Rheology and Processing of Paints, Plastic and Elastomer based Composites
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Lecture 17
Rheology of Adhesives and Sealants

Welcome to NPTEL online certification courses on Rheology and Processing of paints, plastic and elastomer based composites. Today we are in week 3 lecture number 5 the title Rheology of Adhesives and Sealants. So today we are going to look it at for the application of polymeric material from adhesives and sealants point of view. So the concept will be covered here with introduction to adhesives and sealant particularly those who are new to this subject and factor that determines the adhesive strength, the viscosity testing for adhesive particularly from the point of view of handling and stability and then various rheological tests on different adhesives, dynamic time sweep in order to probe into the curing and shrinkage and dynamic temperature ramp particularly important for pressure sensitive adhesives. And then dynamic frequency sweep and time temperature superposition principle same as I depicted earlier in general and of course the rheological test on various adhesives. Once again there are certain keywords which I already discussed with you and if you wish to have a grip on this subject you can use those keywords and search either in internet or in the journals or in books.

So these are some of the keywords related to today's lecture. So without wasting much of time let us try to concentrate on what is adhesives, what are adhesives and sealants. By definition adhesive and sealants are complex formulations used to bind substrates or seal joints or gaps. So first thing when I talk about adhesives it binds substrates, when I talk about sealants the main motto is to it joints or it joints or gap I mean.

So they come in different forms but commonly is a dispersions containing polymeric material or curing agents, surfactants and solvent. So formulation is very simple unlike a rubber formulation which has many complication many ingredients but in this case it is very simple most often very simple formulation maybe you have a mixture of solvents that may be the complication. So adhesives can be reactive or nonreactive. So based on these we can further categorize adhesives into reactive adhesives. Obviously when I talk about reactive that means there is some form of chemical reaction has to go on there.

So adhesion can be induced by mixing two or more reactive components together. See in everyday use what you use arellite, arellite is the trade name but it is a epoxy resin two part. One is a epoxy pre-polymer and other is a amine based hardener. So you mix it, it has a portal live you apply it and then it will try to join two substrates together. So you might have seen a single phase system none other than favikwik.

What is that? Cyanoacrylates. What happens? In presence of oxygen once you take it out from the bottle it tries to polymerize and cross link basically and that is what the favikwik is. So anyway it can be either one part or two part. This two part I meant like you have additional pot life. So unless you mix them together it would not cross link.

And second one by external stimuli like UV or heat you apply the adhesive and then simultaneously or following that you try to apply UV radiation or heat in order to get it cured and having more and more adhesive bonding. And it can be done in presence of moisture also specially silicon based systems you often have a moisture based cure system. So there are non reactive adhesive as well. So for example classic example the adhesive we use for shoes. Those are non reactive classes.

What are those? Those are polymers solvated or solubilized in a particular solvent natural rubber and toluene say for example. You apply solvent evaporates out and it is a polymer which holds the substrate together. That is how it works. So it is a grossly non reactive adhesive. And as I mentioned sealant the whole idea is to fill the gap.

So the primary function of seal joints or gaps. Seal joints gap and prevent moisture, solvent or gases from entering or escaping from the system or to compartment you want to make it separate. Although many sealants are used they have a multiple functions. You can see in this cartoon here one example of sealant. Sealant is applied and then try to you know press it and gets sealed there.

Putting tiles also you might have seen that you use you know sealants at the edges to fix it on a surface basically or floor. So most adhesive and sealants are composed of polymeric materials or containing monomers or oligomers that form a cross linked polymeric network following a reaction. There is a first category I depicted. And consequently the molecular weight and molecular structure of these components are critical material properties both before and after adhesion. One of the point I must highlight here.

Once you apply an adhesive on a substrate sometimes the diffusion is a governing parameter. So how good that your adhesive material diffusing into the substrate also matters. So it is not only the force that is holding on that the tackiness or stickiness but more of like sometimes how much it diffuses across the interfaces that also matters. I will come down there when I will depict about the you know rheology of this you know adhesives from the application point of view. Many adhesives and sealant formulations are two phase system which include emulsion containing dispersed polymer and dispersed solids.

And in both cases particle size and droplet size can be critical to the product performance. Other day while talking about the paints you remember I was talking about the size the droplet size or particle size the pigment size I was talking about. But in this essence you have emulsion what is the size of the droplet, what is the size of the particle that actually matters that actually determines the performance of an adhesive. So, grossly if I talk about the adhesives and sealants it is all about understanding three things the chemistry of it, the physics part of it and the technology part of it. See why physics because it is related to interfaces, surface energy.

When I talk about chemistry it is all about the polymeric material it is cross linking it is that transformation chemical reaction that I am talking about. And about the technology is the design of the adhesive joints. You prepare the adhesives, you design the joint and how best you can have the highest adhesion strength by designing the joint basically or preparation of the joint say for example. So if you want to optimize the bond strength that is often very important. So in order to do that the adhesive interface is important that influences, adhesive bond that is that it forms that influences.

Materials of bonded part and surfaces say arylite although it can it can glue most of the surfaces but it may be bad while gluing two metallic surfaces. So it is a type of material that you wish to bond and its chemistry also important equally to decide the what is going to be the adhesive bond strength. See if you have a two materials you are putting together say rubber and a metal you are trying to apply an adhesive and bond it. You have to show design that before you know the adhesive failed the rubber must fail because amongst the metal this joint and rubber, rubber should be the weakest that is how your design it matters. Then geometrical forms I mean whether it is a button or it is a lapse type of a joint.

The design of the adhesive joints and its exposures to stress mechanical you know thermal or weather those are the factors grossly influences ultimately the resultant adhesive strength of adhesive you are applying. So nonetheless that is about the very basic part of it but let us try to understand two forces. One is the adhesion strength another is cohesion. Adhesion means between two different substrates. So from adhesive point of view it is between adhesive and the substrate you want to bind.

But about cohesion in between the adhesives what is the strength. So typically if you plot the cohesive force vice versa the adhesive force you can really differentiate different adhesives say for example pressure sensitive adhesives labels tapes that every day you use it. So in those cases both cohesion and adhesion should be at a nominal level very low level. But if you go to hot melt adhesive say for example both the cohesive strength and adhesive strength should be appreciably high amount. And if it is the you know structural adhesives you have to join and that structure has to perform with a mechanical load.

In that case both cohesion and adhesions are equally important. So this you must understand at a first place before even understanding the adhesive this is the very basics. The next one if I try to see stress versus strain plot of it you very clearly discriminate between adhesives and sealants the very two words I uttered at the beginning. See for adhesive the stress strain this has to be very high stiffness has to be very high mostly like towards the hard and brittle type of behavior. While the sealant it looks like a plot like a flexible rubber like a pop plot it's a low modulus high elongation.

But there are something in between exist which is called adhesive sealants obviously that's going to be in between it is a ductile material in general. Again two things a load transfer you are applying a stress how load is getting transferred. So that there is no any point of time no stress concentration happening. And second thing is a gap filling. So in that aspect load transfer in y axis x axis gap filling if you plot it then obviously sealants are the you know in terms of you know gap filling it has the highest implication while load transfer it does not have much of a role.

While for a adhesive load transfer is much vital important rather than gap filling here. So quickly into the adhesives once again what I told you if you look at adhesive it's chemically curable then it can be room temperature vulcanizing type. And then it can be thermosetting type and there is something in between both chemical and physical is a reactive hot melt adhesives it has to both the components basically. Otherwise physical solidifying type is mostly comes into the domain of pressure sensitive and that includes contact adhesives hot melt adhesive physically drying and plastic salts that is how you classify. So in this essence when vulcanization or polymerization I take care of it can be poly addition or polycondensation whatever it is.

And it is not very essential to mention here again for your quick recap. The polymeric material the adhesive base is polymer basically low to medium molecular weight polymer or sometimes high molecular weight also. But it is mostly like thermoplastics, thermosets and elastomers. And in elastomer if you categorize one is a thermoplastic elastomer which is actually physically crosslinked one. It is a thermoreversible one you do not put in any it is a hydrogen bonding force ionic interactions those actually binds these two molecule links the two molecules are chained together while in chemically cross linked one like rubber network you have a chemical links like sulphur sulphur it can be carbon sulphur sulphur carbon or carbon carbon sort of a linkage you have.

So anyway hope it gives you some fairly good idea. See another thing once we apply an adhesive on a substrate what you want it should weight it properly that means it should spread. So now the way you can determine just determine the contact angle of its on the substrate. Contact angle is 0 is ideal situation that means it spreads contact angle is more than 90 degree or 180 degree is a hydrophobic or that particular liquid does not like that solid substrate. So if it is a water contact angle point of view we call it super hydrophobic.

So this has a relevance the contact angle has and which is related to obviously the surface energy component of surface energy that balance of surface forces you get the contact angle basically following Young's equation. So now types of bonds I was talking about it can be chemical bond like here in this particular example you can see so nitrogen carbon they forms between the adhesive and substrate these are the bonds it is forming very easily see its waste kind of a reaction it happen NH2 react with carbon bond. The other thing is a hydrogen bonding type is a chemi adsorption type chemisorption type. So then it can be anchoring type also just mechanical interlocking it can be electrostatic where it is some tune less than that of hydrogen bonding but it is a kind of a secondary electrostatic interaction force between two surfaces. And other thing which can be even stronger than the chemical bond which is called the mutual diffusion that I was talking about in that diffusion matters in between two substrate you have adhesive.

Adhesive actually diffuses through the interface on both the sides and it forms a strong bond basically. So these are the some of the ways your adhesive bond strength can vary basically. So now our perspective here is to understand the rheology or viscosity measurement or management in preparation testing and application of adhesive sealants. Why it is so popular? One of the reason is the quality of adhesive and sealant can be checked very very very quickly.

Second, you can reduce the defects. Say for example your viscosity is low at certain shear rate while application that means same as in terms of paints I told the leveling the adhesive will cover up that particular surface. So there will be no air gap of air void there. Then it is a better yield characteristics, yield stress I mean. Then correct properties, efficient processes and viscosity measurement as such is a cost effective measurement technique rather than many other say for example if you have to go for peels test, other test it requires lot of sample preparation so it incurs lot of cost there. So that way your viscosity measurement or rheological measurements much easier.

Let us try to understand the viscosity testing of adhesives particularly from the handling and stability point of view. You made adhesive, how long will be the shelf life? So solution viscosity or melt viscosity those are two other standard metrics used for the in the adhesive industries. It can be solution with the adhesive is applicable as a solution and sometimes hot melt adhesives So melt viscosity is so important for those cases. So viscosity determines how the material handles its long term stability with higher viscosity that means higher zero shear viscosity means what? It will be stored for long time at the same time when you pump it, it will be difficult. However, pumping, spraying, mixing is a high shear rate operation.

So as you can see if I happen to have a response like this viscosity at a low shear rate is extremely high but eventually when I consider a spraying say 10^3 or more s^{-1}, I have sufficiently low viscosity, so it suffices. So that is how you have a check depending on your type of depending on your application you just target or you set up a particular range that gives you the best performance both in terms of storage as well as applications. So that way viscosity shear rate profile of a non-Newtonian adhesive knowing it very very important and the plateau region the first part of it this plateau that actually very low shear rates and if you really interpolate it, it cuts shear and that particular viscosity corresponds to zero shear viscosity that has to be high that is what I mean. That is what is a viscosity plateau I mean the viscosity versus shear rate plot. Beyond this plateau material is non-Newtonian and depending on your application whether you want to apply in the form of a spray or in the form of a with a brush, so you have to quick choose your shear rate.

Sometimes for spraying maybe at the highest shear rate or while putting a brush or rolling you may demand a low shear rate range and there your viscosity is very important. Now as I mentioned it to you whenever you go for dynamic or oscillatory measurements because I would like to really figure out how much is viscous how much it is elastic because your bond strength depends on the elastic component of it. At the same time its diffusion control adhesion phenomena. You need to have a viscous component as well. There is a typically the balance you want to do ultimately that way.

So, oscillatory testing is a staple is very regular for adhesive rheology lab and help to provide the detailed information about the structural properties of the material in a minimally disruptive fashion. So, oscillatory testing can be thought of as a form of mechanical spectroscopy that involves applying a small amplitude oscillatory deformation to a sample and measuring the stress response as I already talked about earlier. So, now what you get it the complex modulus I mean you can think in from the point of view of viscosity as well as I mentioned. A measure of overall resistance of deformation of the material the structural strength. Second thing G prime the storage or elastic modulus is a measure of elastic or recoverable deformation or strength of the material often used as a measure of cohesive strength.

So, higher the G prime that means the higher is the cohesive strength of the material. So, in a nutshell just doing a frequency sweep you can infer that high G prime at high frequency will often give you high peel strength. Whereas high G prime at low frequencies indicate high shear resistance structural strength of the material. So, one thing you would like to have a good peel strength of the material then design in such a way that it has to give at a high frequency very high G prime value that is the thumb rule. So, again G double prime which is loss that is also important is a measure of viscous or non-recoverable component as you all know and is often a measure of adhesive strength it is just other way round.

G prime while I was talking about cohesive strength, but it is more of a adhesive strength with a different substrate. And again for high G double prime at high frequency it always gives you high peel strength while high G double prime value at low frequency it will give you high adhesions shear resistance specifically. So, these are the some of the takes from that and similarly tangent delta which is the ratio bit of G double prime by G prime and that gives you low tan delta gives you high cohesive strength, high tan delta gives you high adhesive strength of the material. So, that is how a damping factor can decide how good or bad your adhesive material is going to be. And Tm is the melt transition and Tg is the glass transition as obvious.

So, melt is only your if you dealing with the hot melt adhesive say for example. Then again you can have a all this you know rheological properties as a time sweep to vary the time. So, if you vary the time you get both storage and loss modulus and this is in terms of cure it is happening like I mentioned for rubber point of view RPA or MDR the similar sort of a plot you get it. So, dynamic time sweeps or oscillatory time sweeps are used to track the development of structural property of adhesive over time. And they are popular for adhesives that are cured or harden over time, but most important thing the blue line you see which is a normal force difference.

If your adhesive undergoes shrinkage or hardening in that case after curing you will find that there is increase of axial forces or normal forces basically happen. So, in grossly what I can say not only you get a cure information from here, but also you will be able to predict that whether my adhesive is going to harden or not. It is not good from the application point of view if the adhesive hardens basically. So, this is what is very very important. Another important thing dynamic temperature ramp test when I talk about temperature ramp test means I mean frequency is constant and amplitude is constant only you are varying is the temperature.

So, why it is important? Because if you get Tg from here in one end other end from the last crossover you can see the highest application temperature. So, your adhesive application is bounded by the temperature range between Tg and Tx, Tx is the highest temperature. So, that is what gives you idea about up to which temperature your adhesive is applicable ok. So, this is very very important for having a temperature sweep ok.

So, I am not going into the details of it. So, this just before the terminal why it is so important. See after the terminal adhesive will have flow it becomes a viscous fluid. So, it will not adhere rather it will flow. So, that is how it is the boundary, but most importantly one of the developmental work you can always do fundamental work that from the plateau modulus and terminal modulus you will be able to calculate out diffusion time and that diffusion time is important for the adhesive to diffuse through the substrates ok.

Although in this context we are not going into details of it. Very grossly for a quick recovery a quick recap ok. If you plot modulus g prime versus temperature you see if you crosslink this plateau part will vanish and gradually gradually you see increment in terms of modulus plateau modulus and finally, if we weigh too much crosslink even glass transition will miss out ok. It will be masked basically because there is no not much of segments to give you segmental mobility there. With the molecular weight obviously, increase the molecular rate plateau part will get extended from here to here to here. So, it is getting extension of the plateau modulus the plateau part of the you know master curve.

Similar so, if you increase the molecular weight distribution if it is a broader you see small molecule will start flowing, but if it is narrower it will try to give you extended you know plateau value ok. So, you have to really pick choose depending on your application whether to go for broader molecular weight distribution, whether to go for you know higher molecular weight and what effect the crosslink it gives into the overall dynamic properties. So, dynamic frequency sweeps and time temperature superposition principle as I mentioned the TTS earlier in details that also plays very very significant role you just in frequency is just reverse ok. And you will be able to figure out the those all crossovers. So, here is the glassy state, glass transition, then rubbery plateau, then terminal region here it is exactly reverse ok.

So, and most importantly most of that rheological machines dynamic rheological machines or DMA's they were limited by frequencies you cannot go beyond say 100 hertz or 1000 hertz. So, in that case if you wish to you know just anticipate what is going to be the response at a higher and higher frequency that you can easily assess by implementing the TTS specifically. So, I am not going into the details as we have already talked. So, axial test I am not going into the details the three major test for adhesives are important and some of them like tackiness, peel and adhesion and cohesion these are the ASTM number by which you can do nonetheless axial test tackiness and peel strength. Then what is axial test? You apply and then try to see the separation between the substrate and the adhesives you applied.

Tackiness is generally described as the speed at which the an adhesive can form a bond with the substrate and that has there the diffusion has lot to do basically. For example, if you have a very long chain molecule you have very less free ends and a small molecules total number of free ends increases. Actually adhesion the best way to conceive the mechanism for adhesion just refer to a Velcro joint. Velcro what you have many loops and some many hooks and this loops comes from the polymer entanglement and this hooks come from the chain end which it can anchor and that is the many a times is described the Velcro joint as a mechanism of adhesion correct. So, peels test is another test which is very important to separate basically ok.

See these two test say adhesion and cohesion you see this failure is a adhesive is still attached you try to separate out this is the adhesive substrate you apply the axial force. So, here see adhesive separates this is the adhesion failure and in this case still you have some adhesive attached here. So, it is a cohesion failure which fails from the adhesive between the adhesive itself ok. So, that way these three test are important, but nonetheless it does not have much of relevance, but for your information, but in that case what I mean to say that structural strength has lot to do. That means, you say refer to elastic modulus G prime and then second thing when you talk about the you know tackiness a diffusion has lot to do ok.

Again with the frequency with the shear rate that shifts. So, you have to your lookouts should be just figure out those fundamental properties and try to have a guess on that. So, rheological test for hot melts again thermoplastic polymers having high molecular weight. However, high molecular weight generally do not have sufficient adhesive power. Reason I told you if you have a very large molecules number of hooks are decreasing although you have number of entangled point that means, you know loops are there, but lack of number of hooks.

So, Velcro joiner will not be good from that example point of view ok. So, we can include in that case lot of plasticizer, tackifiers, stabilizers and hot melt adhesives are applied in the molten state as the name says and the must flow smoothly. So, you can understand at that particular frequency or temperature it should have a flow ability. So, let us try to see two hot melt adhesive one and two. Although initially they look very similar, similar place they gives the crossover coming to the, but in one case you see this adhesive has a much lower modulus so that means, it is more flow able. So, the until the melting temperature is released they are very similar you see, but at high temperatures above melting temperature hot melt one shows better weighting because it and leveling because it is viscosity is low modulus is low there.

So, rheological test is a plastisol is nothing, but plasticized I mean, formulated PVC. It shows you very interesting behavior if you increase the temperature you know always g prime is higher than that of g double prime ok. So, in this case you do try to do oscillatory test the best way I mean this these are sometimes called artificial leathers ok applied on the floor sealing profiles etcetera etcetera ok. So, the best way to describe the temperature-dependent thickness behavior of a plastisol paste is the oscillatory test ok. At constant amplitude and frequency you do the temperature sweep and the onset of temperature of the gelation process is reached when the viscosity and stiffness of the paste increases at typically 60 degree and finally, the plastisol usually reaches its maximum stiffness at oven temperature of 120 degree.

So, what is important here the values of g prime and g double prime increases with the temperature and thickening and gelation occurs. The storage modulus g prime is always higher than that of g double prime this is the behavior typically you get to see for the plastisols and doing its oscillatory test is very mandatory understanding that. Again if you want to probe into the as I talked about for the paints cases if you wish to probe into the thixotropic behavior these are three stages you have to perform the experiment rheological experiment this is for silicon sealants which is often used. See you try to apply the time and different step test you try to monitor in S1 the recovery interval elastic part is immediately above the viscous part the structure will reveals faster than S2.

So, S1 and S2, two sealants if you compare. While in S2 for certain time the viscous part g double prime is still above the elastic g prime and recovery interval initially they form the form is unstable. See initially unstable is slower basically. So, both recovers only partially after out of the cartridge, but S1 shows a better physical stability than S2. So, by performing a so called step test that is what I mean a three interval thixotropic test it is called the material is measured under variable applied deformation and forms small amplitude to large amplitude oscillation and back to the small amplitude oscillation.

This I thoroughly depicted other days while talking about the paints. And a three interval thixotropic test in oscillation provides valuable information on whether the sample is still flowing that means still flowing is g double prime obviously greater than g prime or it's already in a solid state which means g prime is taken over the g double prime elastic dominance happens. So, that understanding you can get it from there. As usual I said if you want to use a adhesive which has to be cured with a UV you can always have a complex air modulus monitor as a function of time.

And you see how it happens. So, you can see 50 percent UV viscosity. So that way the figure shows that the how curing time of UV curing glue as well as the final stiffness are affected by the intensity of the UV radiation. So, this percentage shows how much the UV intensity you are applying from here on to the adhesive basically. So, UV curing is best monitored using oscillatory rheometry as I mentioned. So, higher the intensity more immediately the reaction and earlier the approach to the final value of the modulus.

So, higher UV intensity so obviously it will be cross-linked more. So, hope it gives you a gross idea about the how effectively you can use rheology or oscillatory rheology I mean more importantly for the development as well as testing or assuring the properties of adhesives for the new development to day to day checks. So, we have added this two references here because it deals with adhesives only otherwise the references remain same. To conclude finally, I talked about what are adhesives and sealants and factors that determines the strength of adhesion viscosity testing of adhesives storage stability handling stability from application point of view same as the levelling for the paints, dynamic time sweep test for curing and shrinkage, dynamic temperature RAM for pressure sensitive adhesives, dynamic frequency sweeps and time temperature superposition principle some of the test quickly I mean although I did not go into the details of it, but talked about tackiness, peel and adhesion and cohesion. Rheological test for hot melts, rheology of plastisols PVC we took it as a reference here, rheological test on silicon sealants and finally, we talked about the UV curing of the adhesives. So next lecture we will try to very quickly cover up fibre and plastics and of course, the rubber we will take in due course later.

So that gives you ends you in the last class the most of the I mean components rheological properties how it is important till then thank you very much.