PolCoPUS
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Lecture No -54
Properties of blends

Hello, welcome to another week of classes. In this eighth week, we are looking at viscoelasticity in polymers and we will focus on the blends, some example properties that are relevant.

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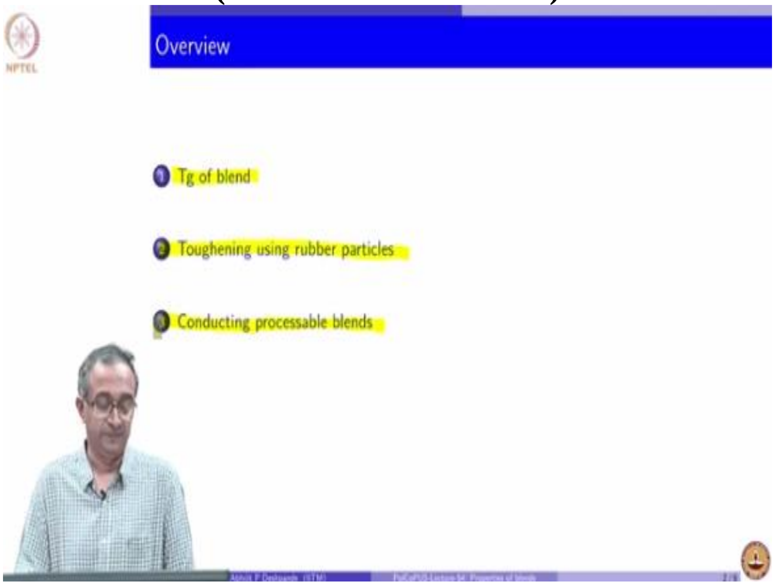

Overview

1. Tg of blend
2. Toughening using rubber particles
3. Conducting processable blends

By looking at first glass transition of the blend itself and how it varies as a function of whether it is partially miscible or completely miscible. And then an important aspect during impact strengths discussion, we did discuss related to the toughening that happens due to addition of rubber particles. So again, we will take a closer look at some of the properties that change when you do rubber particle addition.

In this case for example an epoxy. And similarly the blending is also done for introducing conductivity as a property which may not be there in one of the polymers. So you can make a conducting blend by incorporating a conducting polymer in a non-conducting polymer.

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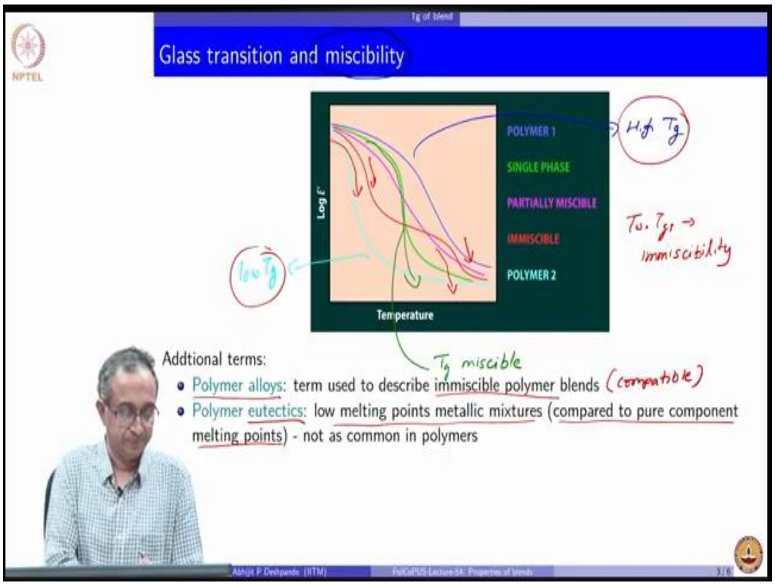

Glass transition and miscibility

Addtional terms:

- Polymer alloys: term used to describe immiscible polymer blends (compatible)
- Polymer eutectics: low melting points metallic mixtures (compared to pure component melting points) - not as common in polymers

So, let us look at glass transition and miscibility. So glass transition measurement is a very good way of determining the miscibility and this could be done by measuring either the E' as it is shown here the glass modulus changes when material undergoes glass transition. We could also measure it using DSC and where we measure the glass transition as a step change in the heat flow curve as discussed earlier.

So polymer 1, for example, has variation and it has a higher glass transition temperature. So this has a high Tg. And on the other hand, the other polymer has a lower Tg. And the 2 polymers therefore are mixed to get a tunable Tg which is in between. But how does the glass transition for the blend behave? And that depends on whether it is miscible or immiscible or partially miscible. And if we recall that; glass transition is associated with segmental mobility, segmental flexibility.

So if they are molecularly mixed, then what happens is segmental mobility of one macromolecule affects the segmental mobility of other molecule because they are molecularly interacting and exchanging interactions. So, in that case, we get the single change and the glass transition will be somewhere in between. So this is the Tg which is in between the Tg of the pure polymers but it is miscible.

So if we observe a single glass transition that is a good indication of miscibility of the polymeric blend system. On the other hand, if they are immiscible then what we will is there will be a decrease associated with segmental mobility changing for one polymer which is the low Tg polymer. So if we increase the temperature further then what happens is we will observe another decrease in the E'.

Because segmental mobility again increases, but this time of the polymer which has a higher glass transition and again e prime undergoes a change. So, therefore these 2 steps, first and second, indicate that we have an immiscible blend. So, 2 Tgs implies immiscibility. And in between if there are partially miscible then we can have more complex variation also. So, of course, we have already said also that alloys are generally for immiscible polymer blends, but which are compatibilized.

So there is some compatible interaction at the interface of these immiscible polymer blends. There is also a term eutectics used in which case it is basically term derives from the low melting points metallic mixtures which are formed because the melting point is low compared to the pure component melting points itself. Generally though this is not observed, there are very few polymeric systems which show this eutectic behaviour.

However, in many textbooks and many syllabi you will see some mentioned related to polymer eutectics, but generally blends and alloys are what is used. Blend is in fact a term which is broad which just implies mixture of polymers. Because there are alloys in metallic domains, sometimes compatibilized blends are also referred to as alloys.

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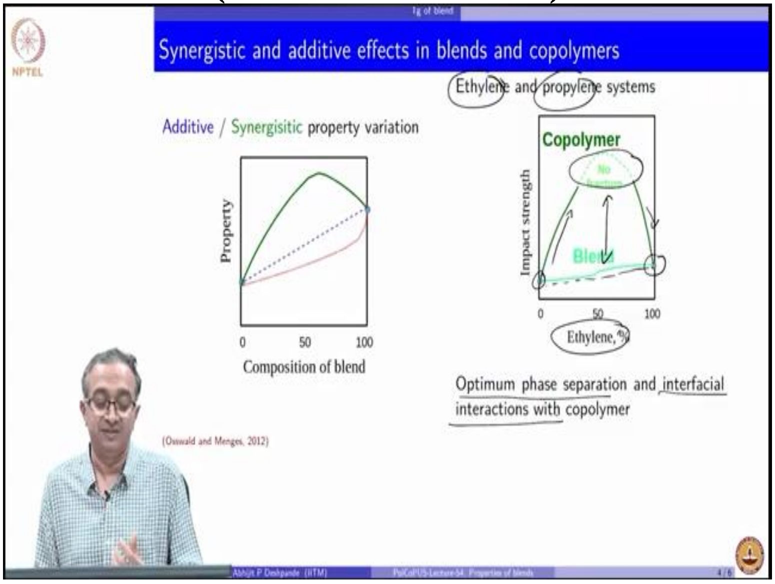

Tg of blend

Synergistic and additive effects in blends and copolymers

Ethylene and propylene systems

Additive / Synergisitic property variation

Optimum phase separation and interfacial interactions with copolymer

(Osswald and Menges, 2012)

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So let us look at the properties of blends from another point of view and contrast it with copolymers because in the end homo-polymers can be combined to covalent bonding into copolymer or homo-polymers can be mixed together to form a blend. So is there any difference? And while we want to look at this it might be useful for us to just classify, what is the property of the blend or copolymer in relation to property of the pure substance.

So, for example, when we think in terms of composition of the blend, we are going from very low let us say value of a property to a high property. So whenever it is 100% one particular component, the property is high. When it is 0, which means the other component 100%, then the property is low. So what is the variation when we change the composition? And the blue line here is basically just a pure additive.

So if I do 50-50, the property will be exactly in between the 2. If I do 25-75, the property will be closer to 1 component and so on. So, this is just a linear addition of 2 properties together. However, what we could also observe is a trend in which we have a property which is much higher than the pure components. And then we call it a synergistic property variation. Of course, we could also have a variation which is much more less than the 2.

And then in that case we could have for example a variation which is given by a very different, for example this. And so you could have a very negative variation based on how the micro structure and other features of the overall plane systems are. Our interest more often than not will be to get synergistic properties. So that we get properties which are better than the 2 components we are adding.

Quite often we should at least get the additive properties which again will be useful from a certain point of view. So now let us look at what happens in case of a specific system which is, let us say this ethylene propylene system. So we have ethylene and propylene and we could form a blend of it and the blend variations of ethylene propylene are not very different in terms of their impact strength.

And so the variation between of the blend also is pretty much small because given that their impact strength are not very different compared to each other. Any blend that you make you will get similar impact strength. And so there is no synergism when ethylene and propylene blends are made. But look at what happens when you make a copolymer of ethylene and propylene. So in fact the impact strength goes up very significantly as you start adding more and more ethylene.

But if you add too much ethylene then again the impact strength goes down. So somewhere in between in fact there is no fracture also. So the material is so much rubber like, an elastomeric like that there is no fracture also observed. So impacts on cannot be measured also under those such situations. That is the influence that synergistic variation can have on the property and some of this is not possible to be guessed without knowing about what is happening at a macromolecular and microstructural level.

So can you think of what is it about the polyethylene polypropylene blend that is so different compared to a copolymer? And somewhere around 50-50 copolymer is completely different compared to the 50-50 blend and why is that the case? And why does it happen for ethylene propylene case? So in this case what you will have to think is in terms of polyethylene polypropylene miscibility.

How do they phase separate, what kind of domains do they form, each of these domains how do they respond to an impact loading? Why is it useful to have polypropylene domains in equal measure as ethylene domains and which plays the role of a crack arrester in case of impact strength, which plays the role of energy absorption in case of impact strength? Because you need both of these features for impacts strength to be very high.

If the material is only energy absorbing, then it may not also again have a very good impact and if the material is only crack arresting, it may not have enough impactions. You need both of these features for the impact strength to be very high. So what in the end we have is optimum phase separation and interfacial interactions between the phase separated domains that gives us this very synergistic improvement in properties.

And that is why ethylene propylene copolymers are used quite often in terms of their impact resistance properties.

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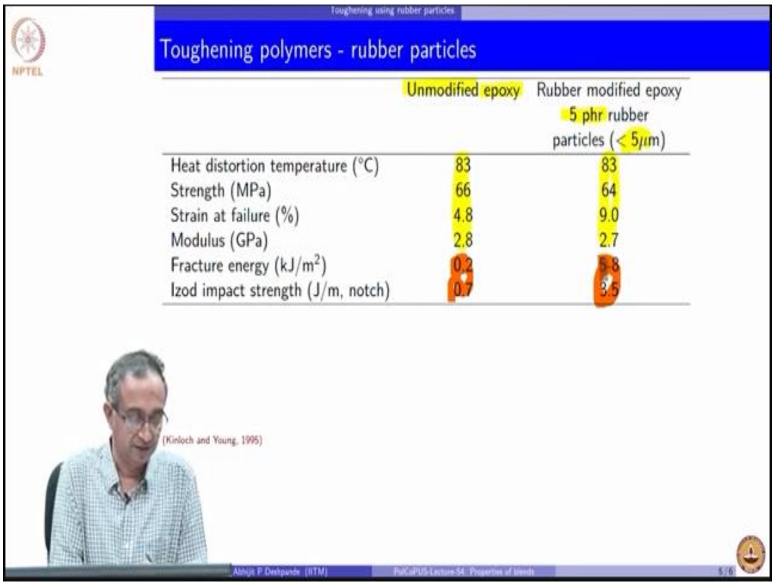

Toughening polymers - rubber particles

	Unmodified epoxy	Rubber modified epoxy 5 phr rubber particles (< 5μm)
Heat distortion temperature (°C)	83	83
Strength (MPa)	66	64
Strain at failure (%)	4.8	9.0
Modulus (GPa)	2.8	2.7
Fracture energy (kJ/m^2)	0.2	5.8
Izod impact strength (J/m, notch)	0.7	3.5

(Kinloch and Young, 1995)

Looking at the addition of rubber particles to many of the material systems, we already saw an example of high impact polystyrene where rubber particles are added. In this case let us look at epoxy. So if we have unmodified epoxy, then you can see that the properties are not very different compared to rubber toughened epoxy. And in this case 5 per 100 rubber particles are added and of a given size.

And but what you can notice is the difference which is there in terms of the impact properties. You can see significant improvement in the impact properties. So therefore toughened epoxy in this case can give you an immediate advantage in terms of impact resistance compared to the unmodified epoxy. And that is the purpose of adding and blending rubber particles in materials such as epoxy.

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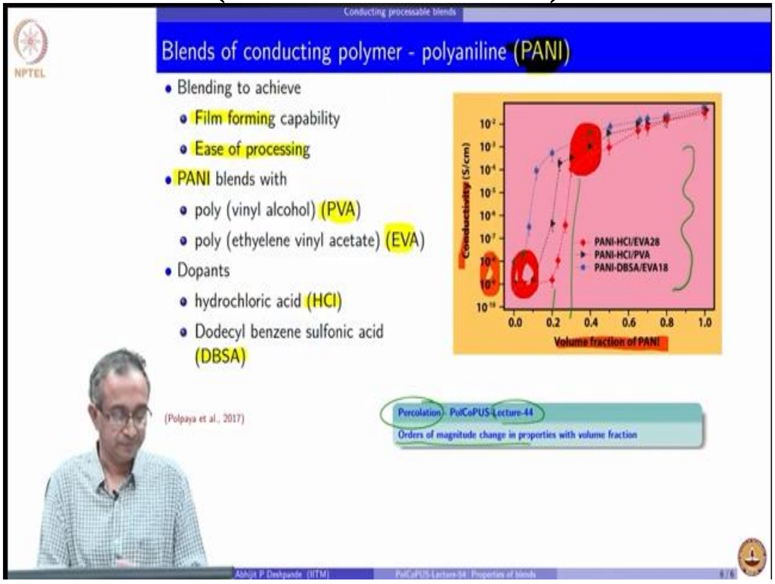

Blends of conducting polymer - polyaniline (PANI)

- Blending to achieve
  - Film forming capability
  - Ease of processing
- PANI blends with
  - poly (vinyl alcohol) (PVA)
  - poly (ethyelene vinyl acetate) (EVA)
- Dopants
  - hydrochloric acid (HCl)
  - Dodecyl benzene sulfonic acid (DBSA)

(Polpaya et al., 2017)

Percolation PolCoPUS-Lecture-44
Orders of magnitude change in properties with volume fraction

We will finish this lecture by looking at another example of blend where the electrical conductivity is of interest. And this is a blend of polyaniline which we have already seen as an example of conducting polymer. But this material is not very easy to handle, very easy to process because the film forming may not be very easy. You may form very brittle films which are not easy to use.

Also processing may be very difficult because solubility of PANI which solvents it is soluble and things like that. So given this can we blend a conducting polymer which is very useful for certain sensor actuator, semiconductor applications. But we cannot use it because of processing difficulties as well as film forming capabilities limited. So you can blend PANI, in this case what we will look at are examples of blend of PANI with 2 insulating polymers.

So both polyvinyl alcohol and ethylene vinyl acetate are being incorporated in the blend because of their flexibility and mechanical performance and film forming capability and ease of processing. Well PANI is the material which gives us the conductivity. But because its processability is difficult and because its film forming capability is poor, we need to blend the 2. And of course in conducting polymers we also use the dopants.

So therefore different types of dopants can be used and what is shown here is conductivity as a function of volume fraction of PANI, the polyaniline which is being added. And at low volume fraction, of course conductivity is very small. This is insulator basically. If you recall 10^{-7} and lower values are insulators. So this is mostly ethylene vinyl acetate, EVA as it is called or PVA, polyvinyl alcohol properties where the conductivity is very low.

But look at how the conductivity varies as we keep on adding more and more polyaniline. And what is remarkable about such blends is by the time we add about 30-40 % of polyaniline, we get conductivity which is in the semiconducting range. So that; this material can be used for a sensor or actuator or any such application. So we do not need to use 100% polyaniline because in that case it is difficult to process it.

But we can use 20-30% polymer, conducting polymer in this case and still get a conductivity which is acceptable for a given application. And what you notice in this case is the orders of magnitude change in conductivity with small amount of volume fraction. You can go from 0.2 to 0.25 or 0.3 and there is 6 orders of magnitude increase in conductivity. And immediately you should recall that what we are discussed in lecture 44, this is the percolation.

So polyaniline is distributed throughout PVA and EVA phase but beyond a certain volume fraction all these get interconnected and a percolation is reached and therefore conductivity increases very significantly. And now since its polyaniline domains which are all connected to each other, conductivity is very close to bulk conductivity and that is what is the phenomenon of percolation which is very synonymous with orders of magnitude change in properties with volume fraction.

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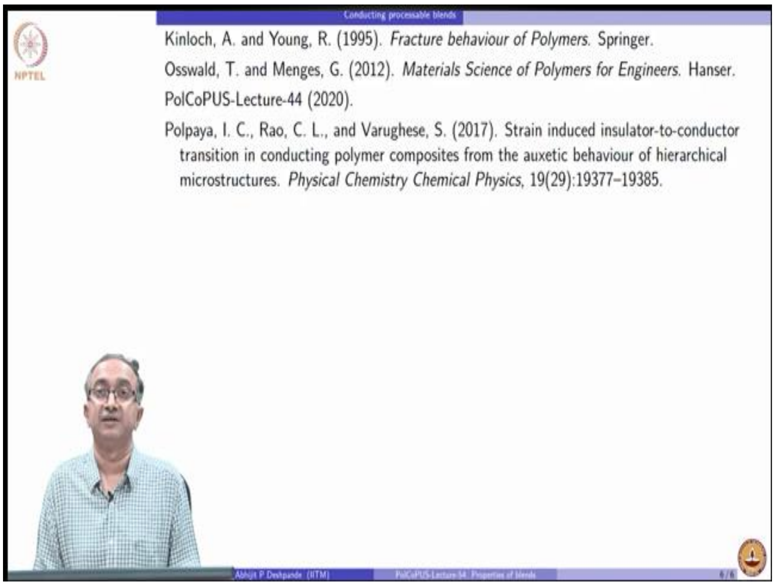

Conducting processable blends

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So with this we come to end of this discussion related to properties of blends. We took a look at mechanical as well as we took a look at some electrical conductivity property. And with this we close the lecture, thank you.