

## Polymers Processing and Recycling Techniques

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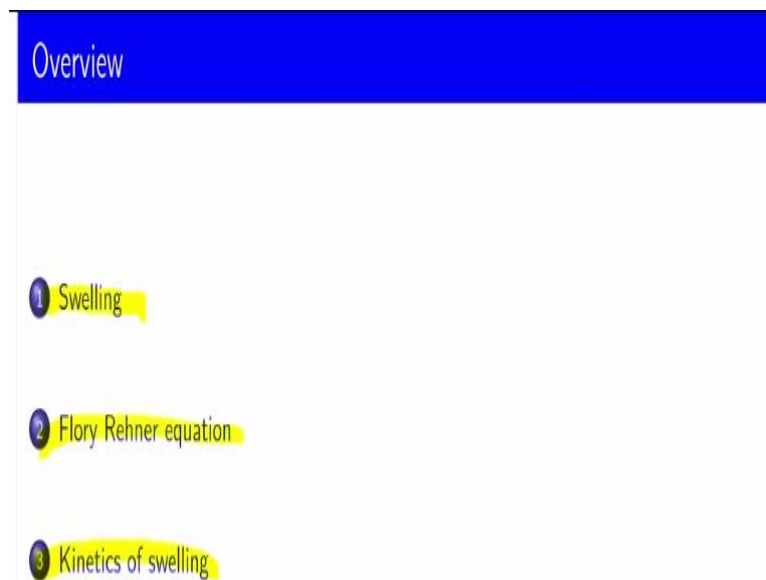
Indian Institute of Technology - Madras

### Lecture – 82

### Swelling of Polymers

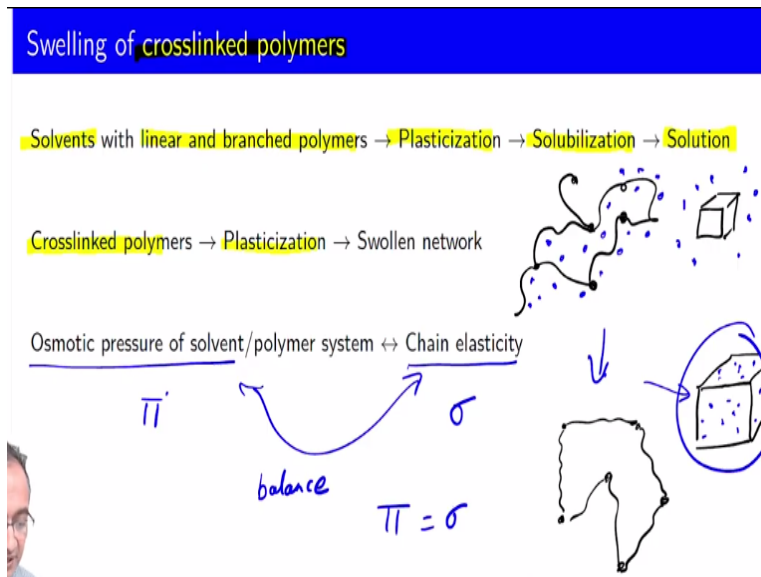
Hello, as we are discussing polymer processing and recycling techniques, one of the important set of polymers that we process are thermosets and rubbers, which are crosslink systems and during their performance as well as just to get to know how much is the amount of crosslinking that's present in these systems, swelling of these systems is an extremely important feature.

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So in this lecture while keeping our focus on properties of crosslink systems, we will discuss swelling. We will look at the elements of theory which is Flory-Rehner equation which can explain how to estimate crosslink density and how to understand how much is the amount of swelling that a crosslink polymer undergoes in the presence of a small molecule or a solvent and we'll also end with discussion related to how does the swelling phenomena happen as a function of time and what are the different phenomena which are required for the overall swelling phenomena to proceed.

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So, swelling of crosslink polymers is involved because if we have let's say linear and branched polymers and we have small molecular systems, what happens is the small molecule will get absorbed into the polymeric system and then they interact with polymer molecule, in turn leading to segmental flexibility increase in these macromolecular systems or plasticization. This of course leads to the glass transition decrease or it may lead to increase in the flow ability or decrease in viscosity of the material and all these features we have seen already.

Eventually, if a lot more amount of solvent and small molecule is present, then what happens is the solvent molecules will basically surround the macromolecule and solubilize it, that implies that macromolecule now is completely surrounded by solvent molecules and so it's called solubilized solvent macromolecule system and so we in the end get a polymer solution, in which case polymer and solvent are completely intermixed with each other. If it's a high concentration, some entanglements would be there, but if it's a dilute system then polymer molecule is separate compared to another polymer molecule and so if we look at linear branch polymer, we end up with a solution due to the effect of solvent, but let's say if there is a favorable small molecule which interacts with a crosslinked polymer, then it will increase the segmental mobility. But because of the crosslinks which are covalent bonds, the polymer molecules cannot get solubilized. So in this case, what happens is, there is a crosslink point which is preventing the macromolecules from getting solubilized. The small molecule which comes into the overall network, it can come in and it can start plasticizing, it can start interacting with these segments and increase the segmental mobility and because the segmental mobility is increased and solvent molecule would like to form a solvation shell around all of

these macromolecules, more and more solvent starts coming in.

Because of this what happens is, in the network which was earlier had lot of flexible chains and since flexibility is there, these crosslink point move away and you get largely stretched chains. Now a sample which had a certain volume because of these small molecules which have come into the polymer, it becomes swollen and so the small molecules cause the polymer sample to swell or increase in volume and this is possible because of the segmental flexibility and stretching of polymeric chains. The two phenomenon which are associated in this case are the osmotic pressure of the solvent or the fact that the solvent is miscible in polymer and therefore rather than remaining as pure solvent it would like to be in mixture with polymer it goes inside the sample. Therefore, solvent which was otherwise outside would prefer by osmosis to go in the polymer and form a mixture of macromolecular solvent system. So this is one feature.

However, there is a limitation to the amount of solvent that can go in because of the crosslink. Once the polymer chains get completely stretched because of swelling, they cannot swell any further, no more further stretching is possible. Therefore, the elasticity of chain how much can it be stretched is the other opposing factor. So equilibrium is reached or the amount of solvent that can swell the polymer is decided based on interplay of these two factors.

At equilibrium if I start with a sample which has no solvent at all and then end up with a solvent rich polymeric swollen network, this state will be determined based on the balance of this, osmotic pressure with chain elasticity. Effectively, I could say that if I indicate this osmotic pressure of solvent as  $\pi$  and if I indicate the stress which is generated in the material due to stretching of chains as  $\sigma$ , then at equilibrium these two have to be equal with respect to each other.

So, this is the phenomenon of swelling where a solvent would preferentially like to mix with the polymer, therefore it comes in, but chain can stretch only so much so it cannot keep on coming in. So there is an equilibrium reached where the stretched chains, the stress felt by them is equal to the osmotic pressure which is due to the ingress of solvent molecules in the polymer system.

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## Swelling of crosslinked polymers

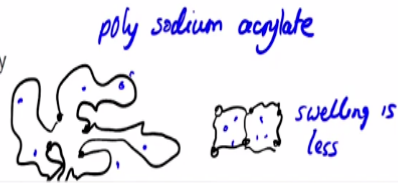
Solvents with linear and branched polymers → Plasticization → Solubilization → Solution

Crosslinked polymers → Plasticization → Swollen network

Osmotic pressure of solvent/polymer system ↔ Chain elasticity

Applications

- Superabsorbent materials
- Measurement of crosslink density
- Hydrogels, organogels



So this can be looked at by looking at the phenomena of both osmotic pressure on one hand and chain elasticity on the other. Why is this very important? Because swelling is a common phenomenon from a performance point of view as well as characterization point of view. So superabsorbent materials which are part of sanitary napkins, diapers, they are also used in agriculture to retain the moisture in the soil, so, there are lot of places where superabsorbent materials are very commonly used and they swell by exchanging a solvent. In this case it happens to be water for agricultural or water based fluids in case of medical applications and other applications such as sanitary napkins and diapers these are aqueous systems which are being absorbed into the polymeric system.

For example poly sodium acrylate is one common material which you will see talked about a lot in the superabsorbent application. Of course, if we can develop a nice theory to explain how much polymer goes in based on the crosslink density, we can then measure crosslink density. I hope all of you can think in terms of you know if crosslink density is more will more solvent come in or if crosslink density is less more solvent come in. So you can just try to think of in terms of two types of network, one where the crosslink density is much less, so therefore, the chain length between two crosslink point is very high or the other situation where the number of crosslink points is much more and the chain length between two crosslink point is much less.

So the question is in which case more solvent will come in and in which case more swelling is possible? Remember how both of these questions are one and the same, will more solvent come in or will more swelling be possible? More swelling is possible implies more solvent comes in.

I hope you can recognize that this is where swelling will be lot less because the chains are already short and they can get stretched in with low amount of solvent and then swelling will stop while with low crosslink polymeric system, swelling will be much more. So if we can develop the relation between the amount of swelling in a polymeric system to its crosslink density, we can measure crosslink density and depending on the solvent which is being exchanged whether it is an organic solvent, then we call it organogel, if it is water then its hydrogel or any other water based systems like salt solutions hydrogels are used.

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Swelling: Flory Huggins theory and network elasticity

Swelling ratio based on weight or volume,

$$S_w = \frac{W_{swollen}}{W_{dry}} ; S_v = \frac{V_{swollen}}{V_{dry}} = \frac{1}{\phi_p} \quad (1)$$

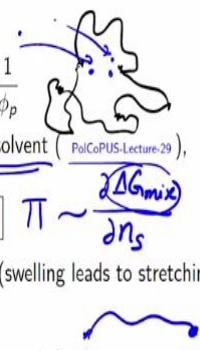
Osmotic pressure  $\sim$  change in  $\Delta G_{mix}$  with number of moles of solvent ( PolCoPUS-Lecture-29 ),

$$\Pi = -\frac{RT}{v_s} \left[ \ln(1 - \phi_p) + \phi_p + \chi \phi_p^2 \right] \quad \Pi \sim \frac{\partial \Delta G_{mix}}{\partial n_s} \quad (2)$$

Network elasticity can be estimated based on ideal chain model (swelling leads to stretching of segments and decrease in entropy),

$$\sigma = C_p RT \left( \phi_p^{1/3} - \frac{1}{2} \phi_p \right) = C_p RT \left( S_v^{-1/3} - \frac{1}{2S_v} \right) \quad (3)$$

$C_p$  crosslink density, in terms of concentration of segments between crosslinks  
 $v_s$  molar volume of solvent



So let's look at the theoretical foundation based on which this idea of estimating how much is the crosslink density affecting the amount of solvent that can be absorbed. Generally, we characterize the amount of swelling by looking at something called swelling ratio, which is nothing but the weight ratio of the swollen or completely stretched polymer chains' configuration, amount of water that has gone in or amount of solvent that has gone in with respect to the dry weight when there is no solvent or no water in the system.

We could also look at it on the volume basis, and in volume basis if we look at, then the swelling ratio is just inverse of polymer concentration, because in the dry state there is only polymer and of course in the wet state there is polymer plus solvent. So the inverse, the polymer divided by polymer plus solvent tells us you know what is the overall volume fraction of polymer in the swollen state. Generally, we can find out the osmotic pressure which is defined as the change in the free energy when we have more and more solvent come in. So when we have this network of polymer and osmosis basically drives these small molecules to come in, now what

we are asking is when an additional solvent molecule comes in, what happens to the Gibbs free energy of this mixture and how much does it change.

$$S_w = \frac{W_{swollen}}{W_{dry}} ; S_v = \frac{V_{swollen}}{V_{dry}} = 1/\phi_p$$

So the change in Gibbs free energy with respect to the number of moles of solvents that coming in or in other words the change in Gibbs free energy with the number of moles of solvent that are coming in if we estimate then that is nothing but related to the osmotic pressure  $\Pi$ . So this we can find out using Flory Huggins theory because it's a polymer solvent system and Flory Huggins theory is one way to estimate how much is the Gibbs free energy change as we have already seen, so we can get an expression for the osmotic pressure.

$$\Pi = -\frac{RT}{v_s} [\ln(1 - \phi_p) + \phi_p + \chi\phi_p^2]$$

Now the other side of it which is related to stretching of the polymer chains, we can see that whenever chain is coil-like then it can have lot of conformations possible and entropy is very high. When we stretch the chain, then the number of conformations possible become very less and therefore entropy goes down. So we can find based on these entropy changes what is the amount of force which is required and because the force will be nothing but the change in free energy as a function of the stretching. So we can evaluate the stress as a function of the amount of solvent in the system and this is based on the ideal chain model that we have already discussed and its related to basically the conformational entropy changing in the polymeric system. So in this  $C_p$  is the crosslink density or the number of chains which are involved between crosslinks and  $v_s$  is the molar solvent, so swelling equilibrium implies that the osmotic pressure which is each incremental solvent molecule coming in and changing the free energy with the stress that is generated, which implies that chains get stretched and therefore entropy reduces and they feel a tension because they are getting stretched. So when these two counterbalance each other, equilibrium is reached.

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$$\sigma = C_p RT \left( \phi_p^{\frac{1}{3}} - \frac{1}{2} \phi_p \right) = C_p RT \left( S_v^{-\frac{1}{3}} - \frac{1}{2S_v} \right)$$

## Flory Rehner equation

$$\frac{RT}{v_s} \left[ \ln(1 - \phi_p) + \phi_p + \chi \phi_p^2 \right] + C_p RT \left( \phi_p^{1/3} - \frac{1}{2} \phi_p \right) = 0 \quad (4)$$

When swelling ratio is very high  $\rightarrow \phi_p \ll 1$

$$\ln(1 - \phi_p) \sim -\phi_p - \frac{\phi_p^2}{2} \quad \text{and} \quad \phi_p^{1/3} \gg \phi_p$$

Flory Rehner equation reduces to

$$\phi_p^{-5/3} = \frac{1}{2} \frac{\chi}{v_s} \left( \frac{1}{C_p} \right) = S_v^{5/3} \quad (5)$$

• Measurement of crosslink density

So Flory Rehner expression is in fact a statement of this, so we equate the osmotic pressure with the stress which is developed in the material and this equation basically relates the amount of swelling which is determined by  $\Phi_p$  with the parameters crosslink density and also the interaction parameter,  $\chi$ , which is exclusive for a polymer solvent system. So knowing a solvent polymer system and its interaction parameter. If we know what is the crosslink density, we can find how much is the swelling or we can do the problem in inverse way where we make a polymer sample. We do not know the crosslink density but we can measure the swelling by looking at the weight change that happens in the material and therefore we can estimate the crosslink density.

If we have no specific chemistry by which we know already what is the crosslink density and we can measure the volume of solvent that has gone in and therefore  $\Phi_p$  which is the volume fraction of polymer, then in fact, we can also estimate the interaction parameter. So you can see Flory Rehner equation is very important in terms of crosslink system and estimating interactions between polymer and solvent systems. When swelling ratio is very high that implies that lot of solvent is there and very less polymer, so therefore, volume fraction of polymer  $\Phi_p$  will be very less than 1. Then we can use some of the approximation, the usual mathematical approximation in terms of a Taylor series for logarithm or also when we have very small number then power less than 1 is usually much greater than the number itself. So using these, the Flory Rehner equation reduces, so this gives us an idea about how swelling ratio changes as a function of crosslink density.

So when crosslink density becomes higher and higher, swelling ratio reduces, they are inversely

related to each other. On the other hand, look at how it is related to  $\chi$  which is the interaction parameter. When  $\chi$  is more negative, interactions are more favorable. So more and more  $\chi$  being negative implies higher and higher swelling ratio. So that means more solvent can go in because of more favorable interactions.

Using this Flory Rehner equation therefore we can actually do measurement of crosslink density and so there are standards available to measure crosslink density of thermoset and rubbers based on this theoretical basis.

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$$\phi_p^{-\frac{5}{3}} = \frac{1}{2} - \chi \left( \frac{1}{C_p} \right) = S_v^{\frac{5}{3}}$$

**Kinetics of swelling**

Combination of

- Mass transfer: diffusion of solvent PolCoPUS-Lecture-61
- Large deformation: swelling of polymer
- Relaxation: macromolecular segmental dynamics

100g sample polymer  
↓  
800g of swollen network  
Super-absorbent



Now in terms of kinetics of swelling some of what we discussed during absorption kinetics, diffusion in polymers all of that has to be combined together in terms of swelling with one major difference that swelling deformation can be extremely high. Superabsorbent polymer can absorb 8 times its own weight. So for example, if we start with a 100 gram of sample which is the polymer material, let's say dry powder, it can become 800 gram of swollen. The swelling ratio in this case is 8. So, that's the amount of solvent that can be absorbed and that's why these are called superabsorbent materials.

Absorption is happening like what we discussed earlier, diffusion is happening where water is going in or other solvent is going in, but the deformation and the polymer chains that are getting



stretched is much higher in this case compared to other systems that we have discussed so far. So when we discuss the kinetics of swelling, mass transfer, diffusion or transfer of solvent has to happen and this need not be fixed diffusion as we had discussed earlier. Large deformations are involved because swelling ratios can be extremely high and of course whatever we have discussed in terms of viscoelasticity and the fact that polymer chains can relax, segmental motion is possible. So, all these three have to be combined together and that makes the kinetics of swelling a more complex phenomenon to describe. In fact, this can be also utilized for generating different types of applications because if you have a very thin film of polymer and let's say if it starts swelling what happens is some places solvent molecule can go in where swelling can happen and some other places if swelling is not that fast, then this film can start wrinkling. So you can achieve different types of shapes by doing swelling and so generating smart polymers, generating sensors, generating actuators, the swelling behavior can be extremely important and we have already seen the example of drug delivery where again swelling and leaching out phenomena are extremely important. So in all these applications not only the amount of solvent that can come at equilibrium, the kinetics of swelling is also equally important.

So with this, we will close this lecture related to swelling of polymers and look at now the next week where we will continue to look at the sustainability aspect in terms of looking at biodegradation in the polymeric systems. Thank you.