

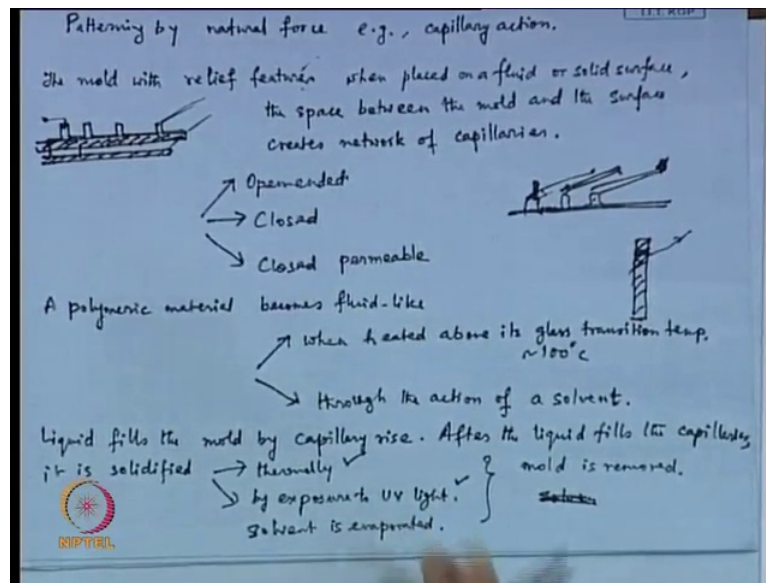
Microscale Transport Processes
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Lecture No. # 34
Plastic Device Making

Welcome to this lecture of Microscale transport process, the topic that we would like to discuss today is this plastic Microfluidic devices. You have already understood that there are certain methods to manufacture these plastic devices from by the use of a mold. So, there are three techniques we talked about, one is casting, another is molding, another is microinjection. Now, we I basically in previous lectures, I discussed this process just as a technique. I mean you have a mold, you have a liquid, you have a polymeric, you have that plastic material above it is glass transition temperature and you pour it, and then after sometime you take it, take the negative part of it and that that serves as microfluidic device. And there are methods how to do the casting and microinjection and we have discussed in this detail.

What I would like to do today is I would like to discuss the theories, the physics that controls this process it is not like I mean just pour something and it will automatically happen. There are certain physics for example, the capillary force which is instrumental in taking that molten taking that plastic melt that plastic melt to go inside that those structures so, these are extremely important. So, you need to understand that there are certain physics which you need to consider, if you want to make a plastic if you make successfully a plastic microfluidic device. So, my intent in today's class is to at least touch up on those issues in physics which you need to know to handle this manufacturing of plastic Microfluidic devices better.

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Let us see what we have here. So, what you have here is basically the you are having; I mean first of all I say that what we are talking about here is patterning by natural force such as capillary action. Why we are saying this is that the mold with relief features. What is relief feature? Relief is the those for example, you want to make a channel. So, there is I mean the negative part of it is would be that there would be a raised portion right. So, with so, there are there are relief features or if you want a raised portion in the Microfluidic device for that you **you** are supposed to have a channel in the negative part. So, the mold with the relief feature when placed on a fluid or solid surface, you may say why am I placing it on the fluid, because I thought we are pouring the fluid on this.

Probably, what this, what I am talking about here is you have a substrate which is flat then you have a mold, this is the mold. So, you bring this, mold bring in contact with this substrate and then you put molten polymer into one of this channels. So, this is bring; this is brought in contact with this. So, they are there is no spacing here so, they are in contact and then you are pouring the liquid at one end and you will see that by capillary action it goes everywhere, this is, this has the third dimension. So, this channels also have third dimension so, you got my point what I am trying to say. So, the mold with relief features. So, these are the relief features when placed on fluid or solid surface. The space between the mold and the surface creates network of capillaries.

Network of capillaries you understand what I am talking about, I mean then this would be so, this spacing is gone. So, the basically the; so if I advance this substrate so, this is the place where the substrate is, so this is the place where substrate is now. So, then you this would be forming so, all these channels or the raise places they will form a network of capillaries, if you will, but if we introduce polymer at at one end of the channel. So, there are network of capillaries this you understand. Now, this network of capillaries there are there are three possibilities, one is open ended; second possibility is closed and the third possibility is closed permeable.

I mean closed though it is permeable, what I mean by this is open ended means; let us see first, what happens if we have a closed capillary? You have a network of capillary, you had a mold. So, these mold has the third dimension here. So, you are bringing this mold you are bringing this mold in contact with another flat substrate. So, you have formed a network of capillary and then you are introducing the fluid; that means, that molten, that polymer above it is glass transition temperature which is in it is very viscous liquid state you pour that here. And you expect that it will go everywhere by capillary action.

Now, if this capillary is open ended; that means, if you have an opening here open to atmosphere. So, you will at least make sure one thing that is that the air that is inside because it is originally filled with air, when you introduce the liquid that air need not get compressed. So, when the as the fluid moves in fluid can move in everywhere and the air can go out because these are all connected. We have connected network of capillary so, air can go out so, you do not have a problem of compressing the air. So, this is one issue here.

The second is closed one; that means, you do not have any air outlet. So, it is all closed except the end through which you have introduced the polymer, that liquid polymer above it is glass transition temperature. So, in that case you will consider this to be closed. So, in that case, if by capillary action you are push; if the capillary action is pushing that liquid, but still air is getting compressed, you need to understand this and the third type is closed permeable, you know that the certain polymers they are permeable; they can they can allow air or vapor to pass through it. There are various mechanisms it is not it is like the students who have studied membranes, they will appreciate it that it would; it will not be that this material is porous, what will happen is

certain vapor will get dissolved in the polymer and then it will go out from the other end. So, there are various mechanisms possible, it is not just; that it is physically there are holes and through holes the air is passing out, it is an intact polymer.

But suppose, I mean why I am talking about vapor is lot of times your; you may not melt it. I mean I am talking about molten, I am talking about polymer melt, but it could very well be possible that you do not melt it, you add certain solvent by which that polymer becomes the polymer dissolves in that solvent and it becomes liquid. And if you can somehow get rid of that solvent then polymer will go back to its own state so that is the possibility. So, if you are using that method then if you can somehow allow the solvent to go out of the system that is all you need, it is not air. And if that solvent if the Microfluidic device, the plastic material that you are using allow the solvent, if that allows that solvent to go through it.

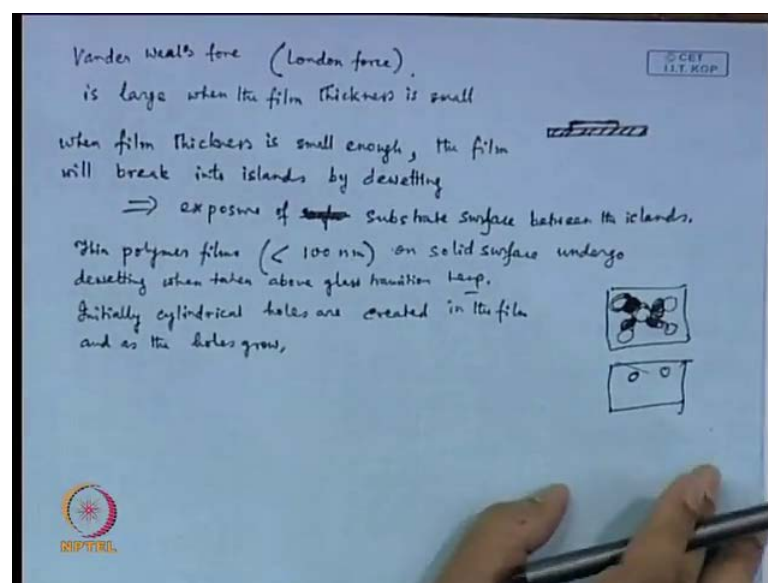
Allowing the solvent means that solvent will dissolve, see if this layer; if this is the plastic layer solvent will dissolve in this material and then permeate through it and then it goes out through the other end. It is not that you have a you have a predetermined pour present through which it is travelling, it is a complex mechanism, I mean it is not it is a physicochemical mechanism not exactly a physical mechanism, by which this transform may take place. So, you have another category which goes by the name closed permeable. So, these are the three possibilities that exist.

Now, couple of things we need to we need to know at this point, one is a polymeric material is becomes fluid like number one, when heated when heated above it is glass transition temperature, when heated above it is glass transition temperature; now, you may ask what is the glass transition temperature for various polymeric material, it is listed and you have access to it. Probably, to get some order if you want to know at what is the order of this glass transition temperature for common materials, it is of the order of 100 degree centigrade. So, actual values you need to there it varies. So, polymeric material become fluid like when heated above it is glass transition temperature or through the action of a solvent; that means, if you bring that through the action of solvent; that means, if you dissolve the polymer if you put the polymer inside a solvent there is a possibility that the polymer will melt which we have seen in our day today life there are solvents in which this polymer is dipped.

Now, when we are talking about this patterning; when you are talking about this filling of capillaries this network of capillaries by polymers, if you try to articulate it in the terms of this Microfluidic manufacturing it would be like this that liquid fills the mold by capillary rise. Rise is not by capillary action would be probably the right word that by capillary action after the liquid fills the capillaries it is solidified. It is solidified by two ways; one is by thermal method, thermally means it was above glass transition, now, you simply cool it. So, it will automatically solidify or by exposure to U V light. Lot of times its pre-polymer it is you have all the ingredients, but the solidification process is initiated once you expose that polymer to U V light so that is also another possibility. And once this is solidified then what you do is? You go for removal of the mold so, the mold is removed.

(No audio from 14:39 to 14:45) So, what you have is? You have a choice of thermally doing it; that means, cooling it basically, or by exposure to U V light. If you have the polymerization to get complete and U V light happens to be the agent to accomplish that or if you have dissolved the polymer in a solvent then you have to make sure that the solvent is evaporated. There is probably the third choice you have solvent, solvent is evaporated. So, if we talk about this filling patterning by natural Or patterning by capillary action or filling of this mold by capillary action this is something which you are actually doing. So, this probably you understand.

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Now, there is another force other than the capillary force, which can also be used for our patterning, but this is probably this is done when the feature size is smaller, that is the use of Van der Waals force. In these terminologies in might people working in this area this is also referred as London force, this the point here is that this force is large when the film thickness is small, what film we are talking about here? If you have a substrate on top of that you have a film, if the film thickness is small, then this force becomes significant. In fact, there is there is dependence which is non-linear. So, more it more the film becomes thin this force increases in a non-linear manner.

So, when it is large film thickness is this becomes large when film thickness is small and what; that means, is that when film thickness is small enough the film will break into islands by process referred as Dewetting and this implies exposure of substrate surface between the islands. That means, this film will start breaking into islands and between this islands substrate surface is getting exposure this film is breaking. The Dewetting phenomena this phenomena is used to fill I mean submicrometer channels I mean when the channel, when the feature size is smaller so, the Dewetting phenomena for so, for thin polymer films by thin I mean less than say 100 nanometer on solid surface undergoes Dewetting. When taken above I mean this thin polymer film this is common that thin polymer films of this dimension they undergo Dewetting, this undergo Dewetting when taken above glass transition temperature.

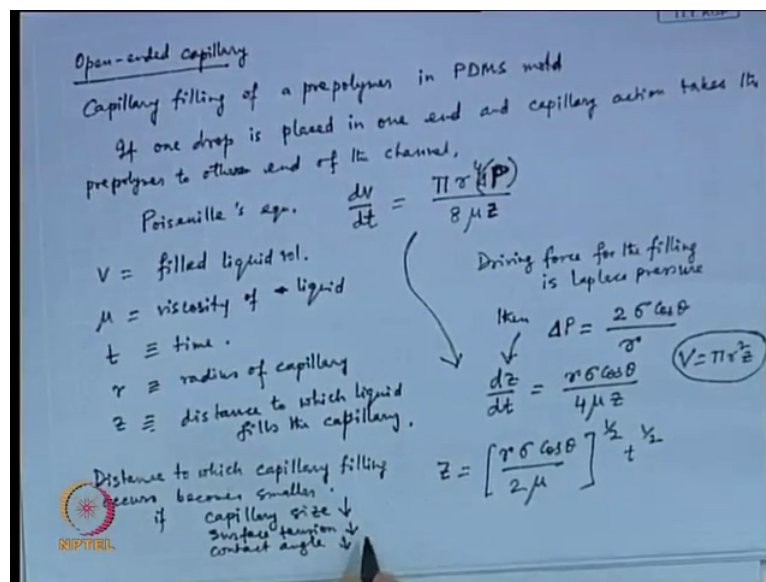
So, what this means is? If you can first form a thin polymer film and then heat it above it is glass transition temperature, you will see this islands being formed. Initially; of course, this this process is much more complex than the way I am presenting it, but I just wanted to wanted you to appreciate that there is such method existing. Make sure that do not have any confusion here. Initially, cylindrical holes are created holes basically, cylindrical holes means if you, if this is surface, you will see this portion of the substrate is getting exposed like this. And initially holes, cylindrical holes are created in the film and as the holes grow the as basically, as the holes grow it, you have a ream here. The it forms a ream and these reams they come in contact with each other they come in contact with each other and then they form instead of holes, you will see droplets existing in between phase so, these holes that has grown at a grown up state.

So, first a cylindrical holes will appear and then you will see that these would be forming. So, these holes are holes are there basically, instead of holes the pattern

becomes that you have a droplet here, you have a droplet there, you have a droplet there, you have a droplet there and rest of the part is all blank. So, if somebody request such feature in the on the microfluidic surface, he can, the person can utilize this force as well, that is what I am trying to trying to convey.

Now, let us, so with this with this background; so I have basically choice of one is capillary action which we have talked about and I said there are these various methods possible. And I said that there is also existing another alternative method which goes by their name which is basically, it is use of Van der waals force and this is applicable for features which are probably Submicrometer scale.

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Now, let us talk about this open ended capillary, because we have we said; I mean I will be focusing on this capillary action here in today's class. So, we talked about this three methods, open ended and closed and permeable. Let us see, how it would appear if you want to focus on the open ended capillary? Open ended capillary, it is let us say we are talking about capillary filling of a prepolymer, I mean prepolymer means you expose it to U V you expect that the polymer it will solidify. Capillary filing of a prepolymer in p d m s mold so, here the mold is made of p d m s. You know the p d m s material is used for the for making of Microfluidic device, but here I am talking about the mold that you are using that is made of p d m s, you understand that is that is highly possible.

So, p d m s mold so, capillary filling of a prepolymer p d m s mold; now, if one drop is placed in one end and the capillary action takes the prepolymer to other end of the channel. Then based on Poiseuille's equation, (No audio from 26:00 to 26:11) if v is filled liquid volume and then t is time. So, $\frac{dv}{dt}$ the rate of change of filled liquid volume, what would that be? That would be the velocity multiply by the area that would be equal to πr^2 to the power 4 ρ divided by $8 \mu z$. What is now, this terms μ is equal to viscosity of this liquid, t is time r is equal to radius of capillary and z is equal to distance to which liquid fills the capillary. So, if these are the terms then you can write using Poiseuille's equation that rate of change filled liquid volume $\frac{dv}{dt}$ is this quantity and on top of this.

(No audio 27:52 to 28:26)

I think this this should be p.

(())

Delta p so, I this is probably, this is should be p or I can say this is delta p yes delta p. Now, if we try to write the driving force for the filling is laplace pressure then you can write this p to be equal to or this delta p to be equal to $2 \sigma \cos \theta$. If you have a yeah this should be included divided by r . So, in that case you can write $\frac{dz}{dt}$ that is equal to from this $r \sigma \cos \theta$ divided by $4 \mu z$ and then you have v is equal to here, because; this is happening because v is equal to $\pi r^2 \frac{dz}{dt}$ that is what you are using. So, if that is so, you get z is equal to $r \sigma \cos \theta$ divided by 2μ to the power half t to the power half. So, this gives you the distance that you would be travelling that distance that z , z is distance to which liquid fills the capillary as a function of time.

So, if one is interested to know how far say at a given time how far this prepolymer will travel inside the p d m s mold this can be figured out. From this equation one thing I would like you to appreciate here is that the distance to which capillary filling occurs becomes smaller. If capillary size goes down, if surface tension goes down, if contact angle goes down so, you want them to be up so that you can have faster filling. And viscosity probably you do not have much control because it is prepolymer that you have here. So, the anyway the for the viscosity it is inversely related so that dependence you can see here. And the other aspect is this whether to use what whether it should be an

equilibrium contact angle or dynamic contact angle that also that point is also there which can be looked into.

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CET
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Air pressure.

impermeable mold is placed on polymer surface
Air pressure impedes capillary ~~action~~ action.

Capillary rise took place @ atm. pr. to height z in a capillary of depth H .

P_0 = initial air pressure. Final air pressure

$$z' = \frac{z}{H} \quad = \frac{P_0 H}{H - z} = \frac{P_0}{1 - z} = \frac{2\sigma \cos \theta}{r}$$

The capillary rise will cease when Final air pressure = Laplace pressure.

$$z' = 1 - \frac{1}{\frac{P_L}{P_0}}$$

No capillary rise will take place if Laplace pressure < 1 bar
Laplace pressure \uparrow with capillary radius $\downarrow \Rightarrow$ Decreasing feature size can cause $P_L > P_0$.

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Now, instead of; so, we talked about this open ended capillary and we have some understanding at what rate it will be filled and everything. If somebody is working with a completely closed capillary, what I mean by completely closed capillary is? That you have suppose, this is a feature, we have and you have put it this is the substrate and you are having a feature and it is completely closed. I should not be putting it here this way probably let us draw it again, you have a completely closed capillary so this is the feature you have. And here, you are expecting that the; so, there is a gap through which the liquid is penetrating here. Now, by capillary action the fluid tends to go up this way so, may be it has gone up to this level so, this is the level up to which the liquid is liquid could fill; however, the air that is there this air is getting compressed. So, you have a air pressure here.

So, what I mean is that this capillary by capillary action liquid will tend to fill this channel; however, by doing that it is compressing the air which is there because air has no outlet. So, what will happen is so this is the case, when an impermeable mold is placed on polymer surface let us say. So, that is what I am saying this we have to assume that there is polymer. So, here it we have the polymer and may be you have the substrate down there. So, you have the polymer should come in and go inside there. So,

impermeable mold is placed on the polymer surface, air pressure will build up I mean that you have already understood in a closed capillary. So, this air pressure impedes capillary action.

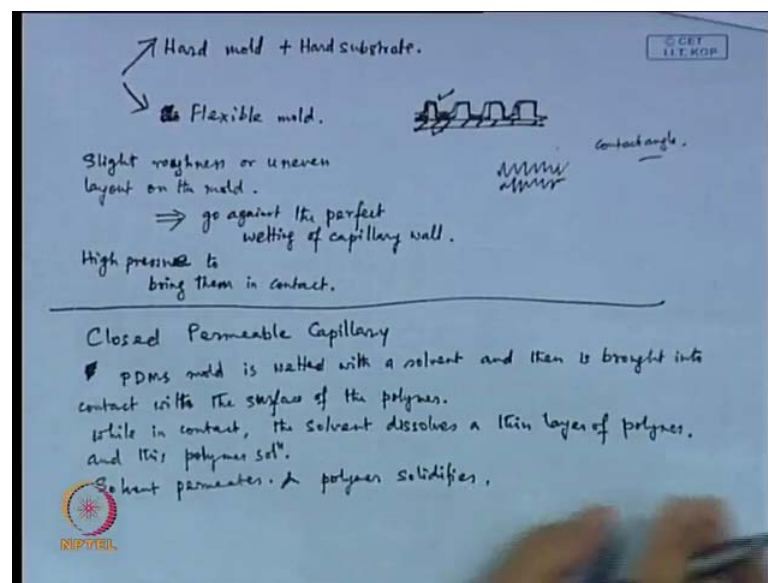
Now, one thing you got to understand that at the beginning this entire channel the air pressure was atmosphere. So, if somebody wants to say let us say this height is z or let us say this height is say h capital H and let us say this level is say Z . So, basically capillary rise has taken place at atmospheric pressure to a height z in a capillary of depth H , let me write it again capillary rise took place at atmospheric pressure to height z in a capillary of depth h . So, the pressure of the trap air in the capillary is what, if we the area remains same so, it is the volume and if we assume that the pressure and multiplied by the volume remains same.

So, what would be the new air pressure? If p_0 is equal to initial air pressure which for all practical purposes would be 1 bar, p_0 is initial air pressure then you can say that the final air pressure would be equal to p_0 into H divided by H minus z or you can write this as p_0 divided by 1 minus say z prime, where z prime is equal to z divided by H . Now, you we are interested in knowing what is z by H , what is z prime for that matter, how far capillary can go again capillary rise also as a limitation. So, how far it can go compressing this air, because if you see that the 90 percent got filled, 90 percent of this volume gets filled. So, you will assume I started with a feature size and then I got 90 percent of it.

So, you better have your features little higher and have this done. So, our thought process works that way. So, if it is that way then the capillary rise. So, one thing you can write here is that the capillary rise will cease when this final air pressure is equal to Laplace pressure. So, if that is so, then you can equate this with the Laplace pressure which is equal to then $2 \sigma \cos \theta$ divided by r . So, then you can come up with this z prime as equal to or you can write if this is the, if you write this as p_L then you can write z prime as tell me if I am wrong here I can possibly write p_L divided by p_0 that can be written probably. So, z prime so 1 minus z prime would be p_0 by p_L or 1 by p_L minus $v r$ I can write it right. So, this is so, if you know the Laplace pressure, if you know see if this is atmospheric pressure. So, you can come up with what would be this z prime.

Now, you need to understand couple of things here is that no capillary rise will take place if Laplace pressure is less than 1 bar, less than atmospheric pressure if it is less than atmospheric pressure no capillary rise will take place that is one issue here. Second point is that Laplace pressure increases with capillary size, with capillary radius decreasing. So that means, decreasing feature size, what this means is decreasing feature size can ensure p_L is greater than p_0 . Now, one thing I would like to then point out then if you have a variable feature size then in. So, you can expect rise also would be variable that is that is another issue here. So, that needs to be looked into as well.

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(No audio from 43:32 to 43:40) There is another point which I need to make here is that why I started that this, I started talking about this p d m s mold; I mean that this by mold I mean this; so, this material is made of p d m s. It has certain purpose I mean if you have this if this mold is made of p d m s basically, what you need is I mean you have a choice of hard mold or you have a choice of soft mold or; hard mold you if you have a choice of hard mold plus hard substrate and or in other words you can have and I do not want to call this soft mold, a flexible, little flexible mold not very flexible, but some flexibility that is actually required. That is why I have mentioned there this is p d m s mold because this amount of, certain amount of flexibility is required.

I can tell you why, I mean from fundamental standpoint you are talking about a substrate, this is a substrate and then you have this mold they are coming in contact with each

other. So, this is made of p d m s this material is made of p d m s. Now, you have to make sure that the contact between this mold and this substrate that contact has to be good. If there is if; so everything has a they have a roughness, this one has a roughness the upper one is a roughness the bottom one has a roughness. So, when you are bringing them in contact with each other you have to make sure that they are really they are contacting with each other.

Otherwise, they could be I mean you may not be satisfying all this requirements of contact angle. I mean you are saying this is the contact angle that you have and that contact angle you are using, but if this is if your upper one is like this, the bottom one is like this and they are not contacting with each other. And then you are having the liquid; if you are calculation is based on that then there could be trouble. So, soft mold will at least no; so you can achieve, what we call conformal contact you can achieve by pressing them hard that is possible, I mean always you can press them hard so that they are; they make a conformal contact. However, if you press them hard, I mean if you are ready to put that much of exercise on this then you may as well squeeze the liquid into it instead of depending it on the polymeric on the capillary phenomena to go everywhere you can just squeeze it.

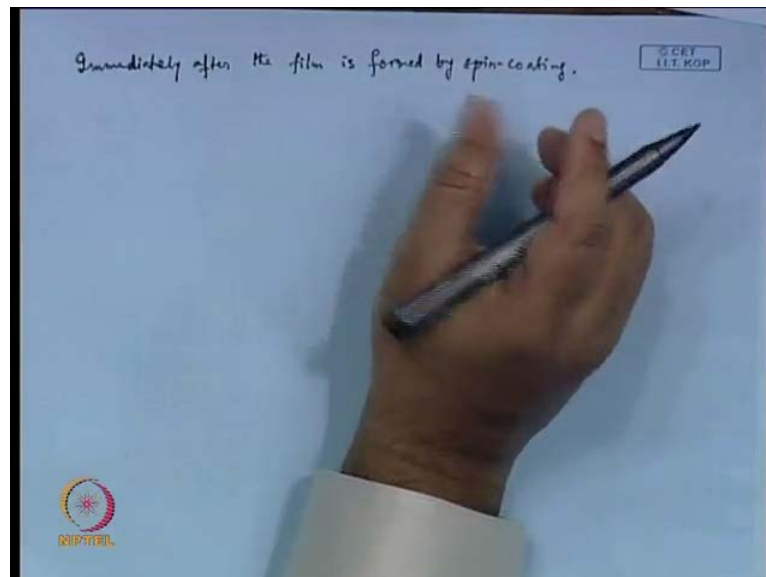
So, these particular issue you need to understand that this slight roughness or uneven layout on the mold will go against, this will go against the perfect wetting of capillary wall. So, you need the choice is you need high pressure. To bring them in contact high pressure to bring them in contact, but then probably this capillary filling by capillary action becomes in consequential; because if you are really employing high pressure then you can you may as well use the squeezing to have this material travel. So, this, so, flexibility in the mold its self has some benefit certain some amount of flexibility should be there to bring this contact. There is; so, the third point I mean so, we have talked about open, we have talked about closed and the third point was when we have this permeation when there is a possibility that some part can permeate through the wall of that mold.

So, we are talking about closed permeable capillary, this is the third point. Now, in closed permeable capillary this is first accomplished by solvent assisted solvent assisted molding. What is that? p d m s mold is wetted with a solvent and then is brought into contact with the surface of the polymer. You can see what is, what we are doing here,

which we reversed it. p d m s mold is wetted with the solvent and then is brought in to contact with the polymer and that polymer is suppose to be dissolved in that solvent, that is the idea. So, while in contact while in contact the solvent dissolves a thin layer of polymer and this polymer solution confirms to; and this polymer solution the solvent dissolves a thin layer of polymer and these polymer solution confirms to the surface topology of the mold by capillarity.

So, basically, if these solvent dissolves a thin layer of polymer and this polymer solution will confirm to the surface topology. So, while in contact the solvent dissolves a thin layer of polymer and this polymer solution would be now, travelling to the nook and cranny of this the features by capillary reaction. So, this is a possibility.

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Next, the solvent permeates by the mechanism that we said and polymer solution solidifies. So, polymeric; polymer solidifies, solvent permeates and polymer solidifies so that is basically, this is what you call solvent assisted molding, probably this is given the name solvent assisted molding. There is another possibility which is which goes which another possibility is there that after the spin coating immediately, after the spin coating immediately, after the film is formed by spin coating. What do you do? After spin coating, you generally, you have that liquid part evaporated. So, you put it after the spin coating you put it in a oven or let it dry. So, immediately after the film when still it is wet it has not been you know evaporated.

At that state if you can bring the mold and put it on top. So, that is also another another possibility. So, you have a thin film and and; so, you have when it comes closed permeable capillary, you have one is solvent assistant molding where you have the polymer which is solid. But p d m s mold that you have is on the surface, you have that solvent and you bring in contact, you bring that and wherever it touches the polymer that those portions polymer get softened or polymer gets dissolved and that liquid that forms. If that will flow through the nook and cranny of those features using capillary phenomena that is one possibility. Other possibility is that you have spin coated the polymer and the polymer still contains; it has not the liquid part has not that solvent part has not been evaporated. The solvent is still there and now you bring in the mold and put it on top. So, then also you expect that with the solvent that polymer will enter into the features by same capillary action and the process will continue.

So, this is also the second method by which you can go for this close permeable capillary filling. So, now, probably you understand that this if somebody is interested in filling the micro features these are the three possibilities they have and these are the, these are probably, I mean I just want you from this lecture. What I want you do is? I want you to appreciate that there is substantial amount of physics involved. And you need to be sensitive to these theories while designing your fabrication process, it is not just some empirical cooking, I mean it is has lot of physics behind this.

And of course, you can one can utilize the Van der walls force if somebody wants to go for feature size below micrometers scale and how it works out I have already talked about that if we have a thin film and more you get it becomes thin. So, you a have thin polymer film and then you heat it and then you see that the features are forming and then at one point you will see that simply it would you are left with some droplets present on the substrate. So, if that is something which you are looking for you can probably make use of these processes to your advantage so that is all I have as far as today's class is concerned. Thank you very much.