Rheology and Processing of Paints, Plastic and Elastomer based Composites

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Lecture 33
Introduction to Two-Roll Mill and Mixing on Two- Roll Mill 1

Welcome to the NPTEL online certification courses on the rheology and processing of paints, plastics, and elastomer based composites. Today we are in week 6 and lecture number 6.3. It is all about introduction to two roll mill and mixing on two roll mills. That is the part 1 of course, we have subsequent parts. So, today we shall be covering grossly the basic introduction to a two roll mill.

We already talked about a bit on that then rheology and mill processability how it can be correlated well. Then material parameter process time mixing and its fundamental. Laminar flow how the flow looks like basically well in course of mixing. Distributive mixing, turbulent mixing, dispersive mixing, mechanism of rubber filler mixing, subdivision of filler I mean, all these five facets of mixing unit processes are deliberate upon.

Once again these are the some of the keywords many of them are common I already talked about in case you want to look through the literature you can use those keywords and have those well, but nonetheless, I will be covering this portion of the lecture from our professor B.R. Gupta's book It is on, and I will give you the reference at the end.So, it is all about rubber and other ingredients; like I said, they have to be mixed well. Mixed well means two major unit part one is dispersion and distribution both has to be done simultaneously.

So, one of the challenges mixing the rubber compounds is the filler because more often filler is a very small site and it has lot of dissimilarity compared to the matrix rubber. Other ingredients including you know antioxidant you know anti degrade I mean other anti degradants accelerator activator they will easily go. So, kind of a if you can crack the hard nut like say dispersing filler rest of the thing will be well taken care of. So, this is what I am going to talk about. So, essentially what you have a machine is two counter root oppositely rotating rolls and in between that the narrow you know separation is called nip the minimum separation and in that you apply brute force and rest part of that mill you have a you know less forces.

So, you have a chances as I mentioned other day brute force is necessary for dispersion and rest are all low shear action is a actually a blending action it gives you a distribution. So, these two combinations are possible in two roll mill. So, in order to understand the mixing further. So, you have to understand deeply the machine parameters the process temperature of course, the pressure and rheological behavior and gum and field why gum and field. So, initially when you deal it with it is a gum rubber and eventually when you start filling it becomes a fill rubber and what the difference it makes it makes changes all together the rheological characteristics of the gum vis-a-vis a filled system as I already mentioned it to you.

In fact, it can change it from a pseudo plastic or power law fluid to a kind of a dilatancy or kind of a other characteristics will be imposed upon going to the presence of filler that is that is how I mentioned here two things a gum as well as filled. So, that you must understand quickly let us take what are the essential parameters that we have to consider of course, the molecular weight and its distribution because as I mentioned it to you always broader molecular weight distribution is better for processing because it gives you a velocity continuity after all and longer is the polymer chain what it ends up with having is a elasticity into the system. So, elastic character means is going to be higher dies well is going to give you higher second normal force difference also as a result you have you will have a melt fracture, skin etcetera etcetera that I already covered in 5.6 I suppose. So, the second thing is a molecular structure you may be wondering I said molecular weight then again molecular structure, molecular structure I means the architecture it may be ladder type, branch type, start type.

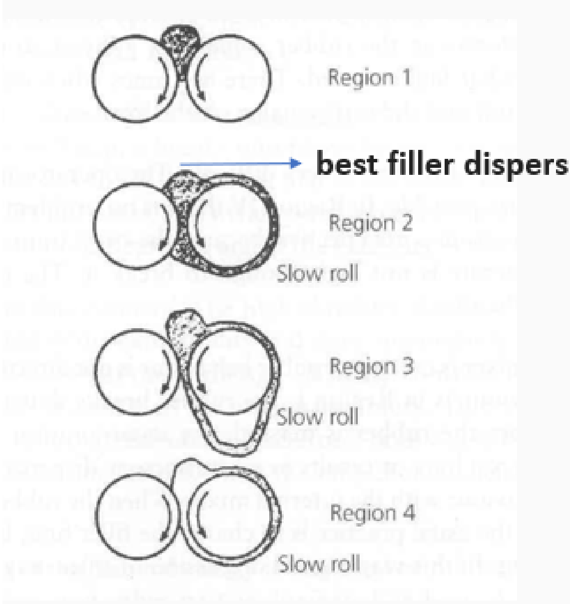
So, depending on that its entanglement density as well as the flow characteristics will change whole lot, and at the same time, if you have a gel content of 10 percent to 20 percent,. So, in that cases also the rheological characteristics will be influenced by presence of gel and not only that think about if you have a gel in the system localized stress concentration will be higher. So, that way think about a filler aggregates I mean in the vicinity of the you know gel it will try to break down very easily. So, sometimes intentionally gels are incorporated into the rubber and that grade of rubber is called superior processing rubber in the sense you will be able to disperse better the filler into the system. So, also of course the filler characteristics is particle size, its particle size distribution, surface chemistry as well as its amount how much pH are as I mentioned many of the rubber formulation, you have more than the rubber filler.

So, in that case as this is also is very important to consider at this stage. As I mentioned structure I mean secondary structure of the filler of it is very very important rule say for example, if you have a higher structure it is quite easier for some sense to disperse it rather than very small structure. So, all together you have to choose a different you know mixing sequence in order to take care of low structure filler by say high structure filler.

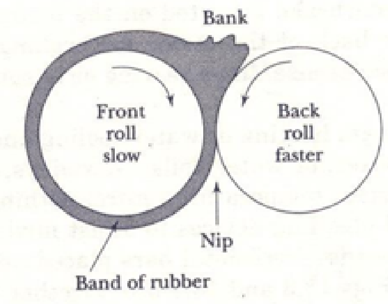
And then machine parameters of course, this is kinematics of it what are those like say roll speed as I mentioned two rolls rotates at a different speed and that is how you define a parameter called friction ratio. Nip gap is important small change even fraction of an millimeter change it changes the shear rate distribution whole work.

So, that you have to consider roll diameter and length because roll diameter decide how much time actually the rubber spins into the nip. Nip area is the most important part once again I will repeat because it actually amounts to the highest shear forces or brute forces you are putting in. Now, let us try to have a rheological sense of it while understanding it. Mooney first as I mentioned Mooney is the first name comes in course of rubber rheological processing. So, Mooney emphasizes the strong relationship between rheological properties and mill processing characteristics of rubbers as those undergoes large deformation while processing.

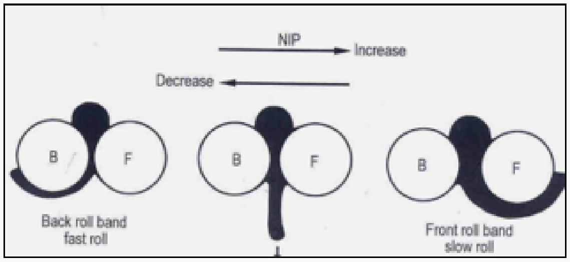
In fact, you will not find many work excepting Tokita and White these two are mentioned few to mention and later on professor B.R Gupta carried it forward. And they actually first time the Tokita and White there they define there are four regions exist see try to do one experiment very quickly let us do. So, I have a you know two roll mill it is rotating I just simply try to put a rubber piece of rubber no ingredients whatsoever. So, initially you will find the rubber is very reluctant to go inside the nip it is a bouncing like an elephant basically it does not want to go.



Regions of mill behaviour of rubbers



Rolling bank



Nip adjustment

So, and then eventually it goes and forms a tight elastic band in one of the roll normally in the front roll front roll and back how do I define the operator faces the roll called front roll and conceptually or conventionally a front roll rotates at a lower rpm. So, that operator gets more chance to handle it with if it is faster you get little chance to manipulate or maneuver. So, this is the region two which is at most important from the starting to end I would like to finish mixing here because I want a tight elastic band. So, that from the roll I will be able to transmit the forces to the filler aggregates or ingredients via rubber matrixes that is important to understand. And then third one if you allow it further remember I am not doing anything I am just try to put rubber inside the roll nip of the roll initially the region one I define it is not going it is undergoing fracture even if I try to force it go through the nip.

In the second instance it is going through and forming a tight elastic band as if it is anchoring the or clinking the front roll that is the region two. Region three if you allow further what happened rolls naturally get heated up and you will find that it will sag like a beard it loses its elastic tension and it is a quasi region mosaic region three. Let me explain why it happens then quickly you will be able to understand. In region 4, what happens is that the temperature goes further up. So, what happens rubber no longer remains elastic it tries to become like a viscous material flow.

So, adhering liquid layer will form on the roll basically. So, you can understand there are these are the four different regions and reason why you know why it happened because as I mentioned it to very beginning at a very low temperature rubber if you just try to go back quickly into the master curve rubber remains in the glassy stage glass transition and then liquid state. Now, this is the behavior of modulus with temperature. If I just try to see quickly this same modulus with the frequency it is exactly opposite. So, practically a machine operates at a high frequency.

So, even if you are I am talking about the room temperature I started the experiment but practically it virtually it goes to a either in the glass transition or glassy state. So, naturally rubbery at this stage when it faces you know roll it is a brittle state. So, it is showing you the behavior region number one and then eventually temperature is going. So, it is forcing it down to a rubbery plateau region. So, it has elastic tension and at the end it actually heated up further.

So, you are in the viscous state liquid phase but what if in the region this is region four region three what happens it is actually mosaic it is neither elastic purely elastic not purely rubbery nor it is a fluid like. So, it is a mosaic phase where, basically, it is instability I am talking about. So, your intention as a as a technologist or engineer to try to confine all your measurement from starting to end to finish it in region two one that is the challenge and as an engineer you must understand the physics of it. So, so far as people used to know that this plural processing was more of art than science. Now, we can understand I could quickly link the region one two three four with the simply viscoelastic properties that means you know modulus versus temperature, modulus versus frequency and it is virtual state viscoelastic state where it belongs and accordingly it is behaving like that.

So, it gives you fairly good interesting isn't it is a good interesting idea to link it the two roll processing with the viscoelasticity. So, quickly define front role is a slow role I will not repeat it again first role is a back role its operator is not facing other side but by the way one thing you must remember sometimes some of the rubbers in special instances special cases it has a tendency to go to the back roll. So, you have to understand the physics of it and try to confine it to take it back to the front roll again quickly. So, that is a challenge as an operator. So, this is the minimum gap is nip gap and this is the reserve bank of rubber actually not reserve bank I am just kidding it is the it is the it is the reservoir as you see all the rubbers one at a time is not going through the nip some are it is like a merry-go-round.

So, one after the other one after the other gets chances and by that process you I will also you have to calculate the batch weight that you mix in a two role name optimally Over-based size is not good; there will be stagnation. So, like if you have too much of money you will not be able to invest much it will be stagnant the same as if you have overburden bank size then it is not good for at this dispersion distribution point of view. So, quickly another thing when you have a let us define another parameter called critical nip gap. See if you take any of the rubber you form a band in the front role then try to push the nip smaller and smaller and then it will switch to the natural in the back role and critical nip gap is between these two instances front and back it neither goes to the front nor it goes to the back it simply drops down because of the gravity and that is what so is called critical nip gap. So, naturally I will not go to the critical nip gap otherwise if you mix in critical nip gap condition then you will not be able to confine the rubber into the any of the roles neither of the roles work.

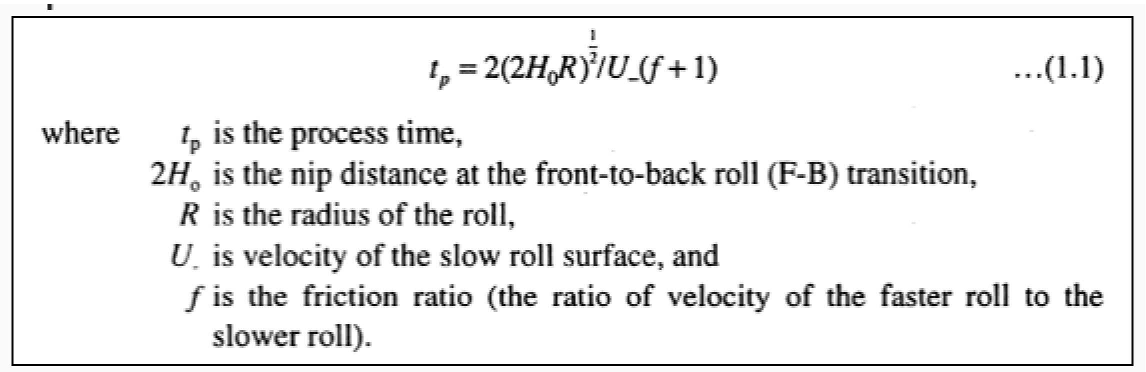
Rather you have to figure out some critical nip gap you have to open it up at some point where it is anchoring to the front role that you have to pick choose basically that is that is that is how you have to work on. So, I am not going into the details I already talked about this there are certain instances shear induced crystallization NR poly butadiene which has to be taken care of. So, it all depends you have to get rid of the degradation. So, you have to have a cooling system as I mentioned it to you at the same time there are some synthetic rubber unless you heat it you will not be able to process it. So, these are the some of the other effects like I said temperature and pressure also plays important role rather than the parameters I defined so far.

So, material parameter I already elucidated a very low relaxation time leads to breaking and crumbling of elastomers. So, I am not going to the details but when I define molecular weight, molecular weight distribution three parameters are important one is zero shear viscosity as I already defined high zero shear viscosity means dispersion will be better because again I will repeat you are transmitting from the roll mill surfaces through the rubber to the filler aggregate the forces shear forces elongation forces pressure forces whatever it is. So, that way zero shear viscosity is very important. Second thing maximum relaxation time what is maximum relaxation time? Time it takes from the you know rubbery plateau to flow. So, you have the you know broader or larger relaxation time means easy to process from the total processing sense.

Third thing is very important to remember is the elongation at break because remember when it goes through the nip the rubber should sustain it should not fail. So, it should have at least 600 percent or 500 percent more than that elongation. So, these thing three parameters namely zero shear viscosity which is defined by eta 0, maximum relaxation time tau max and lambda v which is elongation at break and those three parameters you have to figure out in course of changing molecular weight molecular distribution gel content as well as the branching how it is influential to those three parameters then you will be able to have a better sense out of it. That means again I will repeat higher eta 0, larger tau max and larger lambda v is good in terms of total processing. So, you need to have a combination of molecular structure, molecular weight distribution, gel content in that favor.

So, I am not going into the details, but filler also has a certain role fillers and plasticizers which probably you add in the later stage. So, that also has a sometimes opposing effects also. That you have to counter. Like I mentioned if you have a very high filler loading it actually has a it yields visco plasticity is introduced obviously you have less rubber more fillers in the system also sometime exhibit thixotropic. So, that you have to take care while computing the total shear stress, relaxation time etc.

From rheological sense amount also matters by the way not only the type of filler. So, it is all about as I mentioned it you are already the normal force differences maximum shear forces shear stress distribution second normal force differences it all depends on the elastic memory of the rubber. So, that is also very important while you add filler or not filler does not matter, but you have to really take care of the factor that once you add filler how does it change. So, plasticizer obviously sometimes like I said the example with popped rice and water. So, sometimes if you have learned too much number of filler in order to reduce the visco plasticity you may have to add some oil.



$$t_p = 2(2H_0R)^{\frac{1}{2}}/U_-(f+1) \qquad \ldots(1.1)$$

where t_p is the process time,

$2H_o$ is the nip distance at the front-to-back roll (F-B) transition,

R is the radius of the roll,

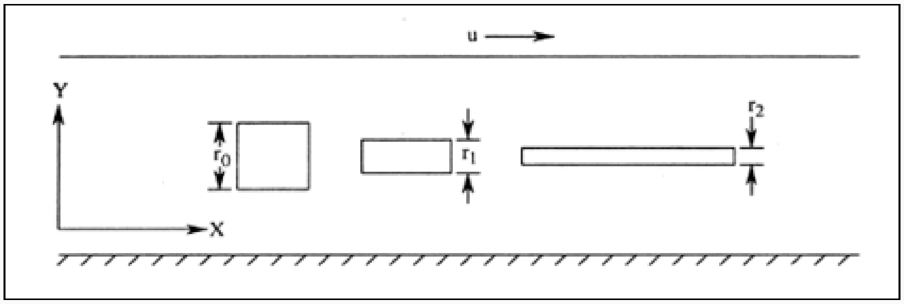
U_- is velocity of the slow roll surface, and

f is the friction ratio (the ratio of velocity of the faster roll to the slower roll).

So, those are the some of the criteria I am not going into the details of it, but rubber processing as such is a kind of a one semesters long course if I have to go into depth of it, but nonetheless. One of the important parameter you have to you must understand what is the state of dispersion end of the day after you mix it that depends on the process time. What process time depends on again a bunch of parameters namely you know critical nip gap 2H0 for the symmetry sake. So, 2H0 is a critical nip gap you can consider half of that H0. Then r is the radius of the roll u minus is the velocity of the slow roll and f is anyway u minus u plus by u minus that means faster roll by u roll the velocity.

So, that is how you can easily calculate in course of your mixing how much time your rubber is really spending in the nip and that remember nip means highest shear action. So, that is how you can calculate. So, I am not going into the details actually this particular equation can be derived from dimension analysis basically. So, I am not going into the details for the paucity of the time here. Once again I will say these are the parameters I had told you that grossly determines good or inferior mill process ability characteristics.

Again when I am talking about mixing I must consider one thing it can be relatively low value viscosity affair when I talk about mixing in a latex stage. Even when I am mixing high viscosity rubber also in solution it is relatively low viscous affairs. But when I am dealing with the visco plastic or viscoelastic fluids I am talking about you know as you remember 100 Pascal second or above. So, under that condition you have to be double sure about those factors. So, most of the ingredients to be mixed with rubber are fine solids and mostly insoluble in the suspending medium, therefore, have to be mixed by imposing the flow in the rubber medium.



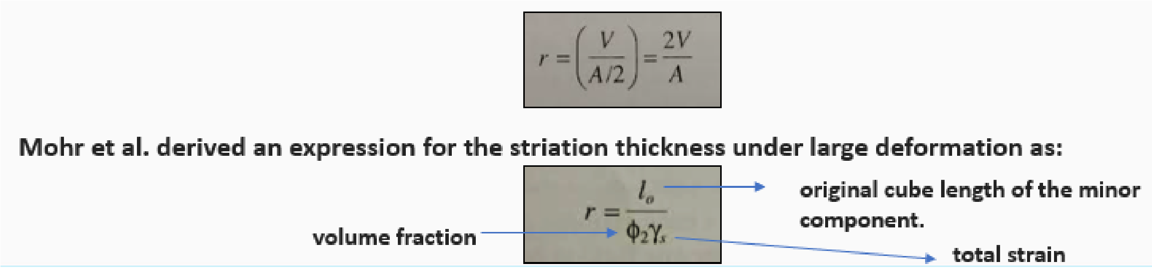
Thinning of the fluid elements due to laminar shear flow between the two parallel plates

So, flow is very very important. So, let us understand the try to understand the flow. So, there are actually certainly to have proper distribution and dispersion some of the mechanisms. See first is the molecular diffusion a molecule through a barrier goes one part to the other. And you know diffusion cannot be the case because you have a very high viscous barrier viscosity of rubber is very high so it is ruled out. AD diffusion also is not possible may be happening towards the later stage of the mixing.

So, main major mechanism of rubber mixing is a you know is a bulk diffusion. It is a kind of a as I mentioned marble color red and other day black you want to mix it literally you have to take it one from that. So, it is a convection bulk convection you can say. So, that is the process that has to be operated by creating AD forces turbulence by turbulence is difficult again to create in a high viscous medium. So, kind of AD splitting frequently applying very high degree of shear force that is how you try to have the convection process on in your system.

Laminar mixing is again it is very difficult to achieve here at this stage. Let us try to understand a particular volume element of the you know rubber. And that eventually is flowing from x direction. So, you see that is getting seared. So, it is getting thinning, thinning, thinning, thinning it reaches some thickness say R2.

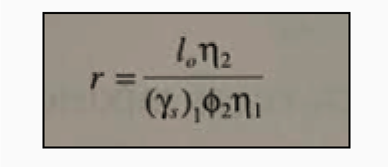
So, exactly what is it is happening you must understand one thing is a gyration thickness R. Physically at some point of time you will not be able to see it in naked eyes, but microscope of course you will be able to examine them and it all depends how much you know ultimately kind of a you know shearing and particle size you are expected to do. Whether it is a nano scale you really want. So, depending on that you have to shear it heavily as simple as it is. So, these are the some of the theories by which the styration thickness you can calculate.



$$r = \left(\frac{V}{A/2}\right) = \frac{2V}{A}$$

Mohr et al. derived an expression for the striation thickness under large deformation as:

$$r = \frac{l_o}{\phi_2\gamma_s}$$

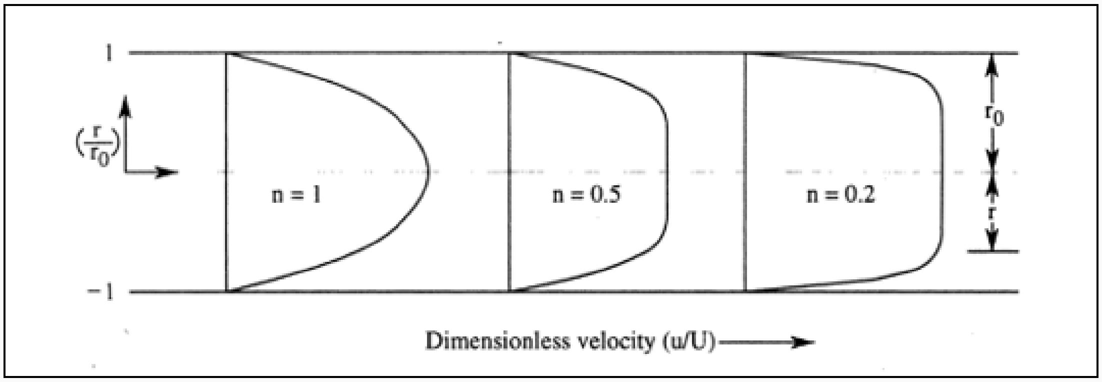


$$r = \frac{l_o\eta_2}{(\gamma_s)_1\phi_2\eta_1}$$

Of course, it depends on the final surface area and total volume. So, volume and surface area total volume is conserved. So, from there you will be able to very easily calculate out. So, similarly from the volume fraction way also the styration thickness at some point of time given you know shear forces you will be able to very total strain what you are applying this gamma s. So, depending on that you can calculate what is the styration thickness.

So, there are many approaches of course to get a track into that and of course implementing the viscosity factor also there are some work people have come up with these are the some expressions. I am not going into the details for the timing by the way. So, as I mentioned it to you the styration thickness and that ratio I mean as I mentioned it is depleted and as you go through from the laminar flow region at the initial this parabolic flow line it goes to fully developed flow and once it goes from in you know initial part to the fully developed one considering I was talking about well considering the well slip etcetera. So, if you consider that your essentially rheologically what is happening n is going towards actually 0. So, n is diminishing that n is the pseudo plasticity index essentially.

So, these are consideration I am not going to the details by the way. So, n value becomes lower and lower lower and lower and your styration thickness is getting smaller and smaller that is what it happens within the channel. Consider between the two roles you can consider kind of a similar environment if a cylindrical flow in sunset. So, you can do the flow analysis in typically nip and around area that way. Although in the next class I will show you not only the nip in the bank region what is happening after it relaxes from the nip also what it happen happens I mean those low shear blending action also I will show you to have a feel.

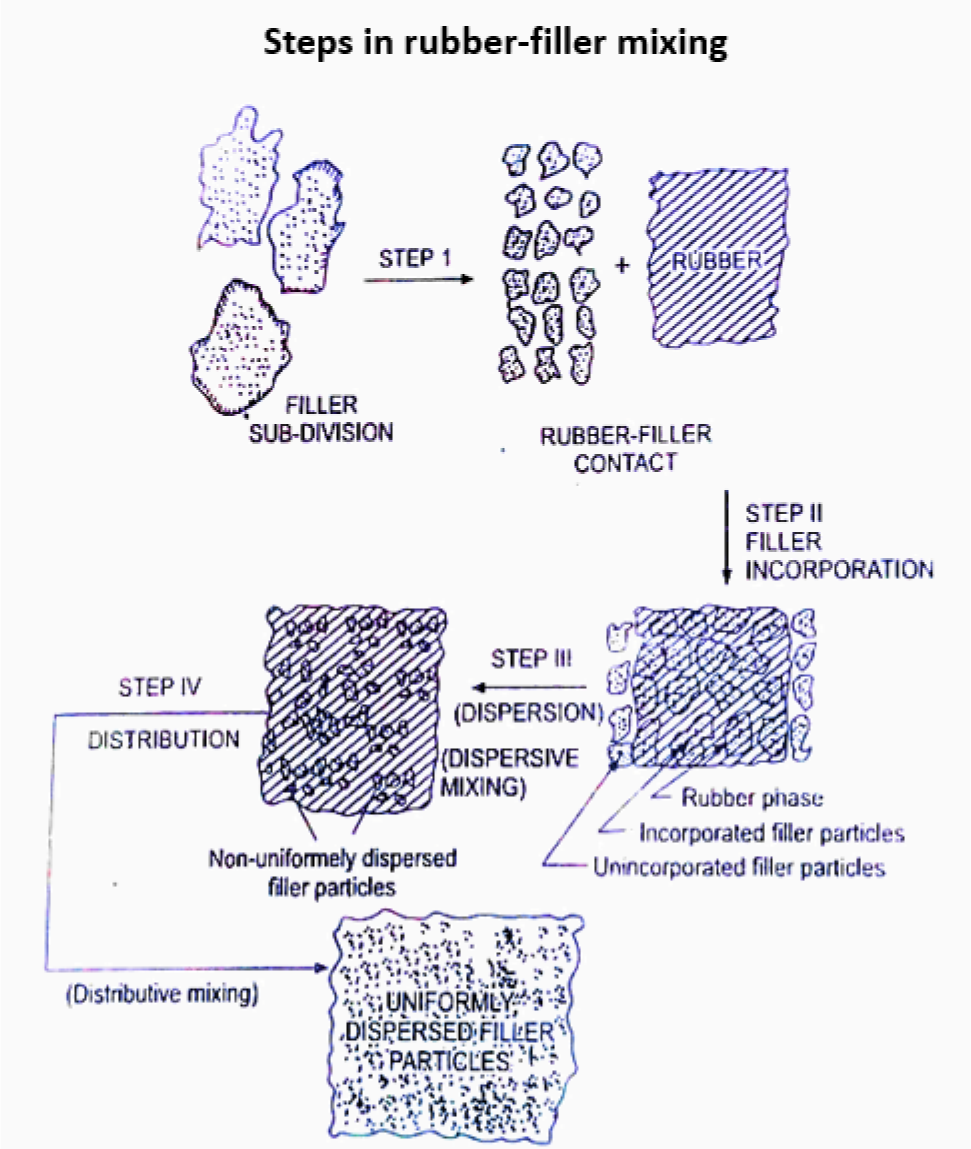


Now, when I talk about distributive mixing as I mentioned distributive mixing is all about low shear blending action. So, if I consider a nip however here it is a very, but here if it is a bank the one which is touching the role surface tries to come over here come over here role stretch is taken alone, but it is a middle man always try to escape. So, there will be that kind of a needing action that gives you the blending basically. So, that is the low shear action I was talking about and when it comes out of the nip also it tries to relax because it was stretched it will try to relax there also you have a kind of low shear blending action. So, that is what and in the nip area you get to see the dispersion the brute breaking down action and so your turbulent mixing is all about in some places or the other you have a kind of a turbulence from the liquid point of view you can consider it.

So, I already mentioned you dispersive mixing happen right at the nip area and rest of the area when stress relaxes and you have a kind of a you know needing action happens on the top of the role. So, that is that gives you kind of a you know blending action or distributed mixing. Let us try to understand this is very important to understand at this stage. See when I consider I have a unique example while considering a mixing unit processes. See think about a train coming to a busy railway station like Howrah Chennai Mumbai unreserved compartment I am considering.

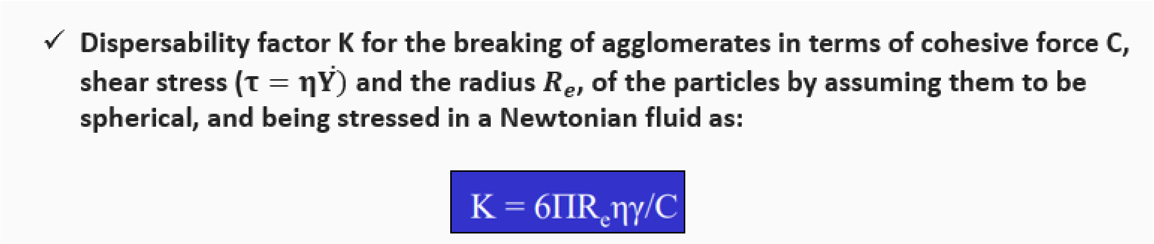
So, what happens first train has to arrive the gate has to be open. So, opening gate means actually lowering down the viscosity which you call mastication. Now, consider people standing are like a filler. So, they will always try to board in faster you board in you get the chairs. So, you do not bother how you go you go with bag and baggages luggages go and there will be through that gate small opening you have to board in and that is the process called incorporation.

The next stage what happens occupying the chairs very fast otherwise you will miss it out 1 hour long 2 hour long you have to travel standing sometimes 24 hours long. So, people will try to occupy the seat but seats are limited. So, what happened then some of the people will go in between the two chairs rows of chair and try to sit there. And as a process will happen the next process after occupying chair there will be little ladies fight each other the little fight between the people and then they try to get distributed within the small passage they get it and they will be very evenly poised. Now, the distribution and dispersion dispersion and distribution first is the incorporation it has to board in second is again dispersion third is distribution and then you see chain registration, Khadabpur station any station the passengers are very free flowing they are very timid by that time.



So, it is the plasticization ready to be processed. So, that is what is happening initially your filler is a large size, large size it does not go rubber high viscous does not go. So, rubber is masticated filler is broken down that is the subdivision stage with the part of the initially before boarding into the train opening the gate up to that. Next stage it goes inside the train is that is what is the incorporation. Next it breaks down is the dispersion occupying the chair.

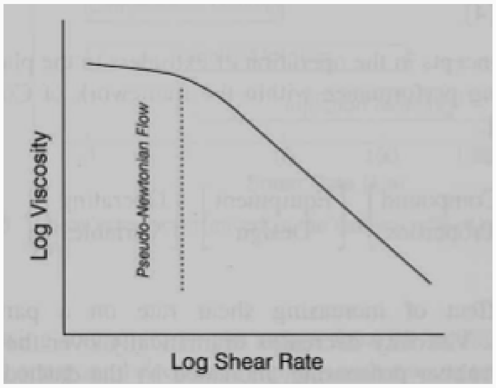
In the next stage it becomes little distributed all ladies are done. So, distribution and the last process is plasticization ready to be processed you adjust the viscosity accordingly maybe add little bit of oil lubricant and you are ready all set your mixing is over and that total mass you are getting ready to be processed. So, this is all about the unit processes and you can go one by one or step by step. The hierarchy wise if you see in filler it has a primary particle size many of the fillers are occupied giving a secondary size you call it aggregate and then all this if you pressurize it compact it it forms agglomerates. So, your idea a agglomerate size is of the scale of millimeter and you have to bring it down to a nanometer actually in the rubber inside the matrix where you do not have a control you have only thing you can control shear stress pressure temperature by which you have to go down and that is what is the challenge basically from dispersion point of view distribution point of view.



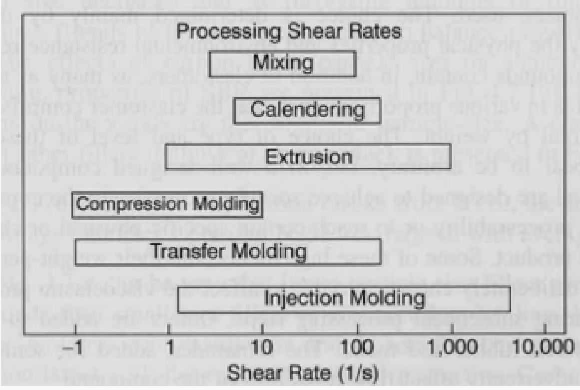
- ✓ **Dispersability factor K for the breaking of agglomerates in terms of cohesive force C, shear stress ($\tau = \eta\dot{Y}$) and the radius R_e, of the particles by assuming them to be spherical, and being stressed in a Newtonian fluid as:**

$$\boxed{K = 6\Pi R_e \eta\gamma/C}$$

So, incorporation as I mentioned you can see to it. So, actually boarding into that and there are two mechanism in fact one is lamination another is comminuation. Lamination means rubber is getting elongated elongated in between filler aggregate comes it gets laminated and comminuation is both of them subdivided and they are getting compacted and because of the you know the forces that it exerts through the through the mill. So, these are the two major mechanisms of incorporation that is grossly divided. Dispersion is a very difficult task tall task although there is a hydrodynamic equation we describe dispersibility due to 6 pi Re into eta into gamma dot eta into gamma dot again considering is a Newtonian fluid shear stress divided by Cc is what is inter particle force.



Pseudoplastic



So, you have to really break down the inter particle. So, obviously smaller is the size your dispersibility will be inferior larger is the inter particle forces dispersion factor will be inferior, but nonetheless this particular hydrodynamic equation does not cannot alone take care of the distribute I mean dispersion from millimeter to micrometer and there is one model called onion model which accounts for like onion you consider you have a several pills. So, in course of putting it and then filler get absorbed here and then gradually as you have more and more pilling and filler are getting more and more filler also get breaks think about if I have some filler aggregate sitting in between these two if it separates out it will try to break it here. So, that way by several such actions like you can realize it from the flow line I talked about is getting thinning thinning thinning thinning and some point of time filler aggregate separates into two and then again that I mean course happens again and again and that is the mechanism is widely depicted as a onion model. So, I am not going into the details plasticization the last step of the unit of a distribution happens throughout the mixing cycle once you start and plasticization is actually you add internal lubricants you try to do little bit more work more shearing. So, that the viscosity goes down eventually and it has more slippage characteristics.

So, that is how you can think about the unit process of and by the way rubber being a pseudo plastic material when you measure it by a Mooney viscometer you get only the low shear portion of it once again you need to have a master curve the whole range reason is why if you consider mixing is happening near about you know 10 to 100 or above second inverse. So, just Mooney alone will not give you information about whether it could be mixed well or subsequently what you are going to do after mixing like say molding injection molding transform molding etcetera extrusion that you do not get any clue. So, if I ask you the question why money alone monoviscometer alone cannot give you idea about the further processing of the rubber to answer the central money works at a very low shear rate. So, what happened rubber being a pseudo plastic at a high shear what is the degree of pseudo plasticity how it behaves it does not give you any clue. So, always keep it in mind before we again come back next day talking more about the two roll mixing.

So, this is the book I was talking about. So, this book I will be covering again in next lecture as well. So, once again in short I try to give you one idea gross idea about you know two roll mixing is fundamental do not forget the example of train if you remember the example of the train starting from mastication then this incorporation then dispersion distribution plasticization will be whole lot easier for you to understand how it happens actually. So, with that again we will come back with the mixing on two rolls, part two, in the next class with that. Thank you very much.