Nature and Properties of Materials Professor Bishak Bhattacharya Department of Mechanical Engineering Indian Institute of Technology Kanpur Lecture 19 Polymer Mechanical Properties

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Today we are going to talk about the polymer mechanical properties. So under this, we are 1st going to talk about the stress train relationship of polymer because this is different from what I have earlier told you about the stress train relationship in metals or ceramics, this is different for polymers, so we have to see that. And also we have to see how we can develop various mechanical models for the polymers.

So, various mechanical models we will discuss, these are also known as the parameter models okay for the polymers. And then we will see the stress strain behavior, so first we will see the stress strain relationship okay how we can mathematically express the stress train relationship and then we will talk about the stress strain behavior. So stress-strain behavior is what we will see once we develop the mechanical models and then we will talk about fracture and fatigue and finally we will talk about the factors that affect the mechanical behavior of a polymer.

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Now the $1st$ point is that what the stress train relationship of a polymer is and how is it different from the stress train relationship that we know for example, for the metals. Now, for the metals for the simplest case if it is a single stress and a single strain that means if you are not about a kind of 3 dimensional representation and tonsorial representation of stress.

And strain for a single you stress and strain, the relationship is $Sigma = E$ Epsilon, so which means that stress is directly proportional to the strain. However, for the polymers is not like that, there are time anomalies in polymers that means not all the stress you will be able to find out at a particular instant, the stresses will be changing with respect to the time and that is also true for the strain.

So, the generalize relationship, we call it as a generalized Hooke's Law is something like this that we have shown here, which is also known as a generalized Hooke's law that the stress along with its derivative, $1st$ order, $2nd$ order till the nth order derivative of the stress, so that is in the left hand side and in the right hand you have strain along with its derivative. So you see the simplest case of the metal can also be represented by the generalised Hooke's law provided you put A 1 to A $n = 0$ and B 1 to B $n = 0$.

So then what you will get is that A 0 sigma = B 0 Epsilon or Sigma = B 0 over A 0 Epsilon, which is something like E Epsilon, where E is B 0 over A 0. So that is why you can say that the simplest case of the stress being proportional to strain is actually a special case of this generalised Hooke's law. Now this generalised Hooke's law we can also write in a little more compact manner as the A 0 Sigma separately and then rest of the terms, similarly B 0 Epsilon separately and then rest of the terms.

If all these coefficients, A 0 to A n and B 0 to B n are constant, then the material is Linear Viscoelastic material. There is no guarantee that always they remain constant, these parameters will not every time, but for certain polymers you call it standard linear solids, where these parameters would remain constant. Now, there are many models that is what these are the mechanical models that being developed in terms of representing various types of polymeric behaviors, so the $1st$ model is the Kelvin Voight model.

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As you can see, in the Kelvin Voight model, you have a spring and a damper, so this is a spring and a damper and they are working in parallel. So for the spring that stress is proportional to strain, so you can write that if Sigma is suppose the stress in the spring, so Sigma 1 in this case in the spring and Epsilon 1 is the strain in the spring, then if the elastic constant is E, which is nothing but the elastic modulus, then Sigma $1 = E$ Epsilon 1.

And similarly, for a linear viscous dashpot the stress here is proportional to strain rate. So if Sigma 2 is the stress here and Epsilon 2 is the strain here, then Sigma 2 is not proportional to Epsilon 2, but it is proportional to the strain rate. So that Sigma $2 =$ Eta times the Epsilon 2 dt. Now, if I am applying a load that is generating a stress Sigma and a Epsilon strain in the material, then this force is actually getting divided into partly in the spring and partly in the dashpot, right.

So you can say that with a suitable area constant, Sigma $=$ Sigma $1 +$ Sigma 2 essentially since the Sigma is working on the same area, it is something like Sigma times $A = Sigma 1$ that is implicit that the A will get cancelled times $A + Sigma 2$ times A and since the A gets cancelled, so you get this relationship that the Sigma stress is Sigma $1 +$ Sigma 2.

And strain wise, the total strain is the same as the strain in the spring or as the strain in the dashpot because both of them are the same integral part of the same material. So you are going to look at only one strain, there will be 2 strains here. So hence, Epsilon = Epsilon $1 =$ Epsilon 2.

So now, if I apply this relationship that Sigma $=$ Sigma $1 +$ Sigma 2 , so Sigma 1 is nothing but your Epsilon 1 and Sigma 2 is nothing but your Eta D Epsilon to dt and Epsilon $1 =$ Epsilon 2, then you are going to get $Sigma = E$ Epsilon + Eta d Epsilon dt because there is only one Epsilon since Epsilon $1 =$ Epsilon 2 and that equals to Epsilon, so this is what will be the relationship.

Now, what is our generalized relationship? That is A 0 Sigma, so generalized relationship I can write for 2 terms that is A 0 Sigma + A 1, D Sigma dt = B 0 Epsilon + B 1 D Epsilon dt. Now let us look at it because here anyway you have up to $1st$ order variations, so we can say that there is a Sigma term in this situation, that means A 0 is there and A $0 =$ unity. There is no D Sigma dt term, so you can write A 1 = 0.

There is a B 0 term because of this E part, so that means B $0 = E$ and there is a $2nd$ constant B 1, which is Eta here so that is what is B $1 =$ Eta. So that means for the Kelvin Voight model, it is a special case of the generalised Hooke's law, where A 0 is 1, A 1 is 0 and needless to say that A 2 onwards all the other terms are 0 and B 0 is E, B 1 is Eta, needless to say, B 2 onwards all the terms are 0.

So what is a special case of a generalised Hooke's law, which is the Kelvin Voight model. Now Kelvin Voight model is signified by parallel combination of spring dashpot, so can there be a serious combination? Yes. If you take a series combination, then we will call that model to be Maxwell model.

Now in this case, is the same force which is passing through the spring and then to the dashpot, so essentially here the relationship is just the reverse here that is the stress is same, Sigma = Sigma 1 equal to Sigma 2 and the Strain here however is partly due to the spring and partly due to the dashpot, so it is Epsilon $1 +$ Epsilon 2. So, if I take the derivative of the $1st$ situation then I will get D Epsilon dt is D Epsilon 1 dt + D Epsilon 2 dt.

So this is actually um taking derivative of strain with respect to time equation one and this is equation two okay. So you get actually equation 3, now actually derivative equation 1. Now, if you substitute the values in the right hand side that means your D Epsilon to dt is D Epsilon 1 dt and what is your Epsilon 1? That is your relationship that Sigma $1 = E$ Epsilon 1 that mean your D Epsilon 1 dt is nothing but 1 over E because D Sigma 1 dt you can write from the spring is actually E D Epsilon 1 dt.

So D Epsilon 1 dt is nothing but 1 by E D Sigma 1 DT, right. So that is your D Epsilon 1 dt and that is nothing but 1 by E D Sigma dt because Sigma $1 =$ Sigma. Similarly, if you look at this part of the relationship, you can write directly that D Epsilon dt is nothing but 1 over Eta Sigma 2. So if you add this 2 together you are getting this relationship, where D Epsilon dt is actually 1 over E D Sigma dt + Sigma 1 Eta.

Now, if you take this relationship and compare it with the standard generalised Hooke's law, you will see that this model A 0 is 1 by Eta, A 1 is 1 over E and then A 2 onwards it is 0. B 0 is 0, B 1 is 1 and B 2 onwards are 0, so that is what is our Maxwell model as a special case of the generalised Hooke's law. Can there be more complicated models? Yes.

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You can have more complicated models like one parameter model, which is linear elastic spring, so these are like simple one parameter models, but from here you can actually come to the 2 parameter models, which I have just now explained, so these are 2 parameter models and then you can have 3 and more parameter models. Now, one parameter model spring denotes actually perfect elastic behavior. And the dashpot behaves perfectly viscous behavior.

So Maxwell model, where the spring and dashpot are in series, they actually predict the fluid like behavior and they do not describe the recovery part. On the other hand in the Kelvin Voight model, they predict more solid like behavior and do not describe the stress relaxation, so that is the typicality of the 2 parameter models.

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More than that, if you go to 3 parameter model then you will get two models, one is called the Standard linear solid model. In the Standard linear solid model, if you look at it that there is a spring and a damper, which are in parallel and also there is a spring and a damper which are in series, so that is the relationship that you get for a standard linear solid model.

That means, if I try to see this in terms of A 0, it is 1, A 2, A 1 is Eta over E 2, A 2 onwards it is 0. And if I look at B 0, this is E 1 and B 2 is Eta times E 1 + E 2 by E 2. And this is B 1, so this is B 1 and B 2 onwards is actually 0. Now let us look at the Standard linear fluid model. For that model, unlike in this case where you have 2 springs in parallel, here you are going to get 2 dampers in parallel and a spring damper combination in series.

So for this case if you work on you will get this one to be the strain relationship. Again here you can write A 0 as unity, A 1 as Eta 2 over E, no other parameters are there, A 2 onwards is 0 with respect to stress. With respect to strain, B 0 is 0, B 1 is find out to be Eta $1 +$ Eta 2 and B 2 is Eta 1 Eta 2 over E and rest of the terms are 0, so that is the again another special case of a generalised Hooke's law.

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Now let us look into the viscoelastic deformation that how the viscoelastic deformation can be modeled as something which is really in between the elastic and the viscous behavior. Suppose, I take a material and then I apply a load which is like a step load as has been shown in this case. That means at time T a, I have applied the load and then at T r, I am unloading the load.

Now if it is elastic material, as soon as you apply the load that means as soon as there will be stress, you will be instantaneously strain will be developed without any loss of time and then as soon as you remove the load, if it is within the elastic limit you will see that the strain will disappear as well. Can a viscoelastic material or can a polymer behavior in this way? No.

Why it cannot behave in this way is because inside the polymers there are many chains and since there are many such chains, each chain has its own dynamics and they are going to interfere with each other, so as a result it will never be a an instantaneous process of strain development. Rather, you will see that the polymer is taking some time to develop the strain and once again the load is removed, the strain will once again disappear from the system.

So, a polymer is essentially if it is totally viscous, it will take time to develop the strain okay and beyond the point of T r, the strain will remain in the system. But in the case of a polymer, it will be addition of the 2 behavior that means as you apply the stress or the load, you are going to get some instantaneous strain development.

So this is the part which is related to called the Glassy modulus part, so this is instantaneous and then gradually you will see that it is deforming more, but is just like the viscous behavior and there you are going to get a additional term, which is the Loss modulus which will come into picture. So both glassy modulus and loss modulus sometimes it is also known as Storage modulus will come into picture in this instant.

And then once you are unloading, you are going to see that it is actually the strain is coming down. So an amorphous polymer may behave like a glassy polymer at low temperature, where it is instantaneous that is why it is actually called glassy modulus. A rubbery solid at intermediate temperature, where it is partly elastic behavior and partly viscous behavior and this happens above T g that is the rubbery phase.

And then a viscous liquid if the temperature is further raised, it will become a viscous liquid, where it will behave totally like a viscous behavior. So for all intermediate temperature, the polymer is a rubbery solid, which shows the viscoelastic behavior, which is a combination of this elastic and the viscous behavior.

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Now if you look at the stress strain behavior, you know that there is the brittle behavior. Some polymers which are highly actually crystalline, they show this kind of brittle behavior. And then there are these elastomers which are like rubber, which does not really does not have high strength, but before it fails it takes a very high strength that is what is like the elastomers typicality.

And there could be polymers which are between the 2 that means it behaves initially like a brittle polymer and then it behaves like an elastomers up to a certain point may be some 4 percent, this is strain in percentage, so maybe up to 4 percent, 5 percent strength and then you will suddenly see that the failure has occurred in the system.

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If you compare it in terms of modulus of elasticity, the polymer's modulus of elasticity is from MPa to just GPa range, something like up to 4GPa. If you compare that with metals, it is something like 50 to 400GPa. So as per as the elastic modulus goes, metals are far ahead of the polymers. If you look at the tensile strength also, the polymers can take tensile strength up to 100MPa but that is the fracture point of the polymer.

And for metals it is from 100 to about 1000MPa. So clearly speaking, metal beats the polymer both in terms of modulus of elasticity and tensile strength. But the point where polymer beats the metal is this elongation capability because before failure polymers can take up to 1000% of its original length kind of deformation, whereas metals fail by a strain which is less than 100%.

So what it means is that polymers are compliant, they try to adjust with the system, they are more adaptive and deform a lot before the final failure takes place. On the other hand, metals do not differ that much in comparison to the polymers so they fail much earlier, less than 100%. But also I told you earlier that ceramics are even weaker than in terms of these that they will even before, they cannot take any high strain at all, so with a very low strain you will see a sudden failure in the ceramics.

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Now this brings us to the discussion on the fracture in polymers, so one point is that polymers have low fracture strength compared to metals and ceramics just because its strength itself is low. And the fracture mode differs from polymers to polymers. For thermosetting polymers, the fracture mode is like brittle material, which means thermosets are highly cross-linked remember.

And for the thermoplastic polymers, both the brittle as well as ductile failures are possible. In such polymers, crack forms at region of localised stress and there will be stress concentration, scratches, notches, sharp flaws, et cetera. The factors that will favor the brittle fracture are temperature reduction, increase in strain rate, sharp notch presence, increased specimen thickness and polymer structure modification for example, by raising the T g of the polymer that is the glass transition temperature of the polymer.

As you can see here that if a polymer is brittle, then something like Melamine or phenolics, then it behaves in this manner, if it is elastomers type soft and flexible like polyethylene, PTFE, will behave in this manner. And if it is in between then it is tough and ductile, ABS, nylons are of this category, which actually takes a much higher stress level and also much higher strain level in comparison to the 2 extremes.

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The fracture mechanism in polymers, there are 2-3 important points in it, one is that there is this amorphous thermoplastic, where for below T g, they are actually brittle so it has a low fracture resistance, it behaves like glassy material as I already told you. Above T g they are ductile, so it gives you higher fracture resistance and there will always a plastic yielding prior to the fracture.

Now the fracture phenomenon that you will see often in such a material is called crazing. Crazes are what; these are the regions of localised plastic information and they will form at highly stressed regions associated with the scratches, flaws and molecular in homogeneities. They will lead to the formation of small and interconnected micro voids. And then the region between micro void you will see the Fibrillar bridges.

Under load, the fibrillar bridges will elongate and break, micro voids will grow and merge, and thus, the crack propagation will happen with respect to the applied tensile stress in the polymer. Let us look into a simple example to see that how this crazing will occur in a polymer. So here I have taken a small sample of a normal plastic bag cutting that his lowdensity polyethylene.

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And his low-density polyethylene, I am subjected it to tensile stress. Suppose your bag is very heavily loaded, this bag you will also notice the same phenomena. So here I am actually trying to stress it, now initially you can see that it has all uniform yellow colour. What will happen if I apply little bit of stress in it? So I am applying the stress as you can see that there are some spots and some lines straight lines which are getting created, these are actually the last attempts of the polymeric chains to orient itself towards the direction of stress.

If I apply more stress, you will see that there are more crazing lines so that means more polymers are aligned and there are some white patches you will see, where actually the colour changes are happening and the micro voids are about to start. Now if I pull it further and you can see that there is a sudden failure and you can see that this sudden failure has happened, where this colour change has happened and there will be formation of such small micro holes, this is one such micro hole.

So the failure could have either happened from the left or from the right side, it is just the chance, where the stress concentration is certainly maximum the failure will take place there. So you can see the colour change, you can see the crazing and you can see this formation of the micro holes. So that is typically a kind of a fracture mechanism that you will see in the polymers.

Now, when a polymer is subjected to cycling loading, then the fatigue comes into picture okay because there are many aircraft structures, et cetera, where there are polymeric wheels and hence there will be always cycling loading that will be associated with the system as the plane takes off and land. So under cycling loading however, the behavior of the polymer is pretty bad in comparison to the metals.

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So they are more sensitive to loading frequency then for metals. High frequencies and relatively large stresses can actually cause localised heating and that would soften the material and leading it to failure. Here, I just want to tell you one thing that frequency and temperature are actually just kind of a you can exchange one with the other by keeping in mind that if the temperature increases then what happens?

Suppose I am drawing the modulus of elasticity of a polymer, initially it is in the glassy phase, then the transition rubbery phase and then it comes to the glass transition happens in the rubbery phase and then the failures occurs. With respect to the frequency, just the reverse will happen. That means the low temperature is actually similar to high-frequency behavior.

So if there is a high frequency excitation of a system, then the polymer will behave like it behaves in low temperature that means it will behave as if it is in the glassy region. That means, under high frequency excitation the polymer will be very brittle. And under lowfrequency it is somewhat similar to the high temperature behavior, so this is the lowfrequency behavior and that is in the rubbery phase and this is your glass transition phase.

So low-frequency, why do we get a rubbery phase because the polymers get more time to adjust itself, the chains get more time to adjust so it behaves like a rubbery material and the low-frequency is exactly similar as the high temperature behavior in the polymers. So number of cycles to failure if you look at it for example, PTFE number of cycles to failure you can see that it can be anywhere starting from 10 cube to 10 to the power 7.

Similarly, polyethylene and the stress amplitude however, it fails at a very low stress amplitude level PTFE. And the high stress amplitude, something like PET can take or polystyrene can take high stress amplitude. So that is the fatigue behavior of the polymers. So what are the factors that affect the mechanical properties in polymers?

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Number 1 is of course temperature, increase in temperature can produce decrease in elastic modulus I have already shown you, it can also create reduction in tensile strength, enhancement of ductility and reducing the strain rate also produces the same effects in the polymers. So as you can see here that PMMA for example, at a low temperature 4 °C, it behaves like a brittle material.

And at 50^oC, you will see that it behaves like a rubbery material, 60^o even so. In between is the phase when the glass transition occurs in the system, so that is the, that is how sensitive polymer is to temperature.

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The 2nd important point is the molecular weight because for many polymers tensile and impact strength increases with increasing the molecular weight and this is due to increased chain entanglements.

Larger is the chin, more is the chance of entanglement and hence the strength tensile and impact strength increases, also the viscosity increases. The $3rd$ point is the degree of Crystallinity, hire the crystallinity, higher the close packing. So higher density would be more strength, high resistance to both dissolution and softening by heating, so that is degree the role of degree of crystallinity in the polymer.

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Finally, the 4th point is the cold drawing, which is analogous to strain hardening in metals, is used in production of fibres and films. Molecular chains become highly oriented in fact, that is why I was showing you that as you are drawing, you will see that this kind of parallel chains were appearing in the system that is what the cold drawing is.

And the properties of the drawn material are actually anisotropy perpendicular to the chain alignment direction, the strength is reduced. So that is why know you will see that in the perpendicular direction, in this direction it is weaker and in this direction it is stronger. And that is why when the cracks occur, you will see that the cracks are occurring and failing in the weaker direction for cold drawing linear polymer. So this is where we will put an end to the mechanical models of polymers. In the next lecture, we will talk about composites now and the classification of the composites, thank you.