Rheology and Processing of Paints, Plastic and Elastomer based Composites

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Lecture 1
Basic Introduction to Polymer

Welcome to NPTEL online certification courses on Rheology and Processing of Paints, Plastic and Elastomer Today we are in week 1, very first lecture 1.1. We are going to talk about basic introduction to polymer. Quickly the concepts covered in today's lecture includes the definition of polymers and classification of polymer. We will start from the scratch. Let us stick to the basics first.

So, the keywords of course, are polymer, rubber, plastic, fiber of course, what it is not given here. Another subclass in terms of application is paints and adhesives although we will be mostly concentrating in present context on paints only not on adhesives. So, now the very basic question and first question is where polymers are used. In fact, it is not a exaggeration if I say our life starts with the polymer ends with the polymer and the day starts with the polymer ends with the polymer.

The reason is that early morning when you wake up the first thing you pick up is a brush ok. And the whole day you use polymer in various forms or the other. Starting from the pen you are picked up. And when you ultimately go to the bed you go to the bed that is made out of textiles there is a class of fiber there is a polymeric material. So, it is not an exaggeration if I say your day starts with polymer ends with polymer ok.

In fact, every day you come to the office, go to the school, go to the college, you you ride on a you know tires and that is made out of polymer which is a sub classification of its an hour ok. So, if we just quickly glance through what are the area polymers are used including rubber, plastic and fibers. It has its implication in manufacturing industry as I mentioned it to you in a finished engineering goods like say tire, conveyor belts from rubber point of view you know your garments, clothes from fiber point of view plastics in the forms of bags, in the bottles, in the in the chairs, tables and where not ok. So, in the manufacturing or day to day application they have you know presence. If you look it at polymers are smart also.

Many a times polymers are used to make the printed circuit board and that you use in mobile phone or color TV those devices ok. Polymers are used as a very extremely very very sensitive sensors and actuators ok, diagnostics applications ok. Polymers are find implication in medicines ok. Today the drug delivery particularly in the you know treatment of cancer, treatment of you know you know chronic kidney diseases is delivered by a control and sustainable delivery system. And that vehicle is made out of a polymer which actually engulfs the drug that does not allow to the to have some side effects.

It will be specifically in a in a stimuli responsive way it will be delivered to a particular organ of a tissue of interest. So, rest will be safer. Similar so, in case of fracture of heart tissues a bone ligaments ok, you have polymers which can used with a cell cell seeding and which can temporarily give the supports as well as I mean over time your cells and tissues will will assimilate it and you do not need a second surgery to mention a few an implication of medicine. And there are a huge amount of implications in medicine because if you look it at our body is made out of soft tissues, proteins, DNA those are actually I mean in in that essence are polymers. Polymers means large molecules made up of small small units, proteins say for example, it is a poly amino acid you can say ok.

So, in the energy it has presence in the form of a solar cells, triboelectric generator, in the space lot of applications ok starting from you know engineering plastics to you know rovers ok and fibres. You have its presence in the mining when you mine something you have a conveyor, you have a you know different types of vehicles that tire everything there. In biotechnology as I mentioned I mean it is very closely overlaps with the medicine, but there is fine line of demarcation there also you have the presence. Agriculture you you you cultivate you retain water you you you try to have the ergonomics ergonomics in a very very better way better engineering way you have the polymer there ok. You have it in electronics as also also mentioned.

So, in that essence when I talk about a polymer it is not of polyethylene carryware, it not about you know tires for the you know for your transport ok. It has presence in a value added products and those gives you thus kind of a smartness. So, when you fabricate this polymers I mean devices or anything engineering material out of polymers its rheology plays very very important role. Unless you cannot make the device however, whatever value added properties you make it end of the day by research in your lab or study that does not have any implication. So, this processing is actually related to the rheology of the material you have to make them flown in a precise manner.

So, that you have a very very good surface finish you have a good aesthetics as well as the precision ok. So, that is what the context is. So, we are going to talk about a organic macromolecules or big molecules, gigantic molecules and we will try to look it at how to understand the rheology and how the better way you can process it ok. So, today you can know I mean earlier it used to be very conventional manufacturing technique. Today you have additive manufacturing, you have 3D printing.

So, in that those essence you you you need to fine tune another only the properties, but the processing as well. Let us go back to the basics as I mentioned what is polymer think about a flower multiple number of flowers you add them together what you end up making is a garland. So, that way a 'mer' is a basic unit small unit you put them together add one after the others and you end up making a gigantic molecule that is what you call it a polymer. But again there is a typical definition how big is going to be the garland? This garland or this molecular weight I will say here molecular weight has to be at least 10000. See for a small molecule you talk about 50, 60, 100 molecular weight in this case it should be at least 10000.

Now, question is that below 10000 what I call it still there of a repetition you call it as a oligomer. So, all these polymers say you know in the form of rubber, fiber, plastics, paints I am talking about it is a little bit more of more than like 10000 molecular weight. Of course, in adhesive or paint certain application it can be little in the oligomeric form also that is a different part of the story, but mostly it is of you know high molecular weight. So, you understand one thing by now for sure the monomer is a basic unit like say propylene is a basic unit you add them together this propylene this double bond consumes adds them joins them and this 'n' is a degree of polymerization how many such you know monomers are united together. And as I mentioned oligomer is a small how small less than 10000.

So, you can see monomer to dimer to trimer you add them together and as if you are making a necklace out of is a small chains or garland out of small small flowers the polymer is slightly solid. So, now when I imagine a molecule simply water molecule you take it example of a water molecule. You take an example of a methane molecule say for instance ok. How do you anticipate you try to have say methane all 4 hydrogen in a tetrahedral fashion bond angle 190 degree 28 minute they add together and you can imagine it is as a sphere. So, basic dimension where you define is a diameter of that particular molecule it is of the tune of few Armstrong, but when you look it at a polypropylene molecule say for example, it is actually cylindrical in feature.

So, you have to define two things length and diameter and rather L by D ratio length by diameter ratio is a engineering term that determines how long is your chain is basically. Now, what is the implication of L by D ratio then? If I have a larger and larger L by D ratio these molecules above those number of one mole of such polymer you put it they will try to be heavily entangled each other ok. So, if it is heavily entangled it is very difficult to take one molecule out of this bulk as a result what will be the difference? Difference will be viscosity is going to be tremendously high. Viscosity means what? Resistance to flow say if I take a viscosity of methane, methane is gaseous anyway if you cool it down it will be liquid. So, water and a polymer melt in the liquid state say.

So, the difference basic difference will be with the equivalent concentration even if in a solution state also equivalent concentration polymer will have to be much larger viscosity. So, it is always offer more resistance to flow. So, that is the basics and why we are so concerned about that? It is a gigantic molecule highly entangled and that I am trying to force it to pass through a small clearance of my interest and how good it is flowing, how it is covering up the nozzles or corrugation of the moles and dyes that ultimately matters because it has a much larger viscosity compared to the small molecules. Now, let us go quickly brush up I know you all have a background on you know polymer, but still let us start from the scratch ok. This course I want it to be self standing ok.

I mean you can start from here end end from here ok. There is a whole intention. So, rheology perspective processing perspective should be self standing this course. So, let us take it source based on source. See mother nature has given us many thing.

So, as is the polymer. If you look it at your hair although I do not have many, but this hair actual is a polymer ok. It is a keratin it is a protein basically ok. So, you can see hair itself you can see it has a very high L by D ratio sort of aspect although not a single molecule is there multiple number of molecules are clogged together giving you to you know fibrous aspect here ok. Another very very very common you know polymer we get it from plant sources which is the largest in the planet ok. It is a cellulosic material cellulose hemicellulose those are all.

I mean repetition of sugar units basically carbohydrate units there ok. So, similar so is the natural lover you get it is nothing, but isoprene what is isoprene? If you just quickly I understand many of you do not like chemistry, but it is a very simple chemistry believe me. It is CH2CH single bond CH double bond CH2 ok. So, this is a butadiene unit. So, out of this butadiene unit if I just remove this hydrogen put a methyl group instead and that is the isoprene.

If you polymerize isoprene nature mother nature does it by biosynthesis route ok. There is a process it is all together a different story. So, it polymerizes and believe me this molecular weight is several lakhs it can be 2 lakhs 3 lakhs 6 lakhs even the molecular weight gives. Of course, one thing you must remember for a polymer you cannot have a you know one type of a molecular weight. It can be with respect to number you call it number average molecular weight.

It can be on the basis of weight weightage how much is the larger fraction you have. This is a weight average you have a Z average also ok. So, likewise weight average has more relevance to flow because it is all about the large molecule and large molecule you know are sluggish fat people are always sluggish to move ok. So, that way that determines the rate of flow. So, more weight average has more implication for the flow rather than the number average which has relevance to the colligative properties ok.

So, I am not going to the for the timing in those aspects. Now, you have a protein you have a starch those are all natural polymers. You have a synthetic polymer which people made it mankind has made it over time synthetically like I showed you the polypropylene one example polystyrene example polyethylene that you use as a commodity plastics basically you have been using plastics also I am not going into that details. But there is in between natural and synthetic which you call it semi synthetic ok. See cellulose sometimes they do not dissolve so easily that does not process so easily little bit of functionalization carboxymethyl cellulose, cellulose ether format ok.

They are all processable you call it as semi synthetic because mother nature has given you on top of that you are augmenting certain functionality got it. So, similar so cellulose ether natural rubber you got it you halogenate it will be oil resistance because you have a polarity induced ok. So, those are called semi semi synthetic class. Now, based on the thermal responses also there are classification. See there are one class called thermoplastics that means, you heat it it will flow you cool it down it will become solid.

So, solid to liquid reversible transition it has most of the plastics are thermoplastic in nature. But there are another class is called thermoset. So, what you do you synthesize the polymer you heat it out give it a shape and it cross links it sets it will not be reverted back. Say for example, epoxy, melamine formaldehyde even rubber when you do not cross link it up to that stage it is thermoplastic because processable. You heat it will flow liquid like you cool it down it will again, but if you cross you cross link say each change which each other that is what you do normally for the rubber application you call it a process of vulcanization it does not really flow ok.

It becomes thermoset and that is a very reason processing plastic or fiber compared to rubber is tricky. When you put rubber for the maximum application you try to put in cross linking agents and then with that you have to process you have a reactive system. So, you have to do all the processing before it sets in and then you try to finally, cross link it ok. So, processing of rubber is all together bit different from fiber or plastic processing because those are all you know thermoplastic in nature. There is one another class which comes in between rubber and plastic it is called thermoplastic elastomer ok.

What it is you know as you know rubber has a typical property you stretch it, it will stretch elongate with a small force release the force it will try to snap back come to the original position original dimension rather ok. Plastics on the other hand you try to stretch it after yield stress there is very small nominal amount it will try to go for permanent deformation. However, you draw the force it will not come back ever ok. Thermoplastic elastomer is a class in between those it is still thermoplastic it has a hard domain and soft domain. You heat it out hard domain will unzip vanish.

So, it will have a flow ability you pull it down it will come back and this hard domain is a physical cross links basically those are not chemical cross link and that allow the snapping back phenomena like just like a. So, your thermoplastic elastomer can be processed like it has advantage processing advantages of plastic and coined with the property advantage of rubber. Let us say different sub class of it ok. There are various variety styrene butadiene block copolymer ok. There is a styrene variety poly-olefinic variety you have ok.

You have rubber plastic blends out of that you will be able to make it. So, that is all together a different part of it ok. So, now again going to the classification say as I said flower. So, you can make a garland out of a red and blue color. You can make a red blue and green color so that means, what you are doing you are changing the type of 'mar' unit monomer unit repeat unit.

When you have a only repeat unit say yellow. So, you are making all yellow chain strands you call it a homopolymer. Say for example, as I exemplified already polyethylene is of that class polypropylene is that class you can represent it a is the monomer its repetition. Now, when you take more than one you call it a copolymer or heteropolymer rather ok. So, it is made up two or more repeating units at as this cartoon source we took it for simplification two already red and blue here ok. You see this red and blue their appearance in the main chain backbone is quite random there is no sequence what say where you call it a random copolymer ok.

You have a alternate one after the other one after the other kind of a repetition ok. That you can make it during synthesis I will come back there how you make it basically ok. That all depends on the reactivity ratio of this monomer when polymerizing ok. Then you have block ok. So, block is like only black, block of blacks and block of red block of black block of red it can be di block it can be tri block it can be I mean randomly I mean it can have multiple blocks also ok.

And fourth class is graft that means, what one class of monomer will be in the main chain backbone and other will be you know coming out emanating for the main chain backbone ok. It is called graft polymer. See fact of the matter is this first two classes you will get a single Tg, glass transition temperature, but later two you will have a multiple Tg characteristics of black and red. And here it is all mix up you can see they are very close to each other.

So, they becomes unified almost ok. So, these are the examples random copolymer SBR, NBR those are the rubber class styrene butadiene rubber styrene acrylonite butadiene acrylonitrile rubber. In alternating class nylon 66 ok. I mean one monomer another monomer one after the other condenses basically. This is a condensation polymer I will come back what is condensation polymer. Block is SBS block is a thermoplastic glass polymer that I exemplified ok.

And there may be graft polymer I mean polyethylene backbone grafted with the butyl acrylate ok. So, there are some reasons why. So, you now try to understand if I have a different architecture of a polymer ok, your flow will be different. Say for example, if you have a small branch polymer is radius of gyration is smaller than the linear one with a equivalent molecular weight. So, in that space graft will easy to flow rather than you know a graft will easy to flow compared to small chain grafting rather than linear one.

But if the grafting is too much it is just like a octopus each hand will try to entangle with other. So, if entanglement increases viscosity of the long chain branched polymer is going to be high. So, these are the small little tricks while understanding the polymer you have some sort of a correlation understanding how it is going to flow. So, rheology again I am going to refer to how I am going to make them flow how easily and not only that rubber is not a polymer is not a purely you know viscous material like water ethanol glycerin it has elastic character. So, while flowing initially it will flow and then it will try to recover elastic recovery and that will act as a in the form of a die swell that will manifest in the form of a calendar shrinkage based on the processing you are doing and it can have a surface roughness also.

So, if you have a product which is equivalent, but it is not you know it has a it does not have a aesthetic you would not buy the product as simple as it is. Let us speed up it can be based on the tacticity ok. See isotactic syndiotactic atactic isotactic is more crystalline. So, you need to have a more energy to make them flow to crystal part to dissolve anyway any polymers semi crystalline crystalline polymer the very first thing you have to do before you make them flow you have to you know melt the crystalline domains. So, that way isotactic has a higher melting temperature than syndiotactic than atactic.

So, that is the order it flows follows. Again based on the architecture as I mentioned it can be linear like your SDP is highly linear nylon polyester highly linear structure, but LDPE on the contrary it has a branching. So, that branching can be in regular interval irregular interval that branch length also can be different ok. It can be star type like a jelly like a starfish ok. It can have a comb type of a architecture it can have a boost type of architecture. So, based on that their architecture the rheological property is going to be whole lot different.

On the contrary if you make cross link can you make this cross link structure clone answer is no because each molecule is attached to other it is a 3D network 3 dimensional network. So, once you have this sort of a structure it is impossible to make them flow. So, that is set that is why thermosets are called thermosets. However, whatever you hit them they will not revert back if you hit higher they will try to degrade rather than flow ok.

So, that is the scenario in terms of processing. In terms of morphology rubbers in general are amorphous in nature plastics and fibers generally speaking either stiffer or they are crystalline or semi crystalline in nature ok. So, that is the basic difference between rubber and plastic in that essence ok. So, semi crystalline means I mean a small molecule can be perfectly 100 percent crystalline, but a large molecule there will be occasional defects ok. Obvious reason there will be crystalline region tie molecule in between crystals and amorphous and another will be purely amorphous no order what ever ok.

So, that also matters amorphous to crystalline polymers. Again strength and physical property wise as I mentioned already to you rubber is a largest in terms of the molecular weight ok. It gives you small modulus low modulus, but large elongation preserving hyper elasticity. Natural rubber is natural sub class of it, it can be synthetic one is BR it can be NBR. Plastics on the contrary they are normally you know polar in nature or stiffer in nature say if you have a aromatic ring on the backbone it will not allow to execute the rotational degrees of freedom.

As a result the molecule will be stiffer ok. So, similarly polyethylene, polypropylene, polystyrene, PVC are considered to be sub class of plastics. They are normally having the lowest molecular weight between rubber plastics and fibre. Fibre on the contrary it is not that large molecular weight as rubber, but higher than plastics, but of course, so they have a more crystalline feature more symmetric in nature and that crystal is more or while manufacturing you make sure that they you know try to orient even further. So, if you have more crystallinity more is going to be the strength ok. So, same nylon 66 say for example, you use it as a plastic, but while spinning it you draw it ok.

So, it will have further you know crystallinity improvised and it will act as a fibre. It It is not that the fibre is a altogether alien molecule different molecule, but same molecules you can while processing have those attribute and strength is going to be way way larger than the normal when it is applied as a plastic material say nylon or polyester say for example. Paint say again is a liquid form I mean it is used with the solvent basically it is a polymer most often is a lower molecular weight segment of it ok. In a paint what you have? you have four things one is your resin that is a polymer ok.

You have solvents, you have pigments and you have some special additives. So, you understand it is a heterogeneous mass same as the rubber is a heterogeneous mass, but it is paint is in the liquid state highly liquid state. So, its rheology also is very important in terms of when you apply it you try to protect sun surface specifically ok. It should form a coherent film and it should I mean embed all these ingredient I talked about. So, starting from its preparation to the application suppose you want to make a panel painted you do not want after painting it should sand ok.

So, to improvise those properties I am going to talk about that as well. From the application point of view if you look it at rubber application I do not have to talk about the very first application when I talk about is the tire comes to your mind, but what you do not see in a automotive wide gamut of forms of rubber products are actually used. Starting from polar to non-polar, starting from synthetic to natural ok. Then so, you can see that automotive, industrial, consumer, construction, medical, catheters, gloves etcetera etcetera. I am not going to go into the details of it for the time being, but if you just open your car in the in the form of a seals if you just under the hood you find in the forms of boots bearing, hoses everywhere different format it is present actually ok.

So, their preparation different shape how to improvise. Remember rubber as I mentioned is a large molecule it is reluctant to flow, but you have to make them flow so that it will have a lustrous appearance so that you will able to industry point of view it will sell it. Plastic when I talk about plastic the first thing probably comes to a might PVC pipes ok. Domestic wearing, packaging polyethylene best, you go into the market you bring it with the polyethylene you know carry bags, automotives, electrical, electronics, medical, gloves, industrial applications ok. In the form of textile as I mentioned there is a very fine line of demarcation between polymer based textiles and fibres and plastics that way, but we will try to discriminate that. Fiber in specifically in construction even you make a bulletproof jacket say for example, the one which gives you strength is textile.

I am talking about tyre is not made out of whole tyre, who gives the you know actual strength is a sitting inside you do not see it actually ok. Like your cat casters is a fibre and automotive convey belt footwear ok. So, everywhere you can see this cartoon all these applications. Now, the last, but not the least how to make those synthetic polymers. There are three ways to make it precisely there are two ways one is addition polymerization ok.

It can again happen with three different mechanisms free radical, anionic and cationic way. So, what is special about an addition polymerization there is no elimination of you know small molecules the monomer they just unites with certain function it is a double bond consumes and keeps on adding them. But condensation say when you make it nylon or polyester when the condenses a small molecule like water eliminates ok. Normally addition polymerization reaction is faster and you can make it a large molecular weight easily ok. But condensation is a very controlled way of polymerization I will depict as and when required ok.

The third class of polymerization is coordination polymerization it is a more of like a catalysis ok. So, these are the three mode by which synthetically you make the polymers. Again when you make it synthetically you have every re-barchy to make the structure, architecture, molecular weight I talked about another class. Another important parameter is molecular weight distribution which is the ratio of M w bar by M n bar.

So, that gives you the fraction of small to large molecules ok. So, broader the molecular weight distribution flow consistency will be there compared to the you know narrow distribution while narrow distribution will give you better properties. So, every now and then a synthetic polymer scientist will try to make that compromise and try to make the polymer for a specific intended application that architecture that molecular weight molecular weight distribution such tune that their flow ability will be can be maneuver so easily ok. So, this is the bottom line. So, we came to the fag end of it the references some of the standard polymer textbook you must have a background that includes I mean you can pick up any book you of your wish. Karovar book is not listed here, but I am sure you know the basic book fundamental books you need to read.

So, finally, to conclude what I try to emphasize upon the polymers are of high molecular weight mostly organic in nature. I did not talk about the inorganic although there are inorganic class of polymers possible. Polymers are classified based on many things, but broadly rubber plastic fiber and paints I talked about which is actually the perspective of this you know rheology and processing lectures courses. And therefore, understanding the processing and rheology that a sense is very very important because as I again I will repeat it the flow depends on the architecture flow depends on the molecular weight flow depends on the many other things. So, that we will try to understand in the next lecture in the form of structure property and process correlation.

So, property also is important at the same time it should be processable good property without process ability does not make sense see you in the next class. Thank you.