Instability and Patterning of Thin Polymer Films

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Lecture No. # 37

Spontaneous Instability and Dewetting of Thin Polymer Film - VII

Welcome come back, the previous class towards the end of the precious class we started to talk about the role of visco elasticity and slippage on dewetting ultra thin films. So, we will continue with that, and in this particular class we will discuss in little bit detail without going too much greeting to the theoretical aspects. We will talk a little bit about how visco elasticity and slippage influences (audio not clear). So, the theories let us take a quick recap of what we know, we know what is a thin film, we know interfacial interaction.

We now know mathematically is the condition under which this interfacial interaction, the surface fluctuations are the undulations can grow, due to attractive long range Vander walls interaction which can result in the formation of hole or spontaneous rupture of a thin film which is known as the spinodal dewetting. We also understand how the haymaker constant essentially influences the possible stability or destabilization, we also have seen subsequent to that the condition or that the morphological evolution sequence that absorb experimentally which is associated with growth of holes, and then qualisent holes formation of rim as a holes forms, because of the mismatch in the rates at which the polymers is dislodges and its redistributed to other intact parts.

We have also seen the very interesting role of surface tension which opposes this instability till the holes opens up till the film ruptures, and though then what is the film ruptures surface tension hits the growth of the hole.

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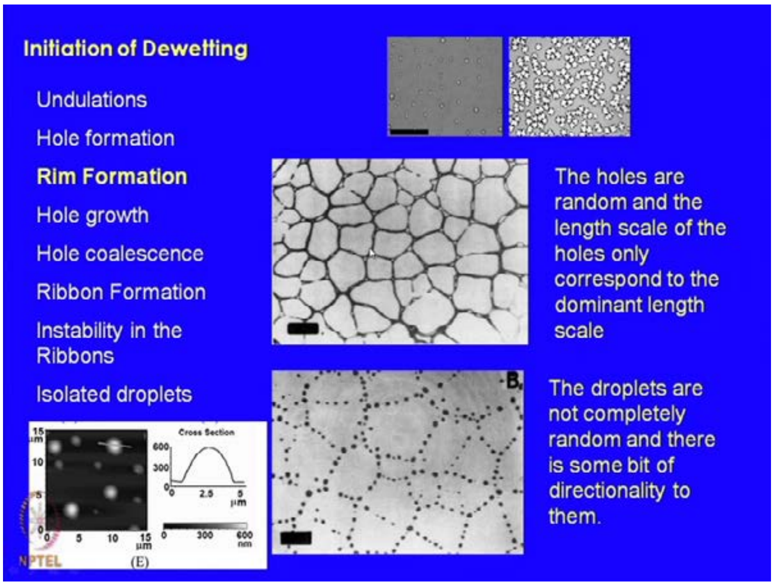

Initiation of Dewetting

- Undulations
- Hole formation
- **Rim Formation**
- Hole growth
- Hole coalescence
- Ribbon Formation
- Instability in the Ribbons
- Isolated droplets

The holes are random and the length scale of the holes only correspond to the dominant length scale

The droplets are not completely random and there is some bit of directionality to them.

And finally, the whole growth can have two distinct regions or a mechanism; one of them is need to attraction of the three phase contact line eventually leading to the formation of the qualysense for the adjacent holes resulting, and which eventually is polymer ribbons break down into isolated drop lets resulting in a final morphogy like this, in contrast one can also have remen stability.

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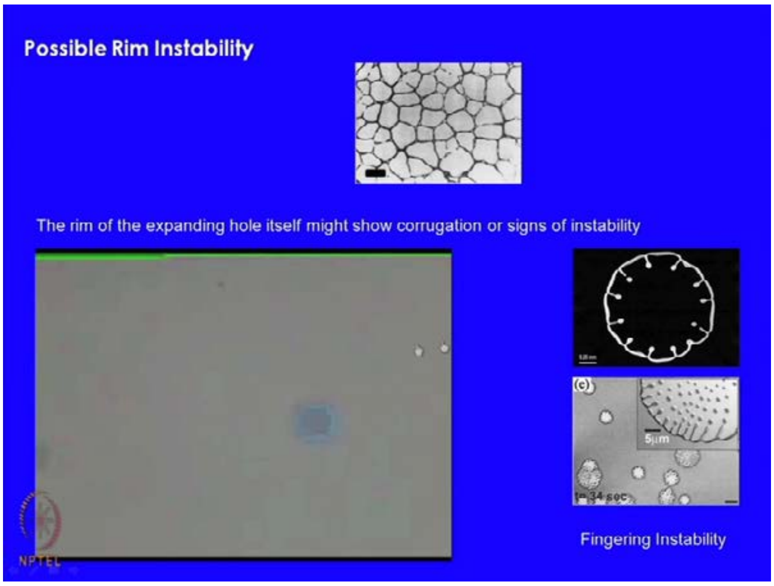

Possible Rim Instability

The rim of the expanding hole itself might show corrugation or signs of instability

Fingering Instability

Where the growing hole is the contact line of the growing hole the rim itself becomes unstable and at least behind drops like this and eventually,

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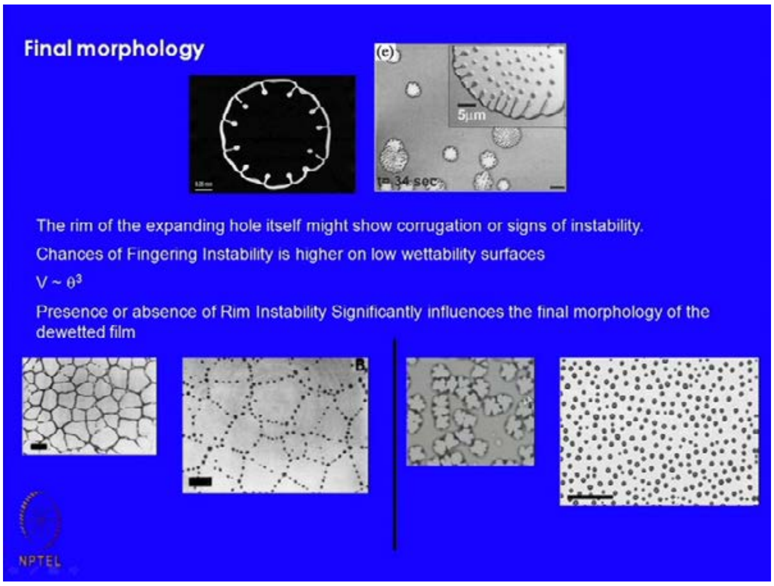

Final morphology

The rim of the expanding hole itself might show corrugation or signs of instability.

Chances of Fingering Instability is higher on low wettability surfaces

$V \sim \theta^3$

Presence or absence of Rim Instability Significantly influences the final morphology of the dewetted film

One results to completely random structures. Subsequently we started to talk about the of visco elasticity and interfacial slippage and we are good that the existence of slippage and polymer film can be attributed to absorbed molecules at the interference.

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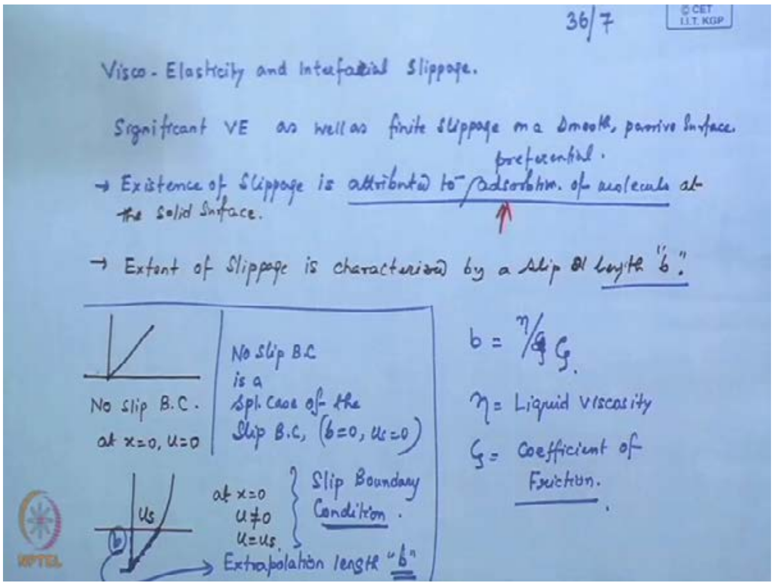

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Visco - Elasticity and Interfacial Slippage.

Significant VE as well as finite slippage on a smooth, passive surface.

→ Existence of Slippage is attributed to preferential adsorption of molecule at the solid surface.

→ Extent of Slippage is characterized by a slip length "b".

No slip B.C.

at $x=0, u=0$

No slip B.C is a spl. case of the Slip B.C, $(b=0, u_s=0)$

at $x=0$
$u \neq 0$
$u = u_s$

Slip Boundary Condition.

Extrapolation length "b"

$b = \eta / \zeta$

η = Liquid viscosity

ζ = Coefficient of Friction.

The extent of slippage is typically characterized by a slip length b, which one can correlate to as the visco the ratio of viscosity of co efficient of friction.

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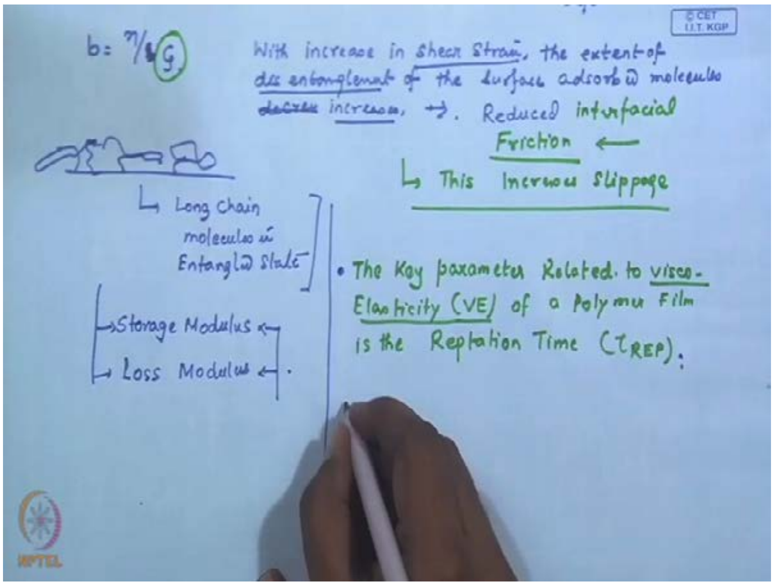

$b = \eta / G$

With increase in shear strain, the extent of dis entanglement of the surface adsorbed molecules ~~decrease~~ increases, → . Reduced interfacial Friction ←

↳ This Increases Slippage

↳ Long chain molecules in Entangled State

↳ Storage Modulus ←

↳ Loss Modulus ←

- The Key parameter Related to visco-Elasticity (VE) of a Polymer Film is the Reptation Time (τ_{REP}):

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And we have also are good that since with increase in shear string the extent of this angle meant, of the surface of molecules increase or they sort of become less entangled or the level of entanglement reduces. This will results in reduced interfacial friction and increases the slippage. The other thing we need to understand key parameter related to visco elasticity of a polymer is the reputation time, which is typically represented by tau ref. Now, I am not giving you coming into any details of what is visco elasticity, please go through to standard literature, because this is something you should have read in your fuel dynamics or some complex fluids.

All you may want to know some critical key words apart from visco elasticity may want to have a clear idea about what is storage modulus, and what is also loss modulus. So, in visco elastic film in an instrument called rheometer, you can eventually individually identify these two parameters which are the storage modules and the loss modules, which are sort of gives you an idea about the extent of visco elasticity of the relative components of viscosity and elasticity of relative dominance of course, one can use a simple Maxwell model to very complicated models, the easiest way to understand visco elasticity of a system is used to consider still the spin dash for the spring stand for the elastic part the dash part of viscous part. So, this I am sorry this is beyond the scope of this particular course to go into the details of visco elasticity, but all we will pick up is that for your polymer bell the reputation time for is a very critical time parameter, because when so we introduced the concept of reputation time for the reason.

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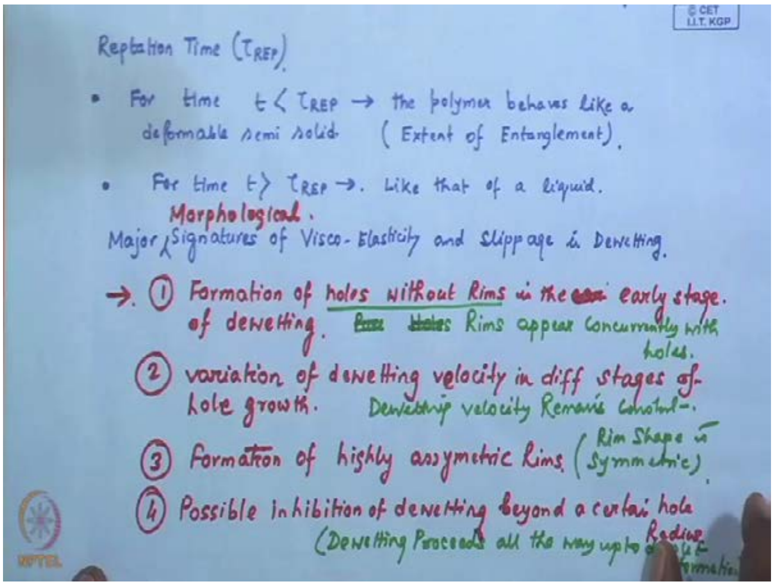

Reptation Time (τ_{REP})

- For time $t < \tau_{REP}$ → the polymer behaves like a deformable semi solid. (Extent of Entanglement).
- For time $t > \tau_{REP}$ →. Like that of a liquid.

Major Morphological. Signatures of Visco-Elasticity and Slippage in Dewetting.

→. ① Formation of holes without Rims in the early stage. of dewetting. ~~Rims~~ ~~Holes~~ Rims appear Concurrently with holes.

② variation of dewetting velocity in diff stages of hole growth. Dewetting velocity Remains Constant.

③ Formation of highly assymetric Rims. (Rim Shape is Symmetric).

④ Possible Inhibition of dewetting beyond a certain hole Radius (Dewetting Proceeds all the way up to [illegible] formation

Why it is important is for time the polymer behaves like a deformable semi solid, one can all go that at this stage the level of entanglement of the long chain molecules is very is pretty high. So, it is related to the extent of entanglement also, and for time t greater than tau ref. The response is like that of liquid.

So, the first thing one needs to understand is that the model that we have talked about the linear stability analysis where we took the governing equation to navier stocks and we have the assumed the nutrineal fluid essentially, we were talking about the region where time was the essentially beyond the reputation time. So, it was the liquid like response that was considered which is though surprising, but not very arbitrary assumption, because this remains pretty valid for short change molecules, which that the polymers which are not very long chain, as well as if you experiment is done at a significantly high temperature.

So, let us say for a polymer like polysyrere p m m a if the glass transition temperature is say 100 to 105 degrees centigrade depending on the molecular rate and you are doing deviating experiment at let us temperature close to 150 to 160 degrees centigrade then well you are in the region, but the response is liquid like. However if the same experiments deviating experiments is done at a temperature which is done very very close to the glass transition. Temperature that is where people have studied the morphological signatures of visco elasticity dividing then the effect of visco elasticity becomes very pronouns. And what we will pick up is the major influence or major signatures, visco elasticity and slippage in deviating particularly the morphological signature. I would say they include firstly formation of hole without rims, in the early stage of deviating radiation of deviating velocity in different stages of hole growth,(no audio from 9:40 to 10:05) formation of highly asymmetric rims. And possible inhibition possible inhibition of deviating beyond the certain hole radius.

Now, let us consider or let us point out what are the differences these means, these statements have when you were looking at the deviating of a purely viscous film. A purely viscous film so, we will write the purely viscous case rim and a purely viscous is what happens holes are or rims appear concurrently with holes. Deviating velocity remains constant rims shape is symmetric. Will talk about it greater detail and deviating goes we have already seen up to now we also know drop let formation. So, these are some of the differences so holes without rims, we will find out some of the reasons why it happens variation of deviation velocity highly a symmetric rims and possible inhibition of deviating beyond certain hole radius.

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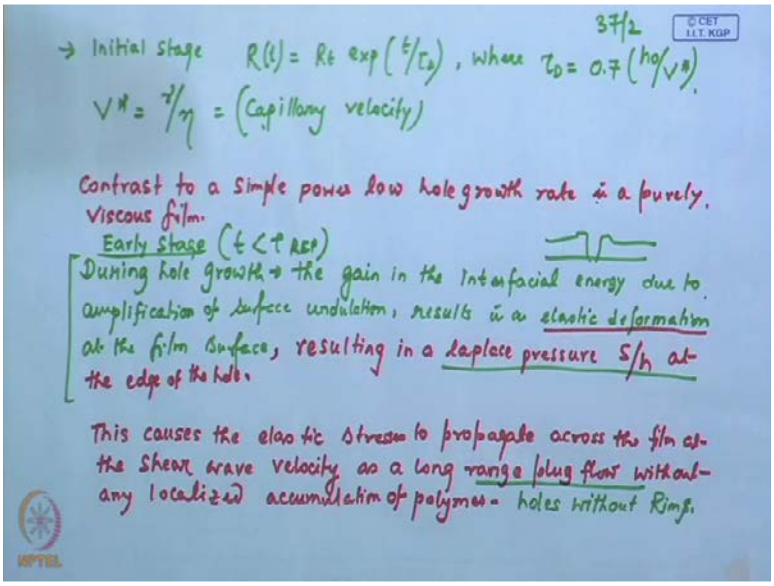

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→ Initial stage $R(t) = R_t \exp\left(t/\tau_D\right)$, where $\tau_D = 0.7\left(h_0/V^*\right)$.

$V^* = \gamma/\eta$ = (Capillary velocity)

Contrast to a simple power low hole growth rate in a purely viscous film.

Early Stage ($t < \tau_{REP}$)

During hole growth → the gain in the interfacial energy due to amplification of surface undulation, results in a elastic deformation at the film surface, resulting in a laplace pressure S/h at the edge of the hole.

This causes the elastic stress to propagate across the film at the shear wave velocity as a long range plug flow without any localized accumulation of polymer - holes without Rims.

So, what happens is an exponential rate of hole growth is initially given (no audio from 12:33 to 12:48) where will see how it matters, where tau D is given as 0.7 height 0 by V star. And V star is given as the ratio of surface tension to viscosity and is known as the capillary velocity. This is so in the stage you see a power low you see an exponential growth rate of holes this is also in contrast simple power law hole growth rate in early in a purely viscous film, during hole growth now what happens is. So, this is a hole that is growing. So, during hole growth the gaining the interfacial energy due to amplification of the surface and durations results in an elastic deformation at the film surface. Now you are talking about this is important so you are talking about visco elastic film in the early stage. So, t is less then tau ref which means, that the response is pretty much like a semi solid or a soft elastic film and therefore, the surface fluctuations which represent on the surface and we know the reason for that results in elastic deformation at the film surface. This results in a Laplace pressure of s by height at the film surface.

At the age of the hole and this causes the elastic stress to propagate across the film film at the shareware velocity, velocity shareware as a long range plug flow without any localized accumulation of polymer which results in holes without rims here. So, this is important. So, in the early stage t is less than tau ref, during hole growth the drain in interfacial energy due to amplification of surface and dulations result in elasticity deformation at the film surface, and which results in Laplace pressure at the age of the hole, and this causes the elastic stress to propagate across the film at the shareware velocity as a long range plug flow without any localized accumulation of any polymer.

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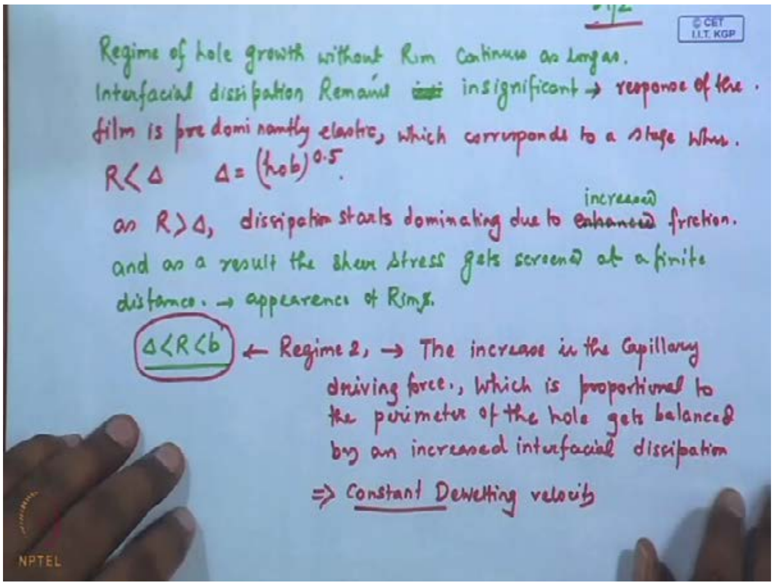

Regime of hole growth without Rim Continues as long as.
Interfacial dissipation Remains insignificant → response of the.
film is predominantly elastic, which corresponds to a stage when.
$R < \Delta \qquad \Delta = (h_0 b)^{0.5}$.

as $R > \Delta$, dissipation starts dominating due to ~~enhanced~~ increased friction.
and as a result the shear stress gets screened at a finite distance. → appearence of Rims.

$\boxed{\Delta < R < b}$ ← Regime 2, → The increase in the Capillary driving force., which is proportional to the perimeter of the hole gets balanced by an increased interfacial dissipation

⇒ Constant Dewetting velocity

So, we get holes without rims. Now this region of (no audio from 18:00 to 18:15) rim continuous has long as interfacial dissipation remains insignificant. On another words predominantly elastic. The rheological response of the film elastic and which which lasts to a stage where the hole radius remains less than delta where delta is defined as height 0 into b b is the slip length raise to the power half as. R exceeds delta interfacial dissipation starts dominating due to enhanced friction and as a result shear stress gets screened at a finite distance. So, earlier what was happening that, the shear stress elastics shear stress was propagating across the film at the shear wave velocity as a long range plug flow without any localized accumulation. So, which resulted in holes without rims and now the due to enhanced dissipation due to entries friction the shear stress gets streamed at a finite distance which results in the appearance of holes appearance of rims. I am sorry

So, in this rims regions this region continues in this radius remains in this range. So, his is the region two the increase in the capillary driving force, which is proportional to the perimeter of the hole gets balanced by an increase interfacial dissipation, and consequently which results in a constant deviating velocity. So, this is important in the initial case we had a deviating velocity which the hole growth rate which are at exponential increase, but now from the region two the deviating velocity becomes constant.

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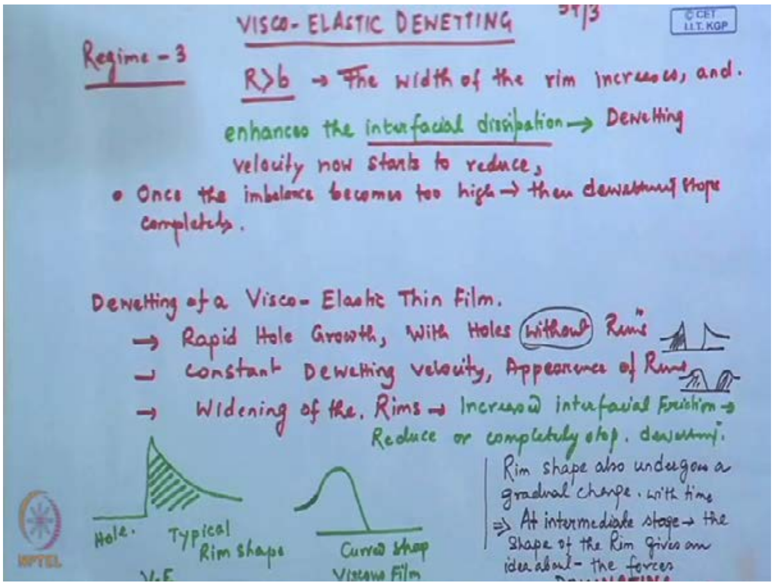

VISCO- ELASTIC DEWETTING

Regime - 3

R>b → The width of the rim increases, and. enhances the interfacial dissipation → Dewetting velocity now starts to reduce,

- Once the imbalance becomes too high → then dewetting stops completely.

Dewetting of a Visco- Elastic Thin Film.

→ Rapid Hole Growth, With Holes without Rims

→ constant Dewetting velocity, Appearance of Rims

→ Widening of the. Rims → Increased interfacial Friction → Reduce or completely stop. dewetting.

Rim shape also undergoes a gradual change. with time

⇒ At intermediate stage → the Shape of the Rim gives an idea about the forces

Beyond R e R is greater than b, the region 3 sits in what happens is the width of the rim increases. Now the width of the rim increases and enhances the interfacial dissipation.

And as a result of which so, interfacial dissipation which was earlier getting balanced with a capillary driving force now starts dominating. So, as a result of which the deviating velocity now progressively reduces. And once the imbalance becomes two high then deviating stops completely. So, these are the regions or three distinct regions one has in deviating of visco elastic thin film. So, first stage with a rapid hole growth with holes without rims, second stage constant deviating velocity and appearance of holes sorry appearance of rims, third stage widening of the widening of the rims which leads to increased interfacial friction and that might reduce or completely stop deviating.

So, this is the key difference of the key signature of visco elastic deviating the other important thing is that in if the effect of visco elasticity is too high this is the typical rim shape. As compared to a much uniform curved shaped absorb in a absorbed in a purely viscous film. In fact, the rim shape also under goes change change with time. So, here no rims appearance of rims initially they are highly asymmetric rims, and at the later stage they become much more circular in nature. So, at any intermediate stage the shape of the gives an idea about the forces dominating the region. So, this is I guess reasonably good level of idea about what about this should be a reasonably a good introduction to the effects of this visco elasticity, on deviating and I do not this is again very advanced research area of lot of activities are still going on, but anyone who is interested they are encouraged to see some of the recent work. So, you can just search the internet with key words like visco elastic deviating. Amongst other thing there was something very very important and interesting that you might have noticed in context of the visco elasticity deviating, and that is the third stage though there is a stage.

So, from Stan point of deviating dynamics for higher the morphological it involves widening of the rim interfacial friction becoming extremely important etcetera etcetera. The other important thing was that deviating completely stops.

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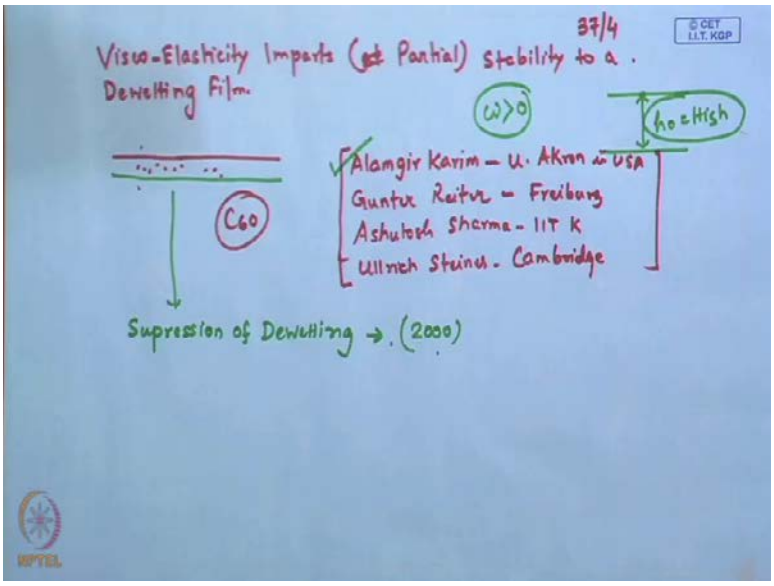

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Visco-Elasticity Imparts (at Partial) Stability to a . Dewetting Film.

Alamgir Karim – U. Akron in USA
Guntur Reiter – Freiburg
Ashutosh Sharma – IIT K
Ullrich Steiner – Cambridge

Supression of Dewetting → (2000)

So which implies that visco elasticity imparts at least partial stability to a deviation film? The other important very important aspect of research on deviating is actually, to understand the mechanism that leads to this instability and then work out strategies which can suppress deviating, because this morphological evolution is perfectly fine for understanding the physics is very rich the moment you get, Omega greater then equal to 0 from your linear stability analysis and the characteristic equation, what did implies that the first few lectures, of this course we had talked that one of the biggest application of thin films lies in coatings and the things like that.

So, what a needs to be understood that there is a significant level of research activity, that is going on at a working out strategies which can suppress the deviating, right. Issues are that when we even when the rooms of your your rooms are getting painted for example, you always tell the painter to apply two coats. So, what exactly you do you essentially by applying this second coat you are making the thickness of your film adequately high. So, now you know that if your thickness is high. So, then the interfacial interactions even if the whenever the nature of the interfacial interaction is attractive, since it is in the denominator and with some higher power height power or height score or whatever that magnitude will be very very low.

So, implicitly without understanding the essential physics we have been applying or adopting this approach for a for a long time now, but what needs to be understand e have also talked particularly in the context of lithography or soft lithography. That now there is a tendency or there is a trained of going in for extreme low feature size. So, earlier any coatings people used to make few 100 nano meter to micron thick. So, any way it would have been stable against any spontaneous stability, but now with extremely lower feature size it may not be possible to always work with extremely very high or very high thickness. So, one has to essentially now work with films which are very thin, and then one has to then talk about if somebody is working or somebody is talking about coating application have to talk about some strategies that can suppress this spontaneous instability. So, work started about roughly ten years back with one of the pioneering work coming from professor alamgir karim groups, he was then misted. So, these are the real top names in the field of thin film instability.

We have been sighting some of their work professor Sharma is at IIT Kanphor. So, that were India has a very strong presence international map on deviating thin film instability of course, we have wool rich Steiner Cambridge university of Heidelberg in Germany university of Aachen in USA. So, these are the real top players in this free land and they are all very actively progressing and publishing so lot of new results are coming. So, about this particular theme of suppression of deviating, one of the first papers that was published was around 2000 was in 2000 macro molecules paper, which said if you had some nano filler particles to this film, and they added C 60 nano particles fulaten nano particles. This showed harem’s group showed that the deviating x completely suppressed so what was r goods.

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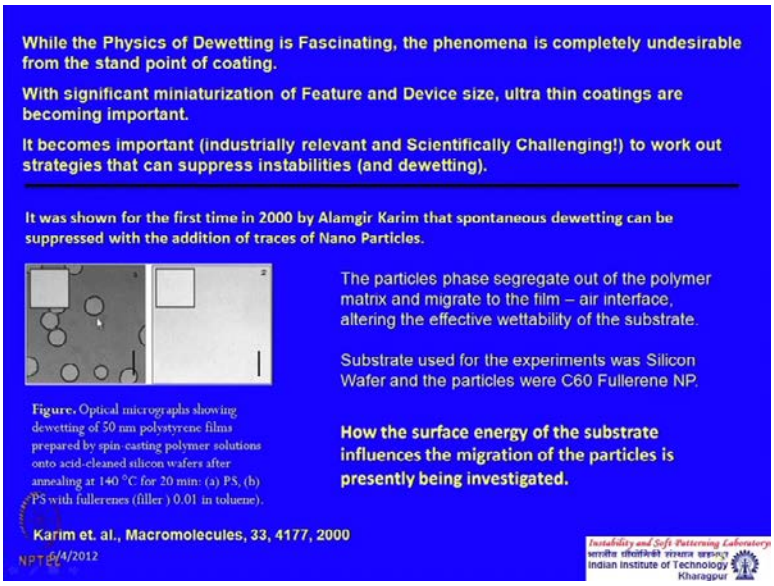

While the Physics of Dewetting is Fascinating, the phenomena is completely undesirable from the stand point of coating.

With significant miniaturization of Feature and Device size, ultra thin coatings are becoming important.

It becomes important (industrially relevant and Scientifically Challenging!) to work out strategies that can suppress instabilities (and dewetting).

It was shown for the first time in 2000 by Alamgir Karim that spontaneous dewetting can be suppressed with the addition of traces of Nano Particles.

Figure. Optical micrographs showing dewetting of 50 nm polystyrene films prepared by spin-casting polymer solutions onto acid-cleaned silicon wafers after annealing at 140 °C for 20 min: (a) PS, (b) PS with fullerenes (filler) 0.01 in toluene).

The particles phase segregate out of the polymer matrix and migrate to the film – air interface, altering the effective wettability of the substrate.

Substrate used for the experiments was Silicon Wafer and the particles were C60 Fullerene NP.

How the surface energy of the substrate influences the migration of the particles is presently being investigated.

Karim et. al., Macromolecules, 33, 4177, 2000

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Instability and Soft Patterning Laboratory
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Indian Institute of Technology Kharagpur

So, essentially what you can see I got the permission from him to show the sledge here, you have a film which is a polybutadine film, which deviates or ruptures the formation of holes you can now understand that this as holes are ruptured, and it has grown without any demon stability. And the moment you had some nano particles of C 60 variety carbon feldene nano particles the deviating is completely suppressed.

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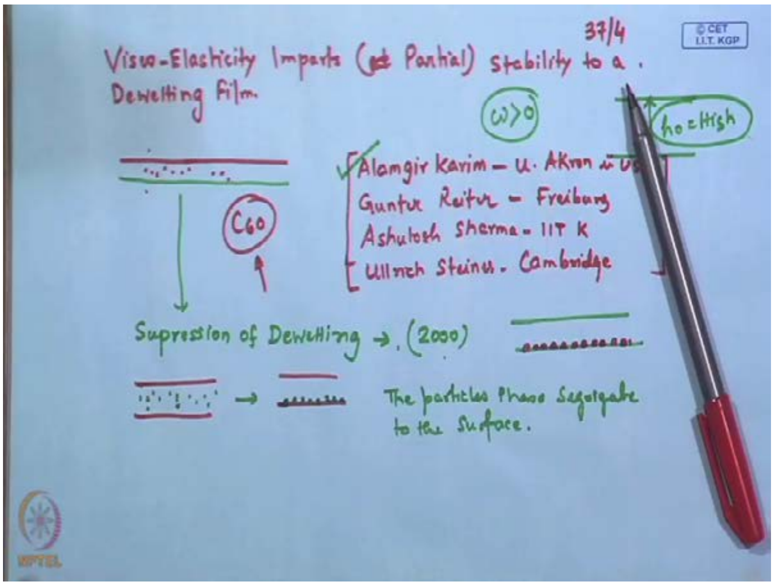

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Visco-Elasticity Imparts (~~at~~ Partial) Stability to a Dewetting Film.

$\omega > 0$

$h_0 = \text{High}$

C_{60}

Alamgir Karim – U. Akron ~ US
Guntur Reiter – Freiburg
Ashutosh Sharma – IIT K
Ullrich Steiner – Cambridge

Supression of Dewetting → (2000)

The particles Phase Segregate to the Surface.

So, what was (( )) these particles actually what happens is these particles though they are added into the polymer. These particles face aggregate on to the surface and effectively.

So, this is how its starts initially the particles are within the polymer film once you heat up the particles due to the preferential affinity towards, the surface or the particles are such they do not buying to the polymer molecules the face aggregate the particles to the surface. And thereby what happens is that there a particle reach layer forms close to the surface. And this layer effectively alters the effective vertibility of the surface and thereby imparts stability to the system. So, this was one of the very very important findings of research where people essentially utilize the concept of understanding the spontaneous instability in a ultra thin film, and then work out strategies to alter the effective vertibility of the surface.

So, what it implies that as a particles face aggregated to the interface. The sign of the effective haymaker constant changed. And you know that film can become unstable only when this haymaker constant is positive. So, what essentially happens is this particle going to the surface it changes the effectively effective variability of the substrate with associated change in the sign of haymaker constants so the system becomes stable.

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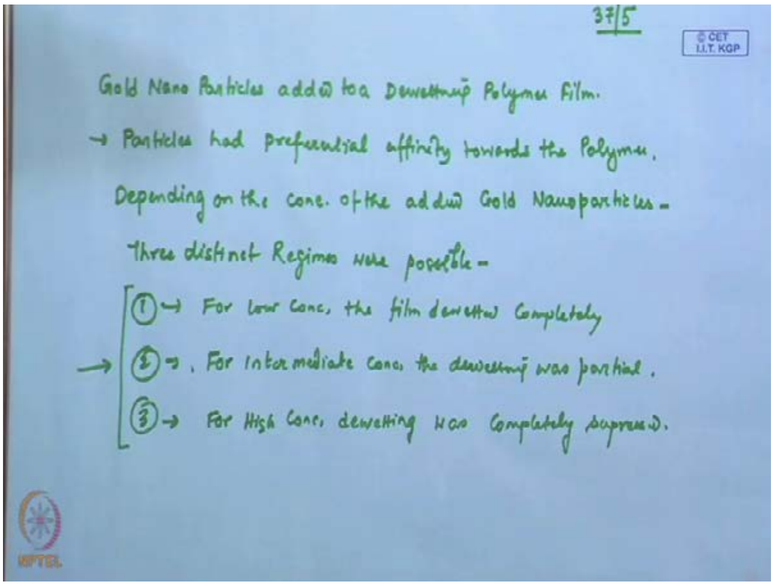

Gold Nano Particles added to a Dewetting Polymer Film.

→ Particles had preferential affinity towards the Polymer.

Depending on the conc. of the added Gold Nanoparticles –

Three distinct Regimes were possible –

① → For low conc, the film dewetted Completely

→ ② → . For intermediate conc, the dewetting was partial .

③ → For High conc, dewetting was Completely supressed.

Recently there was other nice adieu in which people looked at the behavior of the particles some gold nano particles where added to the deviating polymer film. The interesting aspect was that the particles had preferential affinity towards the polymer. So, unlike the previous case where the particles face aggregated the surface here, the situation was such that the particles prefer to be meant within the polymer matrix. And it was seen that depending on the concentration of the added gold nano particles, three distinct regions were possible for low concentration. The film deviated completely for intermediate concentration, the deviating was partial and for high concentration deviating was completely suppressed. So, what happens was the this was the 2010 paper from our group in ACS 10 it is a top journal in nano technology which sort of broke the mystery or broke the myth that was surrounding this area, but you had very little amount of nano particle and immediately the particles becomes completely stable, but there are couple of papers around 2007-2005 people are good that well we are adding some nano particles into a polymer film, and then still we are observing where the film is deviating it is not getting suppressed. So, there was a controversy that was very active it is a are very reason controversy which was going on and people wanted to know whether the claim that Kareem and his co workers put in two house and macro molecules was right or there were something more which was not reported.

So, in deed in certain cases deviating was getting suppressed but in certain cases the film include even with the nano particles where sort of deviating. And so, our results this way this results show that yes it is possible that it is not only a function of whether you apt at nano particles you need to understand what happens. So, what we figure out is that of particular interest was the case where one absurd partial deviating.

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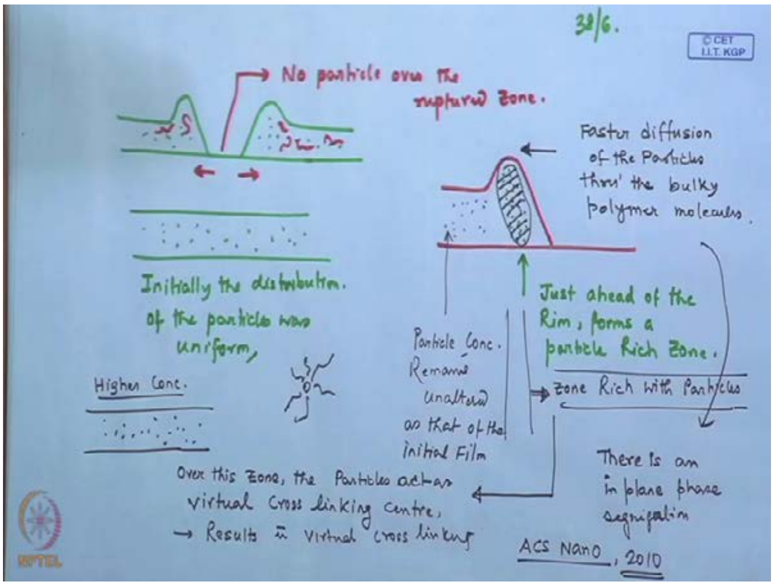

So, what happens is which has been already pointed out with this particular particles where prefer in steady state within the polymer. So, has the polymer film ruptured and the hole started to grow the particles also was there, within the film and there was no trace of particles in the ruptured zone of the hole. So, this implies that a particle did not go to the interface as was the situation with the full added nano particles. So, this was verified but during the whole growth something very fascinating happened and this will really fascinate the chemical engineering as a community. So, you have this surface tension driven bulk motion macroscopic motion macroscopic motion of hole of the hole group you have seen in some of videos of the hole grows. So, effectively there is a component of bulk velocity of shear, and then what you have here is this particle which is embedded in a matrix of these long chain polymers. So, these smaller particles have much faster rate of diffusion as compared to the bulky polymer molecules.

So, this allow this gold nano particles of the nano particles to sort of migrate we are just showing one side of the rim. Migrate at a faster rate as compared to the the long chain polymer molecules which also diffuse as you know that if the rim formation itself occurs, because there is a mismatch at the rates at which the polymer the molecule the polymer is dislodged from the surface and gets redistributed to other intact parts of the film. So, what happens is these timing nano particles are migrate at faster rate and ahead of the rim just ahead of the rim forms a particle rich zone. So, though it is are good that is initially the particle distribution of particle was uniformed due to the bulk motion during opening of the particle there is an impale face aggregation of the particles. So, here the particle concentration remains on altered as that of the initial film (no audio from42:42 to 43:04) but here, because of the faster diffusion of the particles through the bulky polymer molecules there is an imp lame face aggregation.

And this results in a zone which is richer in particle concentration. Now the particles of preferential affinity towards the polymer. So, consequently what happens is over this zone the particles sort of the particles sort of actor is factual (no audio from45:00 to 45:15) martial cross linking center where many polymer molecules sort of get attached to one of the each particle. So, this results in some sort of a martial cross linking, and this zone therefore, becomes almost elastic and therefore, hinders the growth of the holes. So, this is the very very exiting results and this was published in a paper in a joiner called ACS nano in 2010. So, if you are interested in looking at the original manner strepery there you can downloaded or you can just send me a mail and I will be happy share the manner strep with you. For our concentration what happens is any way the particle concentration within the film is high so right from the beginning.

These particles start acting as actual a cross linking centers so effectively imparting some sort of a visco elasticity or high level of visco elasticity or elasticity to the film, and thereby they stabilize the the separation stabilize the instability. So, this is this type of work they have extreme industrial application, and extreme industrial potential particle potential particle application, because these are the type of work that can allow you to make ultrathin coatings coating thin are 100 nano meter for various optical applications various other types of applications, lubrication of names devices and things like that very small lens skill it might be important where you really do not want your film to sort of become unstable. And you want your film to remain stable. So, these can be very nice approaches. The other thing is that since you are talking about addition of nano particles. So, you can use different particles with different levels of functionalities and in the process you can make functional coatings. So, where also these coatings can be stable so these nano particles in that case impart two holes one is to bring in the functionality of their own functionality as well as those particles can act as stabilizing agent as well.

So, lots of research on these areas is going on. So, this is something what we showed or what we discussed about this particle rims, is known what is happening and it was verified experimentally which some careful measurements. The interesting aspect that I will now introduce you may be few minutes are the deviating of a polymer bilayer.

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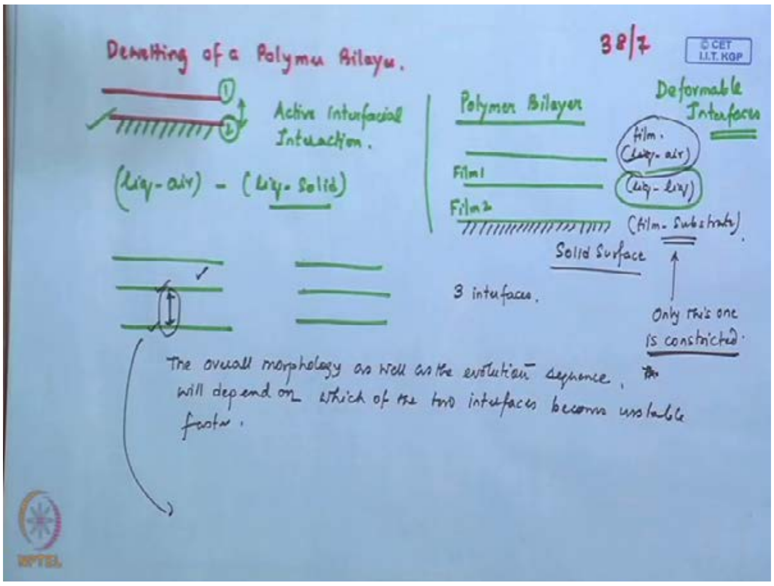

Dewetting of a Polymer Bilayer.

The overall morphology as well as the evolution sequence, will depend on which of the two interfaces become unstable faster.

There can be various other experiments critical concentration, but let us try to understand it in terms of vanderwaals interaction only. So, what we have understood in a in the context of single film that if it is a waiting film. So, it is a liquid film coated on a solid surface, there is active interfacial interaction which can be due to the vanderwaals forces. And what happens is that out of these two interfaces this the liquid solid interface this interface that is smartly to is sort of a rigid interface it cannot be form, because the solid is it involves a solid. So, its shape or geometry is defined by the shape of the solid itself, but therefore, if there is an interfacial for if there is an attraction if interfacial interaction the only deformation is manifested at the liquid air interface. In contrast if you now have a polymer bilayer.

So, you have essentially film one and let us say film two. So, which is now coated on the solid surface? So, what is this case like it is like you know have instead of two you now had three interfaces. One is a liquid air interface, liquid liquid interface, or film air interface, film film interface and film substrate interface. Now the interesting thing is that among this three interfaces only this one is a region interface. The other two both the interfaces both the liquid liquid and liquid air interfaces are deformable interfaces. So, what does what is the advantage or what is the consequence? Consequence is now depending on which of the interface becomes unstable fast faster. The overall morphology which of the two interfaces becomes unstable faster. So, if the interfacial attraction between these two interfaces is stronger and sort of this acts faster as compared to the interfacial between these two interfaces.

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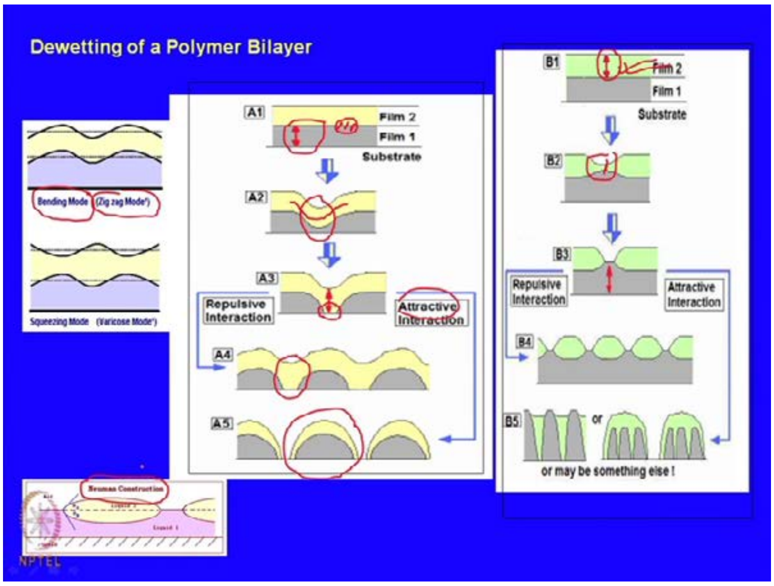

Dewetting of a Polymer Bilayer

Then what is lightly to happen what is lightly to happen is this that, because of this interfacial attraction between the film film and the films substitute interface it is starts to deform and sits since, it starts to deform the other film the top layer film also fallow it. And one might have a situation where the bottom layer has ruptured and then there is direct interaction, now between the liquid air of the film one air interface and the substrate. So, depending on whether this interaction is attractive or repulsive you can have different regions.

So, if this is repulsive you can this layer can also deviate or rupture and can form in a morphology like this or sorry if it is attractive if this interaction now is repulsive it may be there will be no subsequent evolution. So, got embedded structures like this. So, this is otherwise difficult to fabricate. The other interesting thing is that we have seen in the relation of lambda n a and all that also the feature height, it is skills as that the surface tension is also present there. So, the moment do you have a liquid liquid bilayer this is now a interface polymer polymer interface and typically interfacial tensions are roughly one order lower than surface tension.

Therefore, what happens is in that relation of lambda in etc. If you now have the interfacial tension values that surface tension value gets replaced by the interfacial tension and which is order smaller. So, lambda n etc they are going to reduce. So, you also achieve significant feature feature dimension miniaturization by using a bilayer. Now this mode of instability where the deformations are in phase with the deformation of the two layers are in phase with each other, this is what is known as the bending mode of a deformation of zigzag mode of deformation. In contrast you can have a completely different deviating scenario if the interaction between your this interaction sort of starts dominating. And these two interfaces the attractive interaction between these two interfaces becomes or sort of makes the top layer film rupture first. And important thing to notice is that here both the interfaces between which the interaction is going on at deformable interface. So, you can expect to have some sort of morphology like this with a possible with result in rupture of the film over here. Now this is a classic example, of a liquid layer now resting in equilibrium with another on other liquid surface, and unlike the young's equation of young configuration.

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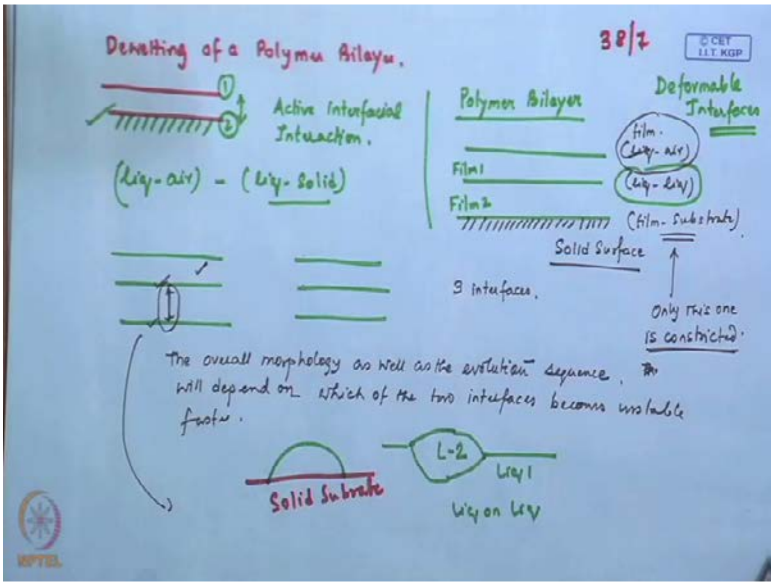

Dewetting of a Polymer Bilayer.

The overall morphology as well as the evolution sequence will depend on which of the two interfaces becomes unstable faster.

What we are more used to seen on a solid substrate, with a liquid equilibrium configuration. For a liquid on a liquid the configuration is known as Newman configuration. So, it is like this this is what is known as the Newman configuration construction not consideration, it is Newman construction and so this is a situation where you essentially did Newman construction. And depending on whether there is interfacial interaction active interfacial interaction between these two later yes or no, because one of the things can be the bottom layer can be very very thick. So, in that case the situation becomes like you have only one deviating layer that is the top layer, but which rests on a on a liquid surface instead of a solid surface. So, depending on whether there is repulsive interaction attractive interaction so you can get different morphologies. So, one of the important thing is the moment you have a bilayer deviating, there are very morphological signatures and I do not think it is important to go into all details.

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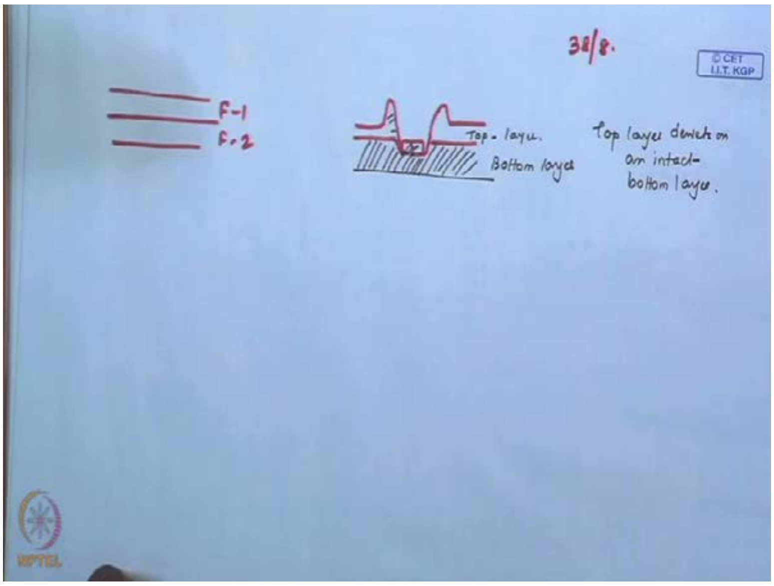

So, you have liquid one and liquid two. So, suppose if your top layer is sort of deviating we know about the formation of these rims. So, one of the critical things that happens is the here you are essentially deviating on a liquid surface. So, what happens is so this is the bottom layer, there is possibility and is particularly happens if the top layer deviates on an intake bottom layer. So, top layer deviates on intact bottom layer, and there is a possibility of the rim penetrating into the bottom layer. So, since the rims are gets penetrated into the bottom layer. So, the dynamics becomes large so this is just an example of what are the complexities that can arise in deviating of a biller, there can be various examples various case studies simulation results in have been just published two there years back, experimental are still active a whole lot of exiting things are happening in this particular area. So, with that I stop my this particular class in the next class we take up how template guided self organization or assembles can be used to guide this random instability structure to make something worthwhile or useful from these patterns thank you very much.