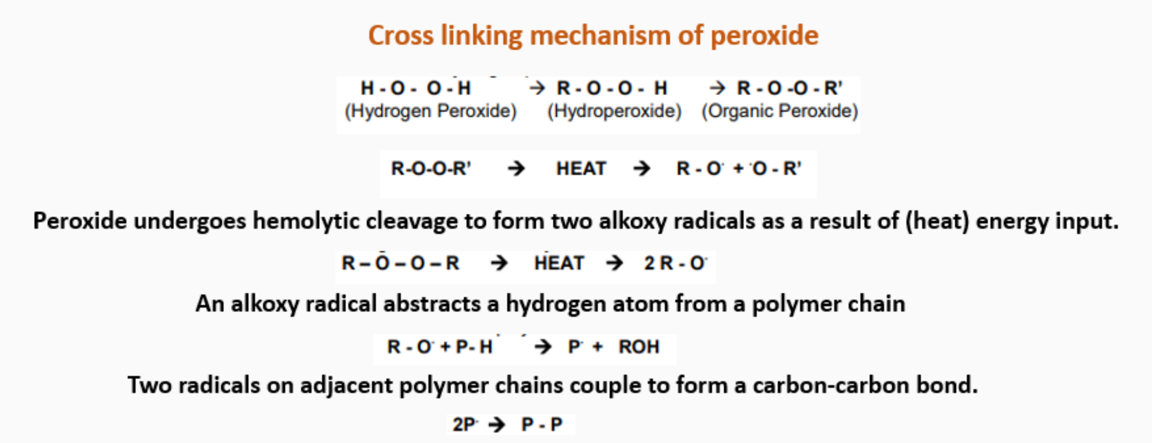






system normally practice with the chloroprene rubber is a metal oxide vulcanization system. Sometimes you use combination of different cure system as well.

So, magnesium oxide along with zinc oxide is used. See this magnesium oxide is known as acid acceptor it scavenges the halogen and forming a bond metal oxide bonds basically with zinc essentially. So, magnesium oxide it initiates and then finally, zinc oxide it settles there as the pop bond. So, there are diisocyanate system used for polyurethane different types of diisocyanate and benzene also diamine systems for acrylics and fluoropolymers.



Cross linking mechanism of peroxide

$H-O-O-H \rightarrow R-O-O-H \rightarrow R-O-O-R'$

(Hydrogen Peroxide) (Hydroperoxide) (Organic Peroxide)

$R\text{-}O\text{-}O\text{-}R' \rightarrow \text{HEAT} \rightarrow R-O^{\cdot} + {}^{\cdot}O-R'$

Peroxide undergoes hemolytic cleavage to form two alkoxy radicals as a result of (heat) energy input.

$R-O-O-R \rightarrow \text{HEAT} \rightarrow 2R-O^{\cdot}$

An alkoxy radical abstracts a hydrogen atom from a polymer chain

$R-O^{\cdot} + P-H \rightarrow P^{\cdot} + ROH$

Two radicals on adjacent polymer chains couple to form a carbon-carbon bond.

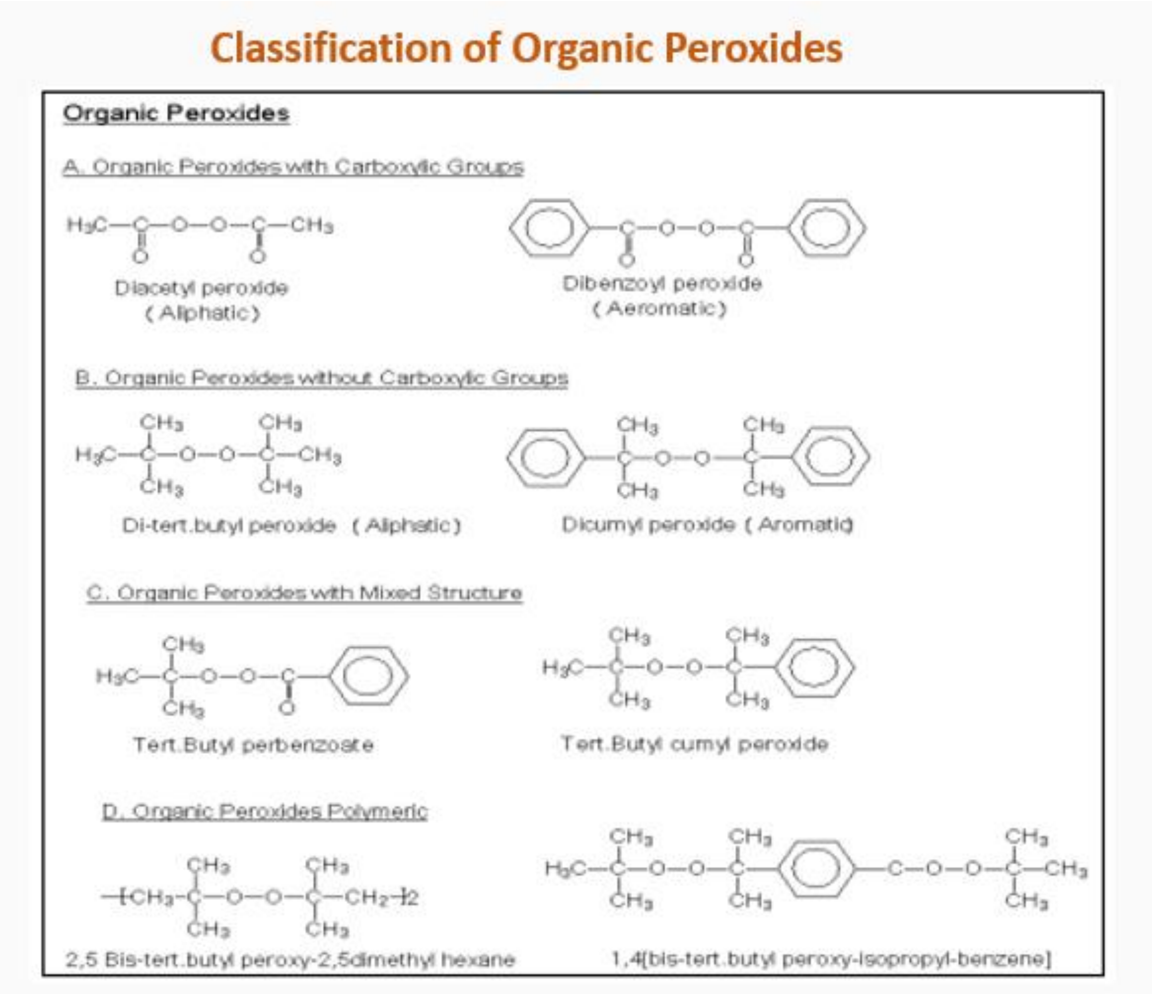
$2P^{\cdot} \rightarrow P-P$

So, there is a one part of it second part is of course, anti-oxidant anti-oxidant anti-degradants how it functions. Like I said, accelerated sulphur accelerators are mainly mainly amine and carbon disulphide condensate product.

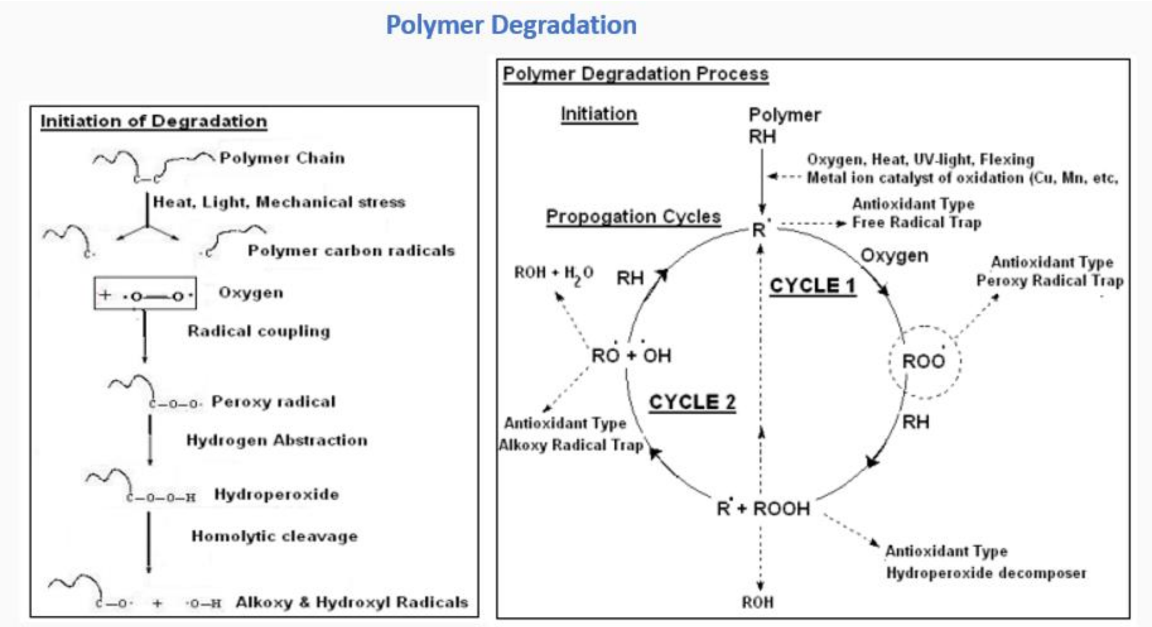
Here the chemistry is aldehyde and amine condensate product mostly. Of course, there are two major types of antioxidants available it can be either phenolic or it can be amine type. But amines are more effective than phenolics, but phenolic has another advantage it does not have a colour. So, that way this is the mechanism of polymer degradation that it happens in course of oxidations this is the whole cycle of it. So, here there are different types of white varieties of antioxidant available that will cut that cycle at different points and based on that the mechanism it works.

So, this is the antioxidant different types are mentioned here I am not going into the details, but nonetheless this is a process by which oxidation of a chain molecules macromolecules happens. So, typically 0.5 to 3.5 depending on the applications. So, another major part is ozone although ozone has a PPM type of a concentration somewhere, but sometimes it is very very dangerous.

Again the antioxidants are majority of them chain terminating type as amine and phenolic as I mentioned. And another mechanism like peroxide decomposes because peroxides forms inside with oxygen reacting with oxygen peroxide or hydroporoxide that it actually phosphites and thioesters works in that mechanism basically. So, once again this is the mechanism and this is what you can see with the ozone what it happens. Classic example if you have a little cheap car when say for example I will not name here any brand name, but little bit economic class you see the window fences I mean windows where you have the glass cans. You will find lot of marks crack marks once your car becomes rolled one or two years that is in is that mostly for the cost point of view they use natural rubber and which has lot of rubber bond and it actually is vulnerable to ozone degradation and specially it happens more when you have applied stress on that and it becomes even worst if you have a dynamic forces acting on the on top of ozone.

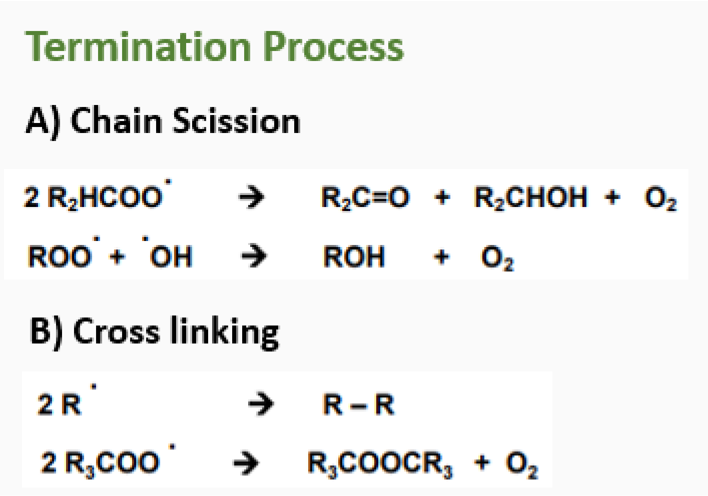


So, these are again some common accelerator for rubber I am coming to paraffinol and diamine these days is banned because it is carcinogenic cancer suspecting, but TMQ is still used phenolic antioxidants are safer. See let us try to see the ozone mechanism if you have a double bond ozone attacks here forms a maleogeonite which is unstable intermediate and once it gets oxidized hydrolyze with the water it spreads. So, essentially your carbon-carbon double bond is gone and that is the mechanism it works. So, you see this mechanism again there are majority of the classes its zwitterion it forms you can turn block the zwitterion it can again you know maybe sacrifice type, but there are many mechanism by which it even the ozone has to come in contact. So, you micro crystal and wax is used which diffuses forms a semi-perverse layers on the surface it does not allow ozone even to penetrate through.



Polymer Degradation

So, those are called physical type of all anti-ozone and again paraffinol and diamines are called you know chemical type it can be autocatalytic or it can be termination of this is how it actually function I will not going into the details, but here these are the physical type and there are certain light stabilizers which are used to improve the light fastness of that and like it gives you in the some UV absorbers or quenchers those are used. So, that will improve its life first fastness it is shown I mean during sort of a different you see this in optical microscopy or scanning electron microscopy way how surface is getting damaged in course of exposure to light and all. So, nonetheless how to select antioxidant system it based upon identify a primary degradation factors understand the underlying mechanism define the service and environmental recommendation may be sometimes only one factor is not see it can happen in presence of chemical oxygen and ozone.



Termination Process

A) Chain Scission

$2\,R_2HCOO^{\cdot} \rightarrow R_2C{=}O + R_2CHOH + O_2$

$ROO^{\cdot} + {}^{\cdot}OH \rightarrow ROH + O_2$

B) Cross linking

$2\,R^{\cdot} \rightarrow R-R$

$2\,R_3COO^{\cdot} \rightarrow R_3COOCR_3 + O_2$

So, you have to do the test simulated test in presence of that and you have to have the measure you have to choose the antioxidant or anti-degradant accordingly. Sometimes telling see how to make a choice between phenolics and amines you are going to make a white compound colorful compound I mean it is not your choice because it has a strong color.

So, that way you have to make your choice, but I am not going into the details of it you can always refer to some of the you know books is already given, but earlier books are rheology, but these three books highlighted here you can always refer for understanding the rubber compounding again the rubber compounding is subjects of its own what I told you so far it is a almost a half a semester stuff I tried to coining within a single lecture. So, in the next class we will try to talk about the other compounding ingredients including the filler. So, in conclusion what I say so you by now you must know what is the importance of compounding particularly for the vulcanization point of view and particularly from anti-degradation point of view. Thank you very much.