Carbon Materials and Manufacturing
Prof. Swati Sharma
Department of Metallurgy and Material Science
Indian Institute of Technology, Mandi

Lecture - 35
Electrospinning and Viscoelasticity

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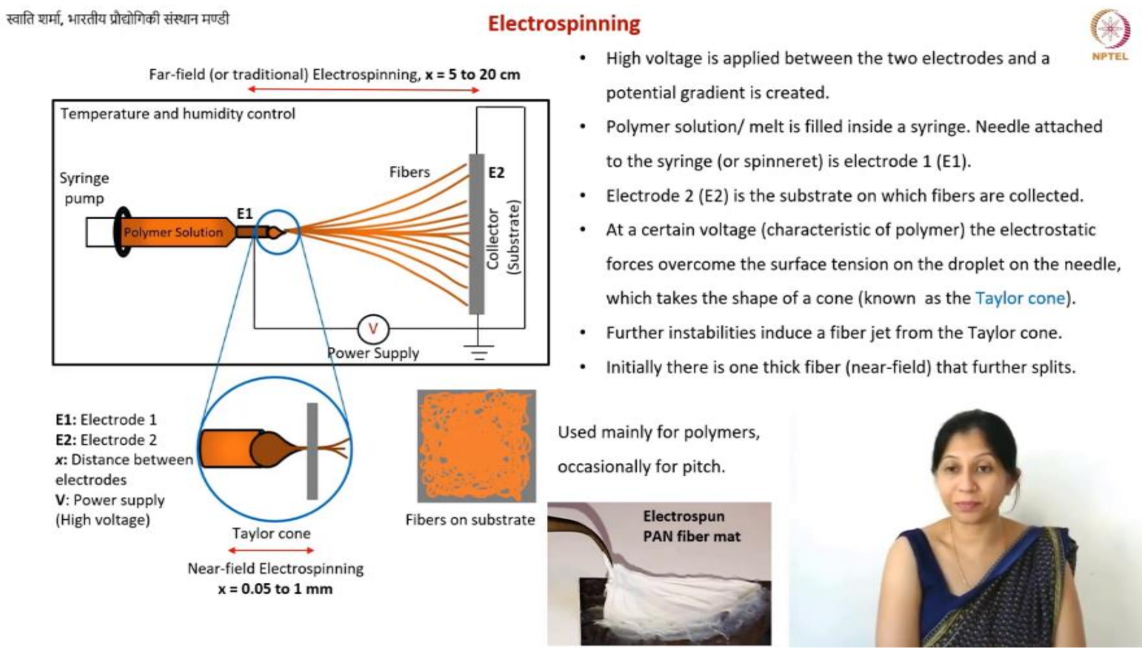

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Electrospinning

- High voltage is applied between the two electrodes and a potential gradient is created.
- Polymer solution/ melt is filled inside a syringe. Needle attached to the syringe (or spinneret) is electrode 1 (E1).
- Electrode 2 (E2) is the substrate on which fibers are collected.
- At a certain voltage (characteristic of polymer) the electrostatic forces overcome the surface tension on the droplet on the needle, which takes the shape of a cone (known as the Taylor cone).
- Further instabilities induce a fiber jet from the Taylor cone.
- Initially there is one thick fiber (near-field) that further splits.

Far-field (or traditional) Electrospinning, **x = 5 to 20 cm**

Temperature and humidity control

Syringe pump

Polymer Solution

E1

Fibers

E2

Collector (Substrate)

V

Power Supply

E1: Electrode 1
E2: Electrode 2
x: Distance between electrodes
V: Power supply (High voltage)

Taylor cone

Near-field Electrospinning
x = 0.05 to 1 mm

Fibers on substrate

Used mainly for polymers, occasionally for pitch.

Electrospun PAN fiber mat

Hello, everyone. Now, we discuss a very important fiber manufacturing technique which is known as Electrospinning. Anybody who has worked in fiber manufacturing, not just carbon fibers, but any fibers polymer fibers for various biological applications, drug delivery applications, membrane fabrication, anybody who has prepared fibers has definitely performed or at least heard of electrospinning technique at some point.

This technique also commercially has been used for over 5 decades. So, this is a very well-known technique and that is why you also have advanced versions of it and industrially for carbon fiber fabrication this is the most commonly used technique. This is how the electrospinning setup looks like.

This is the basic schematic. What do you see here? You see that there is some sort of a syringe where I have a polymer solution or it can also be a polymer melt. So, you have a syringe like structure; you can call it a spinneret and then on top of that syringe there is a needle. Needles are made of metal; syringe can be of plastic, but needles are typically made of metals.

Now, you can also attach pump to a syringe just to push the solution; to put push your polymer out. Now you have a needle and on the other side there is something known as collector. These are your two electrodes. Now, as soon as the polymer comes out of the needle, you are creating a very high voltage difference.

And because of these electrostatic forces now, the droplet that was on top of your needle will ultimately become very unstable and a fiber jet will come out of it. And that then that fiber jet then further splits into thinner and thinner fibers depending upon also the nature of the electric field. If you draw the electric field lines inside your chamber and then you will have this further splitting of fibers and then you will collect them onto the collector.

It is indeed very simple. So, these are the steps that whatever I have just mentioned. I have also written here basic principle of electro spinning. So, you actually apply a high voltage between two electrodes such that you create a voltage difference, a potential gradient and your collector is grounded.

Now, you have a polymer solution melt inside the syringe, E1 and E2 are the names of the two electrodes that I have written here. When this very high voltage is applied which are typically in the kV region, there are charges accumulated on top of that droplet which is just coming out of your needle.

Why is it coming out of the needle? Initially you gave it a little bit push that is why you need the syringe pump. So, you initially sort of just gave it enough push, so the droplet came out and was sitting on the tip of your needle. Now, you created the electric field. And because of this strong electrostatic force, now your spherical droplet its tip suddenly starts to it comes out at some point it starts forming this conical shape.

This type of cone is known as the Taylor cone. So, there is this Taylor cone formation. If you further increase the voltage. What will happen? Now, there are so many instabilities, this Taylor cone cannot remain in the cone conical shape forever. So, what will happen is that cone finally, leaves a jet at certain threshold voltage and then this jet as I mentioned further splits into various fibers.

You can actually get nano scale fibers easily using the electrospinning technique. And, in the case of our carbon fibers whatever fibers we are getting, we are then performing the heat treatment they are also undergoing certain shrinkage. So, it is easier to get nano scale fibers using this technique. However, you see that you are not collecting individual fibers. You see this image I have made here fibers on a substrate.

If I have this collector substrate and I have fibers coming from here what I have on the substrate is sort of a mat, a fabric like structure, they are not woven fabric. Weaving is something that we call when we are weaving the ropes in an organized manner. These are not woven fibers, but they are randomly oriented.

But there are lot of fibers and typically you will have several layers of such fibers depending upon how long you performed your electrospinning and you will have these layer of fibers and that would look like a cloth. So, this is how your fibers will look like on a substrate.

What else? Now, what are the things that you can do with what are the parameters that you can control. So, number 1 – you need to control the properties of your polymer, how viscous is your polymer, how much viscoelasticity it has and now in at the end of this lecture after the two slides I am going to describe the property viscoelasticity. So, that is number 1; that becomes very important.

The distance physical distance between the two electrodes also the characteristic voltage that is just determined by each polymer become important. So, every polymer has a certain range in which this Taylor cone will be formed and then the jet will be released.

Based on the nature of your polymer you will decide what is going to be the voltage that you need to apply. So, this becomes an important parameter. What is also important when you have the syringe pump? Once a droplet gets consumed, there was one droplet in the beginning and you keep on consuming the material as the jet is going and you are collecting the fibers.

Now, you need to refill. You need to also then give it a push. So, your syringe pump is basically pushing the solution through the needle and refilling and making sure that there is enough material for fiber formation. The flow rate at which these droplets are released so, basically the flow rate of your syringe pump that also becomes an important parameter.

Here you see that I have written something called far field or traditional electrospinning and then I made this setup zoomed in structure where I show the Taylor cone. The one goal of that zoomed-in structure was to show you the shape of the Taylor cone and also you see a gray line, there vertical that is the collector.

What happens? if you see in this jet that is formed initially if you zoom it in, initially your fiber jet is like this one big thick fiber which then splits further and it becomes smaller as we go further, but of course, you cannot go too far from the collector because then the voltage difference becomes too low.

So, there is optimum distance again depending upon what is the characteristic voltage for the polymer you have that optimum distance between the two electrodes. In most of the industrial processes and most of our carbon fiber precursor fabrication processes we have this distance between, 10 to 15 centimeters that is generally used. But you can use anywhere between 5 centimeter to 20 centimeter in the case of the standard or traditional electrospinning or we just call it electrospinning.

You know that is the standard or common form of electrospinning. But, there is then a variation of this electrospinning technique known as the near field electrospinning whereas the name suggests the electrode is too close. You still have this one single thick fiber if you place the electrode right there, so close to the needle. So, now you can have higher voltage difference because the distance is so little so, this variation is known as near field electrospinning. Why would we do that? Because in that case you get the single fiber jet.

So, in that case you can practically write with that fiber. So, then it becomes like a printing technique. You can also move your stage, you do not move the needle or the syringe, and then in a controlled fashion. if you move the stage, you can perform controlled writing, you can make control structures using fibers.

However, the disadvantage of course, is that because this is one thick fiber, it is thick. So, that is the problem, it is a thicker fibers. If you want to get nano scale fibers then far field or the standard electrospinning is the one that you can use. Of course, as I said that if you control the viscosity of the polymers, if you control you know the elasticity of your polymers, in that case you actually can get various you can even pull very long fibers or very thin fibers from certain polymers.

In the case of carbon fiber manufacturing however, near field electrospinning is not commonly used and for us what is more important is the bulk industrial carbon fiber fabrication. So, we only talk about the standard electrospinning. This was just for your information that there are other variations that exist.

Now, this electrospinning technique is typically used for polymers, but often it is not used for pitch. However, there are papers where people have reported electrospinning of pitch. Pitch is more commonly used or spun using melt spinning.

This is one image of an electrospun fiber mat and the polymer that was used here is known as polyacrylonitrile or PAN. This is the most common precursor for carbon fibers that is why I have shown it here. So, this is how a mat looks like. You can see this particular mat was spun on top of a silicon substrate. So, silicon vapor and now you have this cloth like structure, so, if I pick it up with a tweezer then the entire sort of cloth like structure comes out.

So, this is how your fiber mat should look like after electrospinning. This is another optimization parameter would be for how long you want to perform the electrospinning, how thick you want your mat.

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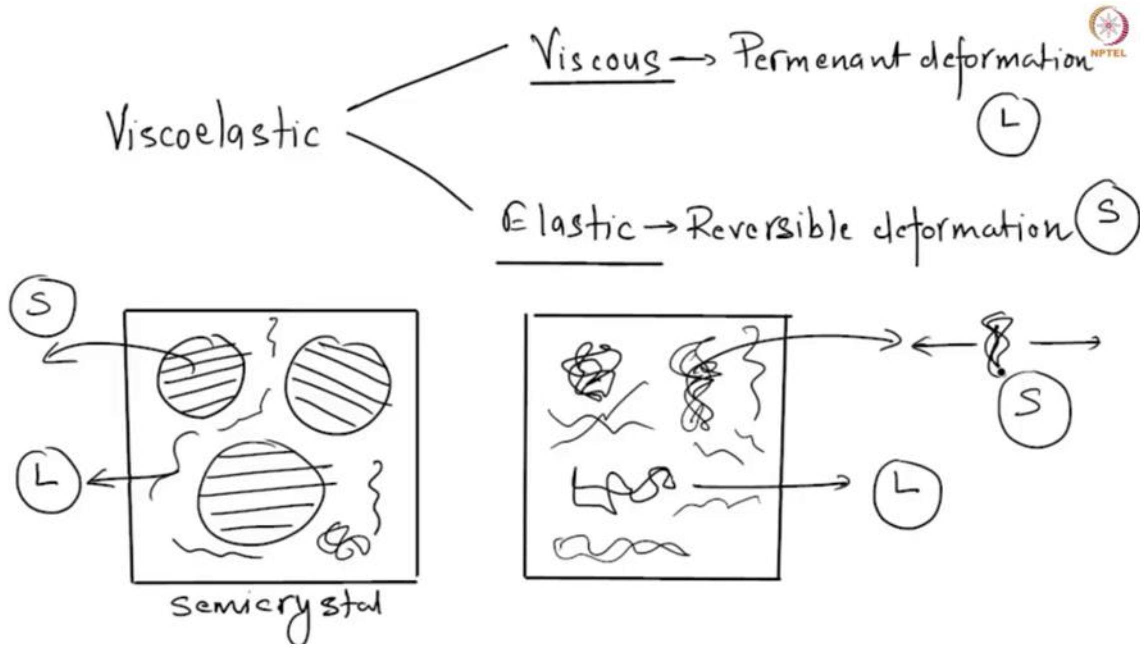

What are viscoelastic materials? You know that viscoelastic materials have two components when it comes to their deformation.one is the viscous component and the other one is the elastic component. What does viscous mean? It means that you have permanent deformation. So, this kind of behavior you will typically see from the liquids.

Once a liquid takes a certain shape, it does not come back to its normal shape. So, in terms of deformation this is the permanent deformation. In the case of elastic materials however, you have reversible deformation. So, it is like a rubber band you stretch it comes back to its normal position. So, you know that this kind of behavior you see from the solids.

Now, the question is why very viscoelastic polymers behave like both liquids and solids. So, let us take an example of a semi-crystalline polymer. You know in the case of semi-crystalline polymers you have either the chain like molecules or sheet like molecules of the polymer. They are arranged in a certain fashion, but these crystallines are randomly oriented.

This is our semi-crystalline polymer material. However, you also have some other polymer chains may be entangled a little bit, maybe not, maybe some small ones, some large ones. You also have other molecules of the same polymer which are in the amorphous region of the polymer. So, they are able to flow freely or relatively freely.

So, this free flowing type material then behaves like a liquid while this material can actually undergo elastic deformation. What does that mean? That it means, it will come back to its normal position. So, we have both components. This is the example where you have semi-crystalline polymers.

However, what if the polymer is not semi crystalline? In that case, we know that polymers have these chain-like molecules and they can be very complex. You can have these chain entanglements which can make very complex geometries. However, again we have some not so complex geometries as well. We may have also chains that are not all of the same length.

Again, we have the same kind of structure. If you take one of these entangled chains and you try to stretch it, then this will try to come back to its normal position because the chain of the molecule will try to pull it back through the entanglement points. However, this part which behaves like a liquid this part is again like a viscous liquid and this can freely flow.

So, that is why you have both of these behaviors in the case of a viscoelastic material. Polymers, pitch, heavy hydrocarbons and petroleum products are also viscoelastic.

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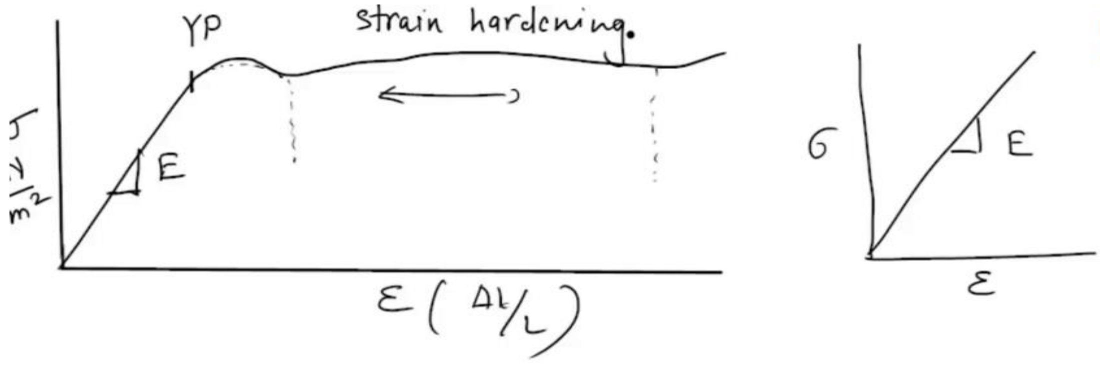

Now, we would like to understand what is the overall deformation behavior of a polymer. If I draw the stress-strain curve. so, this is your stress N/m^2 and this is the Δl/L. So, in this case what happens? you know that for any elastic solid, you have a stress strain curve that looks like this. Now, the slope of this line is your Young’s modulus.

Also in the case of polymers you have this initial elastic region because we do have some elastic component of the deformation right and from here you can also determine the Young's modulus and in fact, that is how the stiffness of polymers is often determined and specified this is the initial elastic region what happens after that.

In the case of solids, you will have a yield point after your elastic region is finished. After that you have a yield point and then you will have further deformation and fracture at some point.

While in the case of polymers, you have a slightly different behavior and the curve looks something like this and the fracture actually happens much later. You will have the yield point also in the case of polymers, but in this region, you have strain hardening. So, strain hardening also takes place in the case of metals and other crystalline solids, but the mechanism in the case of polymers is slightly different.

What you have here is the strain hardening is taking place because of the realignment or rearrangement of the chains. So, this is overall deformation behavior of polymers. Now, let us see if we have some models some mathematical models to represent this kind of behavior.

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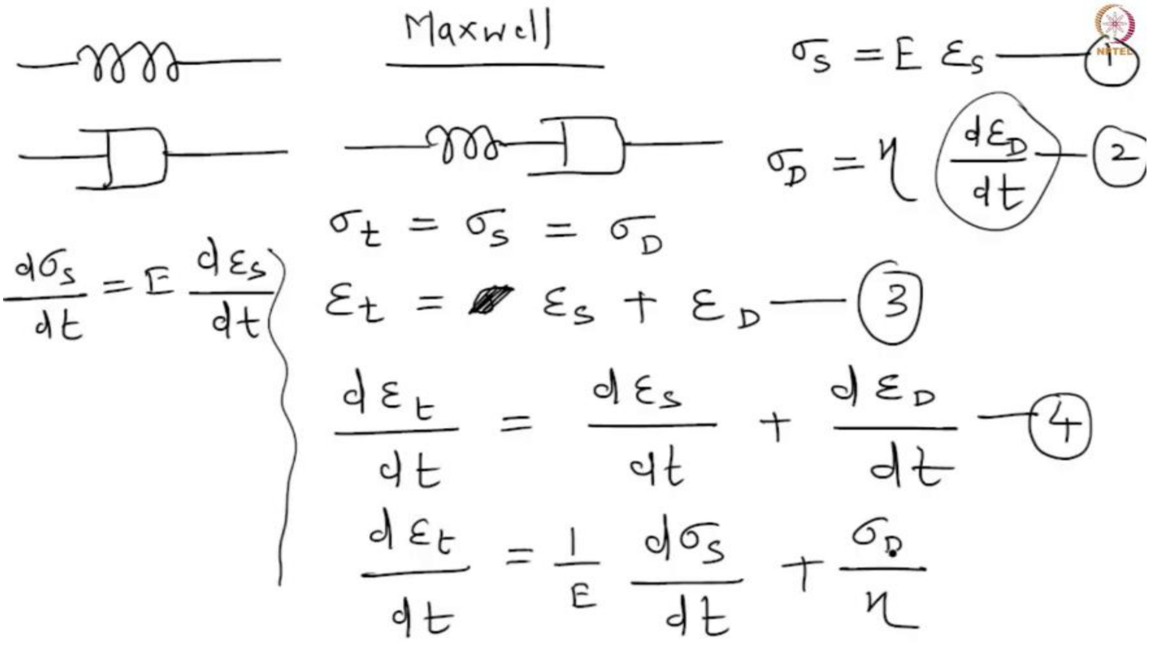

Maxwell

$\sigma_s = E\,\varepsilon_s$ — ①

$\sigma_D = \eta \left(\frac{d\varepsilon_D}{dt}\right)$ — ②

$\sigma_t = \sigma_s = \sigma_D$

$\frac{d\sigma_s}{dt} = E\,\frac{d\varepsilon_s}{dt}$

$\varepsilon_t = \varepsilon_s + \varepsilon_D$ — ③

$\frac{d\varepsilon_t}{dt} = \frac{d\varepsilon_s}{dt} + \frac{d\varepsilon_D}{dt}$ — ④

$\frac{d\varepsilon_t}{dt} = \frac{1}{E}\,\frac{d\sigma_s}{dt} + \frac{\sigma_D}{\eta}$

In the case of mathematical models what do you need? You need sort of two components; you need one elastic component let us take a spring and you need a viscous component; viscous component is represented by what is known as a dashpot or it is also called a damper in some cases.

So, we have these two components and now, we are going to connect them as a circuit element, we are going to connect them either in series or in parallel. So, the first model that we have here is known as the Maxwell's model. In this model you have both of your elements connected in series. So, this is your spring and this is your damper.

before we derive an equation for this model, let us see some very fundamental equations. In the case of elastic solids, what happens? You have the stress proportional to strain and the proportionality constant is your Young's modulus. Let us call it equation number 1. This for the spring system or elastic part.

$$\sigma_S = E\varepsilon_s \qquad (1)$$

In the case of viscous liquids what happens? You have your stress not proportional to the strain, but to strain rate

$$\sigma_D = \eta \frac{d\varepsilon_D}{dt} \qquad (2)$$

Here your proportionality constant is η or this is what indeed is known as viscosity.

Now let us see what is the overall stress and overall strain on the system in this model. Now, you can see that the overall stress

$$\sigma_t = \sigma_S = \sigma_D \qquad (3)$$

However, that is not the case with strain. So, the total strain

$$\frac{d\varepsilon_t}{dt} = \frac{d\varepsilon_D}{dt} + \frac{d\varepsilon_S}{dt} \qquad (4)$$

So, these are the two equations that you have. Now, we can take the derivative of the second equation. So, let us call it equation number 3.

So, we have this derivative of this entire equation the epsilon total. Why are we doing that? Because our goal is to find out what is the total deformation of the system and what is the total strain on your system. So, that is why we are taking the derivative of this. Now, we need to find out the values of different components. So this is our equation 4.

Now, from equation 1 and 2 we are going to insert some values here. If we see equation one in that case if you take the derivative of this equation 1, what do you get?

$$\frac{d\sigma_S}{dt} = E\frac{d\varepsilon_S}{dt}$$

And, the second one the value of the second term that we can easily get from here we already have the value. So, this is basically $\frac{\sigma_D}{\eta}$. So, this is your equation, this is your model. Now, you can make some other modifications you can for example, you can just replace σ_S and σ_D these terms with σ_D or you can just call it σ, in this equation

$$\frac{d\varepsilon_t}{dt} = \frac{1}{E}\frac{d\sigma_D}{dt} + \frac{d\sigma_S}{dt}$$

So, let us talk about model number 2.

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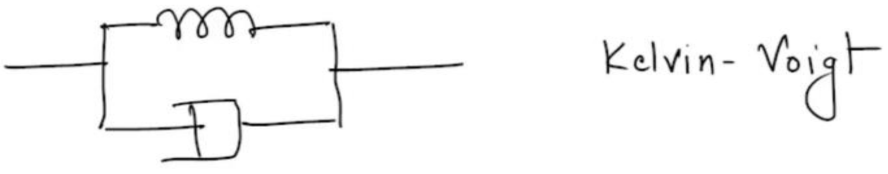

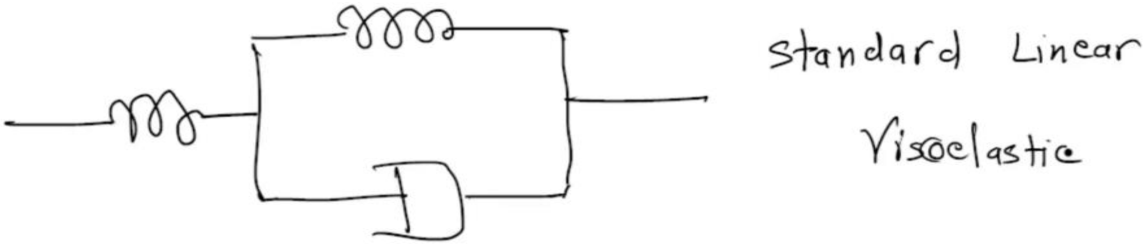

Model 2: I am not going to derive it because again it is very simple. The only difference is that here both components are not connected in series; they are connected in parallel. So, now your stress value will be the addition. So, total stress on the system will be the addition of the stress in on each component while the strain will remain equal.

$$\epsilon_t = \varepsilon_S = \varepsilon_D$$

So, you can solve this one for yourself. This 2nd model is known as the Kelvin-Voigt model. Now, the model number 3 this is kind of a combination of the two models you have a spring and then in series you have this spring dashpot system connected to it.

So, again you can solve this model for yourself. This model is known as the standard linear viscoelastic model. So, standard linear viscoelastic model. So, you can solve all these models for yourself. Now, the point is that there is nothing like which model is good and which one is bad.

It is more about what is the type of your polymer –what is the viscosity component of your polymer? what is the elastic component in your polymer? Depending upon the properties of the polymer how many and what kind of chains you have and so on and that is how you will find out which model is more suitable for your system.

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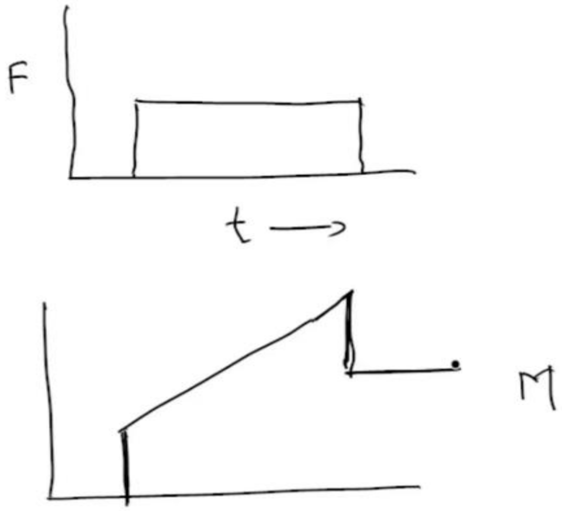

Now, I would like to also quickly tell you how these models actually represent the deformation? if I apply a certain force onto this polymer for a given time t. So, I apply the force and then I hold it like that and then I release the force. In that case what will be the deformation? How will the deformation look like according to each individual model?

In the case of your first model which is your Maxwell model, you will have certain elastic deformation in the system in the beginning. Then there will be a linear change in the properties in the deformation and then when you release the force then this elastic part will come back.

So, whatever is the magnitude of this part will be the magnitude of this part and then you will have a relaxation. So, this is how the deformation will look like as per the model number 1.

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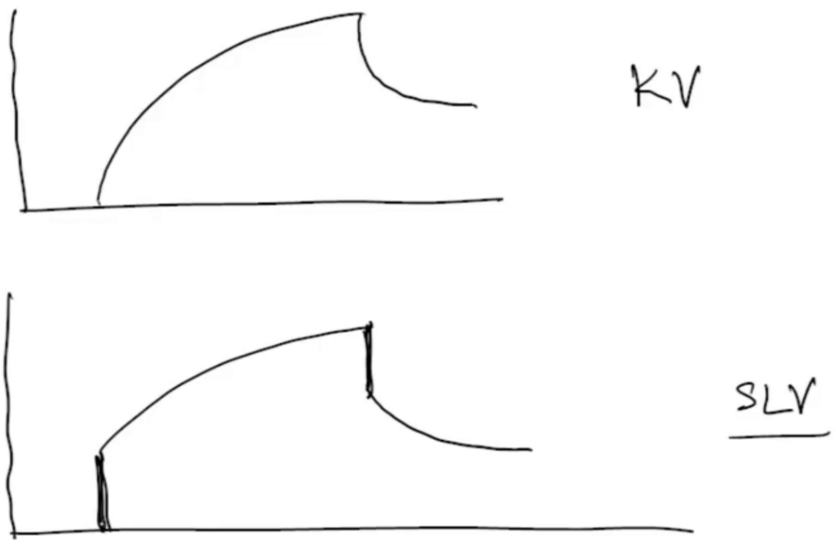

Now, what happens in the case of model number 2? It indicates that the deformation is not linear and also the relaxation is represented like this. So, this is your Kelvin-Voigt model. This model is very good for representing creep in the system. In the case of third model it looks something like this.

So, you have an elastic component in the beginning, then you have this kind of behavior. So, you do have a certain creep in your system. However, after you release the load, then you have again the same magnitude; you have the elastic component coming back, but then you have a relaxation mechanism. So, this is your 3rd model. So, as I mentioned before that according to the nature and chemical properties of your polymer, you can select the model that is suitable for you.