Basic Construction Materials Prof. Manu Santhanam Department of Civil Engineering Indian Institute of Technology, Madras

Module No # 09 Lecture No # 43 Polymers and Composites – Part 2

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Again thermoplastic versus thermosetting, what is being shown here is that how does the molecular weight of the materials affect the way that it responds to temperature. If you make a polymer with a very high molecular weight consisting of very large number of chains, you will have to significantly increase the temperature to cause it to change its behavior. So that's what is being shown here.

So in thermoplastics as we said there's a little cross linking. These are highly ductile. They will show very large levels of deformation before failure. These soften with heating, they start flowing with heating. So these are the examples provided of the linear and branched copolymers.

Thermosetting materials are having very large cross linking or they are almost networked or reticulated. These are hard and brittle as we talked about before. They don't soften with heating. You continuously increase the temperature, at one point it will simply burn. They do not soften with heating, they just go and burn. Examples include vulcanized rubber, epoxy, polyester resin,

phenolic resin. All these are essentially components that are used in different engineering disciplines. Epoxy is used a lot in civil engineering, you will learn later when you take about repair of concrete structures. Epoxy is a very common material for repairing concrete structures.

So now what is this diagram showing you here? At low molecular weights, even at reasonably low temperatures your material is already a mobile liquid. That means it is a liquid with very low viscosity. As you increase the molecular weight, the materials or polymers basically will show a viscous liquid sort of a behavior.

At high molecular weights and at high temperatures you will experience a rubber like behavior. High molecular weight automatically means that you have a material that is almost a solid, but then because the temperature is high, it will experience very high levels of deformability. That's why we call it as a rubber like behavior.

At this high molecular weight, when you reduce the temperature, you get what is called as a tough plastic. And then when you further come down in temperature, you make a partially crystalline solid. And you have a crystalline solid when your temperature is extremely low. So depending upon the molecular weight of the polymer that you are forming and the temperature to which you are processing it or exposing it to, you will form different types of material characteristics.

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In case of thermoplastic materials as I said, it's going to be highly sensitive to the temperature. An example is given here of data from a semi-crystalline polymer polymethyl methacrylate which we also know as plexiglass. So here the stress is plotted against the strain and you can see at 4 degree Celsius, it's almost exhibiting a brittle behavior. When you change from 4 to 20, you start seeing some plastic behavior. At 40, it becomes more plastic and at 60 it becomes extremely plastic and it goes to 1.3 strain. This is not 1.3%, this is 1.3 strain, that means a deformation that is 1.3 times that of the original length. So you can see what kind of behavior these materials exhibit when you change temperature just from 4 degrees to 60 degrees, which may be quite a lot in the range of operation that you expect.

So for example if you consider this material and you apply it for an application in the exterior environment. At least it will have variation between 4 degrees and 40 degrees depending upon the temperatures in your region. So your material behavior is changing significantly. So when you decrease the temperature, you increase the modulus, you increase the strength and you decrease the level of elongation. That means you make the material less ductile as you decrease temperature.

When you increase strain rate, you get the same effect as decreasing temperature. So increased strain rate means that you are testing at a very rapid rate. When you test at a very rapid rate, you get a higher strength and modulus but you get a lower ductility or deformability.

It's very important for you to understand what is meant by viscoelasticity. You may have learnt a little bit about this in the material behavior chapters earlier. Viscoelasticity deals with flow in solid materials. When we talk about liquids, we only talk about viscous behavior. But when you talk about flowing solids, we call them viscoelastic materials. In fact most materials are viscoelastic, although the viscous response in most materials like steel or metals may be negligible as compared to the elastic response.

In concrete you do get a significant response but it's nothing compared to what you get with polymers. So for polymers it is very essential for us to understand this sort of a response. Again think about the most common polymers that we know of, that is bitumen, which is used for road construction. Now what will happen with a continuous loading in this material is that it will undergo a very large amount of creep. And because of that it will have a significant change in its material characteristics. The way that it responds to the driving will change significantly over time. So let's talk about how viscoelasticity is typically studied in polymers. Usually viscoelasticity is studied with the help of the stress relaxation test.

Now creep means you have a sustained load and then you measure the strain which changes in the material. You can also do an experiment where you have a sustained strain and you measure the change in stress in the material. So what will happen is if you stretch a material and hold it in that position (that means you have a constant strain), the material in the interior will start rearranging itself in such a way so as to lower its stress. It will rearrange to lower its stress. So that's basically called stress relaxation, lowering of stress levels at a constant strain.

So again here in the tensile test, the strain is kept constant, the stress is time dependent and it changes with time. Stress decreases with time. Creep test is opposite. In creep what you do is, you have a constant stress and the strain basically increases with time.

In creep, stress is constant and strain increases with time. In relaxation, strain is constant and stress reduces with time.

Now here we define a parameter called relaxation modulus which is equal to the time dependent stress divided by the original strain which was applied. Now what is given here are data for amorphous polystyrene and what is plotted is the temperature in the x-axis and there's relaxation modulus on the y-axis relaxation. What you see here is that when the temperature is low enough, less than 100°C, you have a rigid material. You have a material that is rigid. That means it is almost behaving like an elastic solid. You experience a change here when the material starts flowing, that means it has got a very low relaxation modulus, why because the stress is reduced significantly in this material. Because it starts flowing, the stress basically gets relived significantly. And you can call this temperature at which this transition occurs as the glass transition temperature.

As you increase the temperature further, you have a very large relaxation and your stress level drop to very low values. That essentially conveys that the material now has become viscous liquid. So what you are seeing here is that your material will experience a large range of possibilities in its state of existence as you change the temperature. Now here the temperature is being changed from 60 to 180, it is not really a large variation mind you. In most engineering applications you need to think very carefully about where this transition actually occurs. So because of that, the glass transition temperature values of certain polymers which are commonly used in engineering are provided here.

When you have a low molecular weight polyethylene, the glass transition happens at -110. That is why when you take these polyethylene sheets, some of the bags that you take for shopping, which are banned now by the way. If you take them and you start stretching these bags, they will continuously stretch.

If you go to more thicker high density polyethylene sheets, they have a slightly higher glass transition temperature. But then still at room temperature they are all highly deformable. Polyvinyl chloride, a common material used for making pipes for instance has a glass transition temperature at 87°C. So if you have to carry boiling water through polyvinyl chloride pipes, you have to think twice. That is why in most countries where they have hot water supply directly to your bathrooms, the hot water is generally supplied using metal pipes and not PVC pipes. PVC is only used to carry cold water.

Polystrene is around 100 as you saw here and polycarbonate is about 150°C. That means it has got a more higher level of applicability in terms of temperature.

So when you are choosing polymers for applications in engineering, depending upon the conditions of exposure you will be choosing the type of polymer. That's very important with respect to polymer chain.

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So just to summarize, polymer behavior as we said compared to metals and ceramics or concrete, the general drawbacks are that the modulus of elasticity, the temperature of application, the fracture toughness, these are generally small. Deformation is temperature and time dependent. Very important to remember that. And again, sometimes you can improve the characteristics by composite reinforcement. What do you mean by that?

So if you have a polymer or a plastic and when you put fibers in it, it may increase the extent of strength of the polymer and that's what we will talk about in terms of the polymer based composites.

Thermoplastic materials like polyethylene, polystyrene, polypropylene, polycarbonate, they have smaller elastic modulus and smaller temperatures of application. You cannot really apply them at very high temperatures. They are easier to form and recycle. You can recycle, you can melt them and then reform them.

Elastomers like rubbers have very large reversible strains. That lead them to have a very good characteristics with respect to engineering. Where do we use a lot of rubber in engineering? We use that for the bearing pads in a bridge. If you have a bridge deck which is supported on piers or columns, you typically have a bearing pad here. A rubber bearing pad is used between the bridge deck or bridge deck girder or beam, that rests typically on this bearing pad made out of neoprene. These are neoprene bearing pads. That's one of the application areas for polymers like rubber for instance.

Now thermosetting materials like epoxies and polyesters, which are also applied a lot in civil engineering, have larger modulus of elasticity and a greater range of temperatures over which they can be applied.

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- · Impact resistance
- · Fatigue resistance
- Tear strength and hardness

So having looked at polymers and polymer behavior, we can also look at and briefly talk about some engineering properties like impact resistance, fatigue resistance, tear strength and hardness. Now of course impact resistance is not going to be as good as what you have for metals or concrete but because impact implies a very high rate of loading, you will experience a much greater strength level for the polymers.

Fatigue is a common problem with most polymeric materials, a lot more than it is with concrete. Fatigue happens because of repeated loading. For example again a roadway pavement, you have an asphalt or bituminous pavement which is subjected to continuous movement of traffic, number of cycles of loading happens and that reduces the load carrying capacity of the material still further. And in polymers it can be quite significantly affecting the characteristics of the polymer.

Tear strength and hardness, now how easily can the material tear off? How can it easily tear of? For instance, one of the common aspects of polymers is the application of coatings on concrete or in steel. How hard is the material to scratching and how easily can tear off from the surface? So these are also characteristics that you need to consider for polymers that as applicable to construction materials.

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You can strengthen polymers by using additives. You can strengthen polymers or you can alter the temperature response significantly. What are these additives? You have fillers, very fine fillers essentially that will improve the strength and hardness. And they will also improve the thermal stability and dimensional stability. For example fine sawdust, silica flour, sand, glass, clay and so on are very fine particles and they can be mixed with the liquid polymer at the time of its preparation and that will lead it to have a more rigid sort of a structure.

Plasticizers will improve ductility and toughness and also flexibility of the polymer. Of course when you are increasing ductility and toughness, you are going to be reducing the rigidity of the material. So generally these are liquids with low vapour pressure and low molecular weights and these may be used in forming thin sheets for instance where you need a lot of pliability. One of the common things that you see is the food wrapping sheet. See how nicely it deforms and it you can cover the food quite nicely with it.

Stabilizers basically improve the resistance to the environment, particularly we are talking about ultra violet radiation. Most polymers will degrade, actually all polymers will tend to degrade when they are exposed to sunlight, when they are exposed to ultraviolet radiation. That's basically the process of aging of the polymer itself. And stabilizers help to prevent that aging to some extent.

Sometimes you can color the polymer differently. You can have dyes and pigments that are added to the material to give different colors. And in some cases you may want to put flame retardants which can reduce the effect of fire on polymers.

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So we talked about polymers and let's take a look at how we can make these polymers a lot more versatile for engineering applications by making them into composite materials. First of all why do we want to use composites? Simplest example is reinforced concrete. Why are we using the composite because concrete is good in compression and steel is good in tension. We combine the good characteristics of both and give a composite that produces a synergistic effect. So that's a combined action.

Now if you think about regular composites, even concrete as a composite, we talked about the fact that concrete can be a 2 phase composite. One phase is cement paste phase which is cement and water together. The other phase is the aggregate phase which are the particles of aggregate distributed in this matrix. So you have the matrix phase which is continuous and the dispersed phase which is embedded in the matrix.

So in concrete, the matrix will be cement paste and the dispersed phase will be the aggregate. So based upon how these 2 phases are different, you can call your composite material in different ways. One is a particle reinforced composite where you have particles dispersed in the matrix, which could be large particle or dispersion strengthened particulate composites. The other is a fiber reinforced composite, in which case you can have continuous fibers in some cases and discontinuous fibers in other cases.

So in concrete, sometimes we use short steel fibers to improve the load carrying ability of the concrete and to improve the deformation resistance of the concrete. And these fibers are typically added in a discontinuous non-aligned fashion. They are distributed all across the structure. They don't really align themselves quite nicely. But there are other fiber reinforced composites where the fibers can be aligned or a continuous fiber.

Again these discontinuous fibers could be aligned or randomly oriented. So in fiber reinforced concrete, we get randomly oriented fibers. Now other than combining materials together, you can also take materials individually and put them together structurally and form what is called as a structural composite, like a laminate.

Think about plywood. What do you do in plywood? You have essentially thin sheets of wood which have grains in different directions. So your grain orientation in one sheet is in this direction, in the next sheet the grain orientation is in the other direction. And then you stick together these individual sheets together to form a slightly thicker wooden or plywood. Plywood is basically a laminates of wood which are connected to each other with grains oriented in different direction. That means it will have equal strength in all directions. So that's a structural composite.

Another structural composite could be a material which is a sandwich panel. So we have the exterior panels which are made of a very stiff material and an interior panel which is made of a light weight composite. So in that way your structural composite will be able to take large loads because of the exterior panels and you don't have to waste a lot of material in the interior. And you can get some deformability and pliability because of the low stiffness material that is filled up inside.

I also talked previously about the hollow steel tubes that are filled with concrete. That's also a structural composite.

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Now how do you determine the engineering properties of composites? Obviously the engineering properties of composites would be dependent upon the engineering properties of the individual materials that go in to forming the composite. And what sort of formulations do you apply to get that? So think about a simple composite with 2 phases, 1 and 2 and with modulus of elasticity of E_1 and E_2 . And volume fraction of V_1 and V_2 , volume fraction V_1 means the volume of phase 1 divided by total volume. V_2 means volume of phase 2 divided by total volume.

So the rules governing the engineering properties of a composite from the engineering properties of the individual constituents propose that the engineering characteristics of the composites will be in between a set of upper and lower bounds. So let us take a look at what this upper and lower bound is. What is plotted here is the data for copper matrix with tungsten particles.

So you have a continuous space that is copper and then tungsten particles are strengthening this phase. What is plotted here on the x-axis is the composition in terms of copper and tungsten. The volume percentage of tungsten increases from left to right. That means here you have pure copper and here you have pure tungsten. So as you increase from copper to tungsten; if you take the modulus of elasticity of copper and plot it here, the modulus of elasticity of tungsten is here.

Tungsten is a stiffer material and you are embedding that in the copper matrix. As a result the composite modulus can increase along that line. And that line is the upper bound. Upper bound means that your composite cannot have a modulus that is higher than that line. For example, if I choose a 50-50 composite, that means 50% copper 50% tungsten, it is likely to have an upper bound value of about 240 GPa.

It is likely to have an upper bound value of about 240 GPa. Now that does not mean it will have 240, but it cannot have more than 240 is what the upper bound rule is trying to say. So how do we actually formulate these rules? And again there is also a lower limit. So in the upper bound, you typically say that the modulus is equal to the weighted or volume fraction average modulus. So Ec, the modulus of elasticity of the composite is equal to the volume fraction of the matrix (Vm) into the modulus of elasticity of the matrix (Em) plus volume fraction of the particulate ingredient (Vp) into modulus of the particle ingredient (Ep).

$$
E_c = V_m E_m + V_p E_p
$$

So here of course the matrix is copper and the particles are that of tungsten. So you just substitute and you will get your upper limit as far as the rule of mixtures goes.

Now of course there are several ways of looking at how you can produce composites with two different materials and estimate the engineering properties. For example the energy minimization approach is one more way to do this. But let's take a look little bit more closely what would be a

simple arrangement that will lead to the upper and lower bounds. We call them otherwise as parallel rules and series rules. Let us take a look at that briefly.

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So let's say we have a material which is combined like this. This is phase 1 and this is phase 2. A composite is being formed by mixing phases 1 and 2. And they are arranged in this kind of a fashion. In the second example we will consider the materials to be arranged like this 1, 2 and this is the direction of loading. So now what do we do here? So in this first case, if P is the load that is applied, how is that load going to be taken by the phases 1 and 2? And here in this case what is going to happen to that load?

We know that in the second case, this load P is equal to the load in phase 1 and that is equal to the load taken by phase 2. In the first case, $P = P_1 + P_2$ because they are connected in parallel whereas here they are connected in series. This is parallel, this is series. What about the strains? Now in parallel obviously the strains are going to be equal. So strain equal to strain 1 and that is equal to strain in 2.

$$
\varepsilon = \varepsilon_1 = \varepsilon_2
$$

What about the strain here? Strain is equal to $\varepsilon_1 + \varepsilon_2$, because each one is deforming separately. Although they are subjected to same load, they are getting deformed separately.

So now how do we estimate modulus? For that we will have to look at these relations $P = P_1 + P_2$ and $\epsilon = \epsilon_1 + \epsilon_2$.

What is load? Stress multiplied by area and that should be equal to $\sigma_1A_1 + \sigma_2A_2$.

$$
\sigma A = \sigma_1 A_1 + \sigma_2 A_2
$$

Now stress multiplied by area, stress is nothing but $\epsilon EA = \epsilon_1 E_1 A_1 + \epsilon_2 E_2 A_2$.

$$
\varepsilon EA = \varepsilon_1 E_1 A_1 + \varepsilon_2 E_2 A_2
$$

So let us just keep E here, that is equal to $(\epsilon_1 E_1 A_1$ divided by $\epsilon E) + (\epsilon_2 E_2 A_2$ divided by ϵE).

$$
E = \frac{\varepsilon_1 E_1 A_1}{\varepsilon A} + \frac{\varepsilon_2 E_2 A_2}{\varepsilon A}
$$

We just said the strains are equal right. $\epsilon = \epsilon_1 = \epsilon_2$. So you can cancel of these. Modulus of elasticity of composite is now equal to E_1A_1 by $A + E_2A_2$ by A.

$$
E = \frac{E_1 A_1}{A} + \frac{E_2 A_2}{A}
$$

That is nothing but E_1 into the area fraction of $1 + E_2$ into area fraction of 2.

$$
E = E_1 A f_1 + E_2 A f_2
$$

Now considering this in 3 dimensions, we can equate that to the volume fractions, E_1 volume fraction of $1 + E_2$ volume fraction of 2.

$$
E = E_1 V_1 + E_2 V_2
$$

And that is exactly what was there in the upper limit. In the upper limit of rule of mixtures, the composite modulus (E) is equal to the modulus of the first phase (E_1) into the volume fraction of that phase (V_1) plus the modulus of the second phase (E_2) into the volume fraction of the second phase (V_2) . And that is what we also got. We derived it out of a simple arrangement of the material.

Now of course this is just imagining that the materials are sitting right next to each other. In a composite it is not going to be like that. That's why the possible maximum is defined by this rule. But the possible minimum is defined by this sort of rule. Again let us just take a look at what that is.

Now let us consider this series case. Remember I had mentioned that strain equal to strain in 1 plus strain in 2. I am wrong there. You cannot equate strains. You have to equate the deformations. So delta, total deformation should be equal to $\Delta_1 + \Delta_2$.

$$
\Delta = \Delta_1 + \Delta_2
$$

You can only equate the deformations. The total deformation is equal to deformation of 1 and deformation of 2. You cannot say the same about strains. So, Δ_1 is nothing but E₁L₁ or ε_1L_1+ ϵ_2L_2 .

$$
\Delta = \varepsilon_1 L_1 + \varepsilon_2 L_2
$$

Just coming back to this, so the total deformations have to be the total deformation of 1 and 2 tougher have to add up to the deformation of the composite.

So the deformation of the composite is nothing but the strain in the composite multiplied but the length, that should be equal to strain1 into $L1 + \text{strain2}$ into $L2$.

$$
\epsilon L = \epsilon_1 L_1 + \epsilon_2 L_2
$$

So this one here is wrong, we cannot equate the sum of the strains to be the total strain of the composite. We can equate the sum of the deformations of the 2 materials to be equal to the deformation in the material. So when you get this again, keep ε to this side and take this as ε_1L_1 by $L + \varepsilon_2 L_2$ by L.

$$
\epsilon = \frac{\epsilon_1\,L_1}{L} + \frac{\epsilon_2 L_2}{L}
$$

Now epsilon itself obviously we are considering the material in its elastic state so that is sigma by E should be equal to σ_1 by E₁ into L₁ by L + σ_2 by E₂ into L₂ by L.

$$
\frac{\sigma}{E} = \frac{\sigma_1 L_1}{E_1 L} + \frac{\sigma_2 L_2}{E_2 L}
$$

So in this case we are assuming that we have unit area. Since loads are equal, the stresses are also equal. Since loads are equal, if you considering a unit area of cross section, the stresses will be equal since the loads are equal. So that means 1 by E now becomes 1 by E_1 into L_1 by $L + 1$ by E_2 into L_2 by L.

$$
\frac{1}{E} = \frac{L_1}{E_1 L} + \frac{L_2}{E_2 L}
$$

Now this L_1 by L and L_2 by L are nothing but the same as the volume fractions of phases 1 and 2. Because you take L_1 and multiply that by the unit area, you get the volume of 1. Take L_2 and multiply by the unit area, you get volume of 2.

So 1 by E here becomes V_1 over $E_1 + V_2$ over E_2 and that is exactly what the lower limit has been defined as. That is, one over the composite modulus is equal to the volume fraction of the first phase divided by modulus of the first phase plus volume fraction of second phase divided by modulus of second phase.

$$
\frac{1}{\mathrm{Ec}} = \frac{V_1}{\mathrm{E}_1} + \frac{V_2}{\mathrm{E}_2}
$$

Now this need not just apply only to the modulus. Even if you want to consider density of the materials, you can apply the same sort of a rule of mixtures.

But the real values will be somewhere in between these 2 bounds. The real values of the matrix will be somewhere what you actually determine by experiment you will see that they will lie in between these 2 bounds because the materials are obviously not arranged so nicely as what is shown here. In the parallel and the series cases, you do not have the materials correctly arranged just like that. So with simple elastic calculations we are able to determine how these materials will respond to the load.