Physico - Chemical, Mechanical and Electrical Properties of Polymers

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Lecture – 44
Properties of Composites

Hello, in this journey of understanding about polymeric materials. We are in sixth week, where we are focusing on properties and given that we have looked at so many polymeric systems of different kind, let us look at properties of composites in this lecture.

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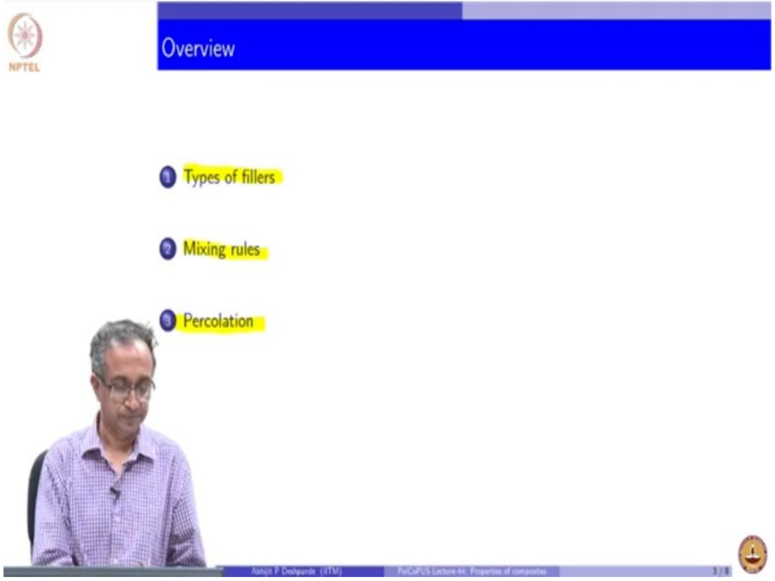

Overview

① Types of fillers
② Mixing rules
③ Percolation

And we will do this by first looking at what are the different types of fillers or reinforcements, which are used in these composite materials, because the type of fillers will determine the eventual properties of these material systems. And then we will look at some simple mixing rules which are guidelines to look at how the properties of a composite system depend on the constituent properties. And one of the important ideas related to percolation whenever we have a continuous network of filler being there in the system.

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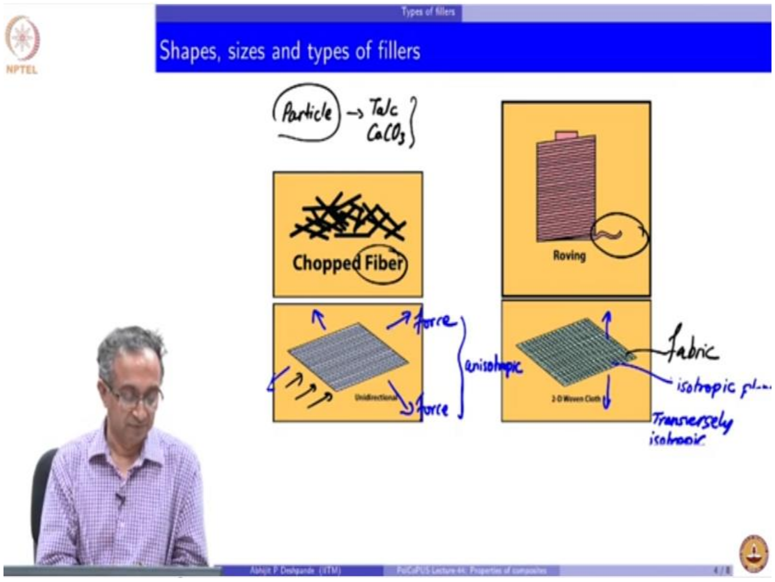

Types of fillers

Shapes, sizes and types of fillers

So, the examples of types of fillers that are used quite often we may use just the particulate filler itself and spherical particles or talc powder for example, this is a filler which is used talc or calcium carbonate. So, these are all particles which are used and quite often when we use particles, the purpose is to reduce cost. That is not always the case for example, when we add carbon black into a polymeric sample; it is to induce conductivity at times and so, there the specific role of carbon is to introduce a property into the material which is otherwise not there, in an insulating polymer a conducting carbon is added. But quite often particulate fillers are added as mineral fillers or fillers which can reduce cost, they of course, modify properties also stiffness can improve, modulus can improve, barrier properties can improve. However, it may also happen that strength may decrease depending on the specific interaction between the filler that is added and the polymeric material.

When we start increasing the aspect ratio of the fibre and we saw this already in earlier lecture, that ease of processing becomes less and less when we increase the aspect ratio of the filler, but property improvement is more and more when we add. So, for example, instead of adding a particle we could add a chopped fibre. So, many of the filled polymers chopped fibre is quite commonly added. We could use a roving, basically a fibre which can be taken off of a spool and then incorporated into a polymeric materials. We could use a unidirectional arrangement of the fibres or we could make a fabric out of the fibres and you can see that this is going to be anisotropic. If forces applied in this direction, the property is going to be very different compared to property in this direction.

So, therefore, this is going to be anisotropic material while this will be isotropic. However, what about the thickness direction? So, if I were to ask you the question that what will be the property in this direction. So, you can see that since again fibres if we stack different fabrics like this again the property in that direction is going to be because there is no fibre which is going to be oriented in that direction. So, these materials are called transversely isotropic, because they are isotropic in the plane alone, not in the thickness direction. So, these are different types of fillers which are incorporated and quite often rather than just taking them by themselves, we premix them with a polymeric material before they are used in a fabrication.

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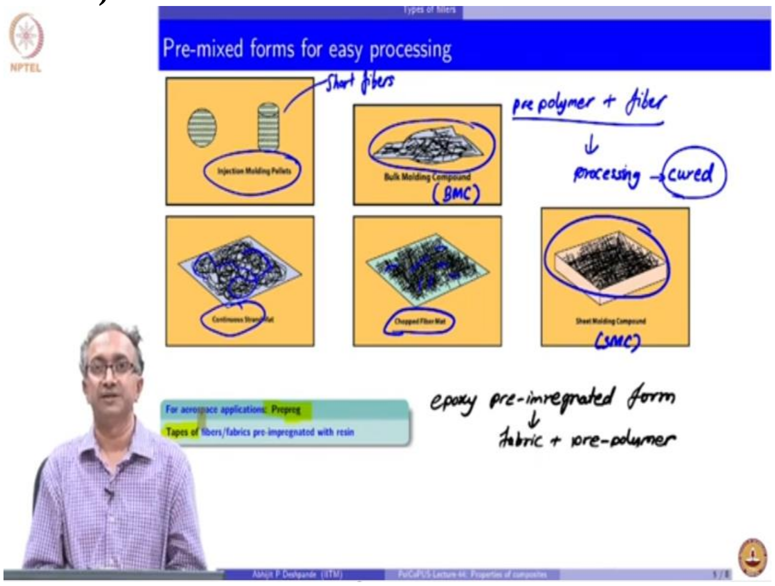

Types of fillers

Pre-mixed forms for easy processing

For aerospace applications: Prepreg

Tapes of fibers/fabrics pre-impregnated with resin

So, for example, with the short fibres, chopped fibres can be incorporated along with a thermoplastic material and then we can have injection molding pellets. So, instead of molding pellets of just a pure polymer we can have injection molding of these reinforced pellets and this is quite commonly done with glass fibre or a variety of other fibres. There are several other ways and especially, this is for thermosetting compounds, we can form a bulk molding compound or a sheet molding compound.

So, here again the pre-polymer plus fibre are mixed together and then during processing this mixture is cured. So, since it’s pre-polymer and fibre, then this can be molded, you can shape it and once shaping is finished, then you can induce curing in the material and therefore, curing can happen. Curing would imply basically higher temperature so that crosslinking reactions can take place. So, for thermosetting materials usually SMC or BMC as they are called are composite forms which are used. Thermoplastics on the other hand, one can impregnate with chopped fibre or a continuous strand mat, and as the name suggests, there is continuous fibre which is just everywhere and in this case, there are fibres which are located and these sheets then can be used to form the final part, you can stack multiple sheets on top of each other.

Each of these you can see that one of the important aspects is the length of the fibre as well as its orientation. Because these sheets for example, in the thickness direction is only if polymer which determines the properties, in the plane the fibres are there. So, therefore, most of these materials may end up being transversely isotropic as opposed to being isotropic in all 3 directions. And so, anisotropy is usually associated with reinforced materials such as composites.

One other common way of making polymer composite and this is especially true for aerospace for example, epoxy prepreg is nothing but a pre-impregnated form. So, the fabric as we saw earlier fabric is taken and so, fabric of a reinforcement plus epoxy pre polymer is added together and we prepare tapes of these materials and we can keep them as rolls. And, in fact, it is quite interesting to observe how complex parts such as aerospace wing, aeroplane wing or large parts which are required for aerospace applications are made, if you just search for prepreg hand layup, you will see that these prepregs are unrolled and then they are by hand laid on top of each other and then this whole assembly is put in the autoclave as we saw in an earlier lecture, and the autoclave can be size of rooms and bigger rooms and halls and things like that depending on the size of the part that is being cured. So, in all of these ease of processing is not there, because of these continuous fabrics which are there in the material. However, from a material performance point of view, excellent performance is obtained, because of the continuous fibres being present in such systems.

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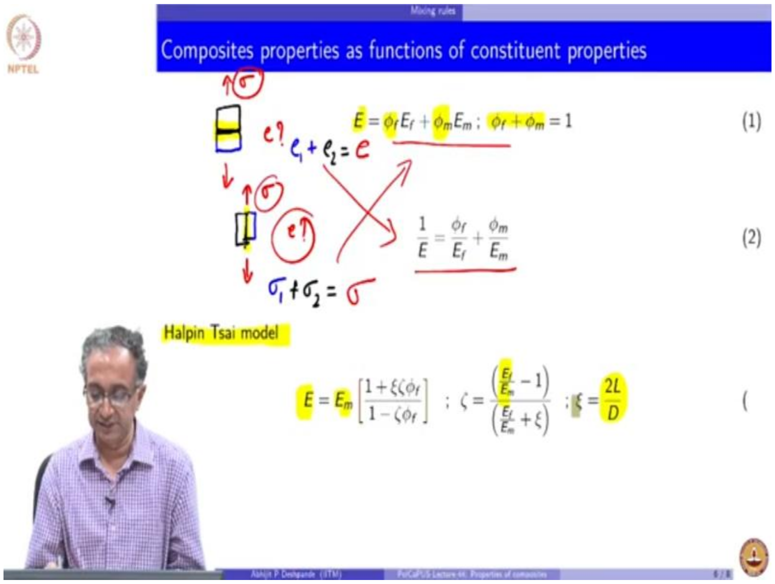

Mixing rules

Composites properties as functions of constituent properties

$$E=\phi_f E_f+\phi_m E_m\,;\ \phi_f+\phi_m=1 \tag{1}$$

$$\frac{1}{E}=\frac{\phi_f}{E_f}+\frac{\phi_m}{E_m} \tag{2}$$

Halpin Tsai model

$$E=E_m\left[\frac{1+\xi\zeta\phi_f}{1-\zeta\phi_f}\right]\ ;\ \zeta=\frac{\left(\frac{E_f}{E_m}-1\right)}{\left(\frac{E_f}{E_m}+\xi\right)}\ ;\ \xi=\frac{2L}{D} \quad ($$

So, what are the properties of composite once we mix the fibre and so, fibre and matrix are mixed in certain proportion with of course, the volume fraction of both of them summing to 1 and the modulus can be a rule of mixture where there is a parallel and then there is a serial addition of these. For example, if you have two materials, which are bonded to each other with a perfect bond, and then we are applying a force on this and the question is, what will be the strain in the material? So given that there is a stress in the material, what is the strain in the material? And we could have the same material combination in another way, this idea, we will see again later on when we look at models of viscoelasticity also. So here also if we apply sigma then what is the strain and this is again a perfect bond. So the bond surface is perfect in both cases. However, what will happen is in this case, it is the same sigma which is seen by both the materials while the strain in the two materials may be different, while in this case, it is going to be the same strain which is seen, but the stress in the two materials will be different. So, in this case, σ1 + σ2 will be equal to sigma, while in this case, we have e 1 + e 2 equal to the total strain. So, the series parallel combinations are what based on these mixing rules and can you try to say which one is parallel and which one is series?

$$E=\phi_f E_f+\phi_m E_m\,;\qquad \phi_f+\phi_m=1$$

$$\frac{1}{E}=\frac{\phi_f}{E_f}+\frac{\phi_m}{E_m}$$

$$e1+e2=e$$

$$\sigma 1+\sigma 2=\sigma$$

So, if you are able to look at the fact that strain sums up in one case and in other case, stress sums up, because stress is related to modulus times the strain. So, we can quickly see that, this is related to the mixing rule, while this is related to this mixing rule. And so, these mixing rules are guidelines by which we can try to analyze the response of a composite material. However, the mixing rules are very simplistic and there are several other models, which are present for example, Halpin Tsai model, which has been around for 2, 3 decades or even more, and where, depending on the aspect ratio of the fibre and depending on how the arrangement of these is, we can calculate the overall composite properties in terms of volume fraction and the aspect ratio of the filler.

$$E = E_m \left[\frac{1+\xi\zeta\phi_f}{1-\zeta\phi_f}\right] \quad ; \quad \zeta = \frac{(\frac{E_f}{E_m} - 1)}{(\frac{E_f}{E_m} + \xi)} \quad ; \xi = \frac{2L}{D}$$

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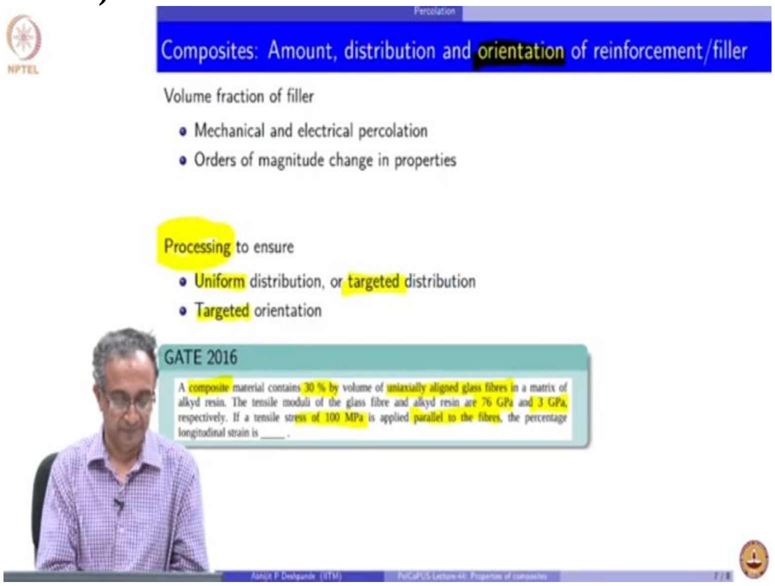

Percolation

Composites: Amount, distribution and orientation of reinforcement/filler

Volume fraction of filler

- Mechanical and electrical percolation
- Orders of magnitude change in properties

Processing to ensure

- Uniform distribution, or targeted distribution
- Targeted orientation

GATE 2016

A composite material contains 30 % by volume of uniaxially aligned glass fibres in a matrix of alkyd resin. The tensile moduli of the glass fibre and alkyd resin are 76 GPa and 3 GPa, respectively. If a tensile stress of 100 MPa is applied parallel to the fibres, the percentage longitudinal strain is _____ .

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One of the other things that we have to consider while looking at the properties of composites, one is amount which we have already discussed. So, higher the amount will lead to greater reinforcement. However, distribution of the filler is also equally important. When we are processing a polymeric part the fibres can get distributed differently and we can observe some regions where there is only polymer and some region where there is largely fibre and very less polymer. So, such possibilities will lead to a maldistribution of fibres and clearly properties will vary from point to point. Sometimes of course, this can be used as a tunability aspect. So, if we have a weaker part in our overall engineering design, we want more reinforcement, we could design the flow in such a way that fibres accumulate there, so, that there is strengthening of a weaker part. But, more importantly, what we need to understand here is there is a very good correspondence between how the filler is distributed and what is the property of the material.

So, not only do we need to know the overall amount of the filler, we need to also know its distribution and its orientation. And one of the aspects which is also important related to composite property is the idea of percolation. Whenever we add small amounts of filler, reinforcement is going to be not very high. As we start adding more and more filler, we reach percolation where fillers start touching each other.

So, for example, if we use let us say chopped fibres in a sample, so, let us say we are preparing a composite sample and we use some chopped fibre if we use them in low percentage, you can see that all the fibres are not interacting with each other and we say that percolation limit is not reached. However, if I increase the percentage of these fillers and then what happens is again they are randomly oriented. But now there is a percolating network of these fibres.

Now if these fibres are conducting while the polymer is not, then we can in fact reach electrical percolation. These fibres certainly will carry the load more than the matrix and therefore mechanical percolation is also reached. So by measuring modulus, by measuring conductivity we can also find out whether a percolation is there. And one of the reasons for percolation to be important let us say for example, for conductivity is the fact that conductivity as a function of volume fraction can increase order of magnitude.

So this can be 7 orders of magnitude or even higher. Can you guess why that is the case because if let us say there is 0 volume fraction of the filler, then basically the material is insulating and conductivity will be 10^{-7}, which is 10^{-10} or 10^{-14} and once carbon is added which starts connecting with each other let us say a nanotube is added or a graphene sheet is added or any other fibre which is conducting is added then what we have is electrical percolation and then conductivity can increase all the way up to 10^{2}. So, we have not just 7 to 10, 12 orders of magnitude of change of this conductivity. So, one idea associated with percolation is this orders of magnitude change in properties. And so, whenever we reach these phenomena of percolation, this kind of significant change in properties is observed and this is done this is also observed for many composites materials.

The other key therefore is, processing technique has to ensure that we either achieve uniform distribution or targeted distribution. So, as I mentioned, if we want a certain part of the polymeric part which is thin and it needs to be strengthened, we can design it in such a way that it may have higher fraction of fibres, but then this target distribution has to be achieved using the processing technique and the flow rates and whatever molding conditions temperature pressure we are using.

And just to look at the load carrying capacity that we have been talking about, so, if a composite material will consist of 30% by uniaxially aligned class fibres; so, clear that orientation is very important and the fibre properties and the matrix properties are given and then if you apply 100 MPa parallel to the fibres. So, depending on the mixing rule that we discussed on the previous slide, we can then evaluate the strain which is there in this material.

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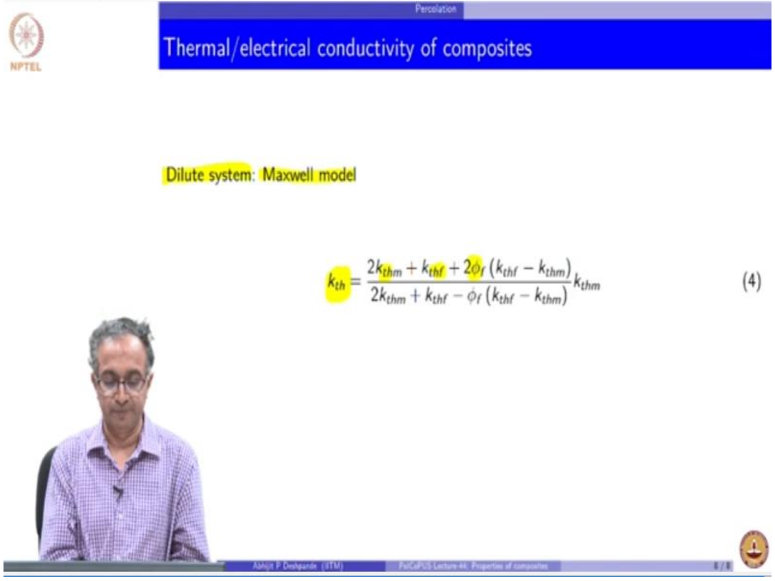

Percolation

Thermal/electrical conductivity of composites

Dilute system: Maxwell model

$$k_{th} = \frac{2k_{thm} + k_{thf} + 2\phi_f\left(k_{thf} - k_{thm}\right)}{2k_{thm} + k_{thf} - \phi_f\left(k_{thf} - k_{thm}\right)} k_{thm} \quad (4)$$

The other aspect of composite material performance is related to electrical or thermal conductivity as we have discussed and here again the model which is used for a very dilute system is related to Maxwell development, where the conductivity of fibre and matrix is related to the overall thermal conductivity of the composite. So, depending on the fibre volume fraction, the filler volume fraction this can vary and it this is again the simplest possible model to estimate electrical or thermal conductivity in the material.

And there are more complex inter empirical and semi empirical relations which are also used by different practitioners of polymeric composite industry.

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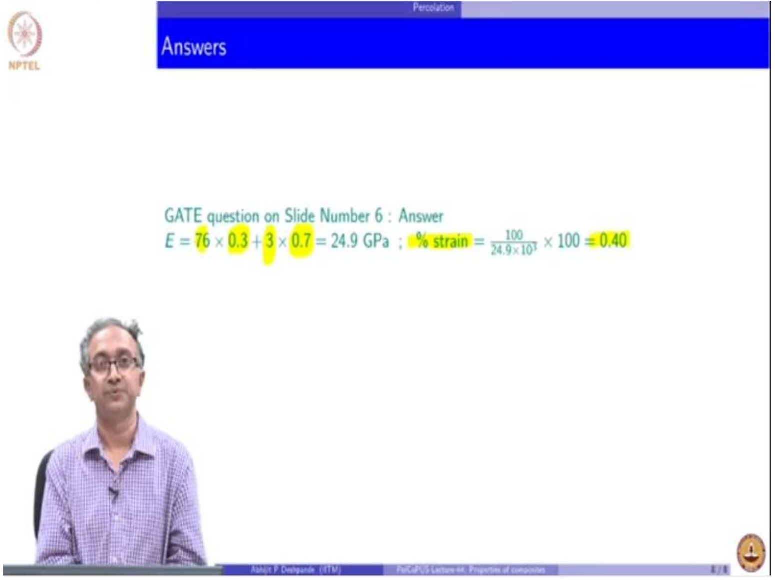

Percolation

Answers

GATE question on Slide Number 6 : Answer

$E = 76 \times 0.3 + 3 \times 0.7 = 24.9$ GPa ; % strain $= \frac{100}{24.9 \times 10^3} \times 100 = 0.40$

So, with this, I am sure you can, looking at the mixing rule, calculate the overall percentage strain that is possible. And it just depends on what is the volume fraction 0.3 and 0.7 that is added and the properties of matrix and the fibre. So, with this we will close this lecture, and we will continue our journey for exploring more properties of polymers in a lecture later on. Thank you.