Polymers: Concepts, Properties, Uses and Sustainability
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Week 9
Interaction of Polymers with Other Materials

Lecture-62
Compatibilizers

Hello, welcome to the course on polymers, in this week we are discussing interaction of polymers with other materials and also we are focusing on the interfaces in case of macromolecular systems and compatibilizers are important sets of materials which are essential in terms of designing an overall polymeric system and especially we discussed so many different types of polymeric materials where we do mixing of different components. So, we mix different polymers in blends or we mix another substance with the polymer to form composites and compatibilizer is added to make sure that the interaction at the interface between macromolecular systems is optimized. So, that we get the requisite performance. So, the emphasis will be on uses of these compatibilizers.

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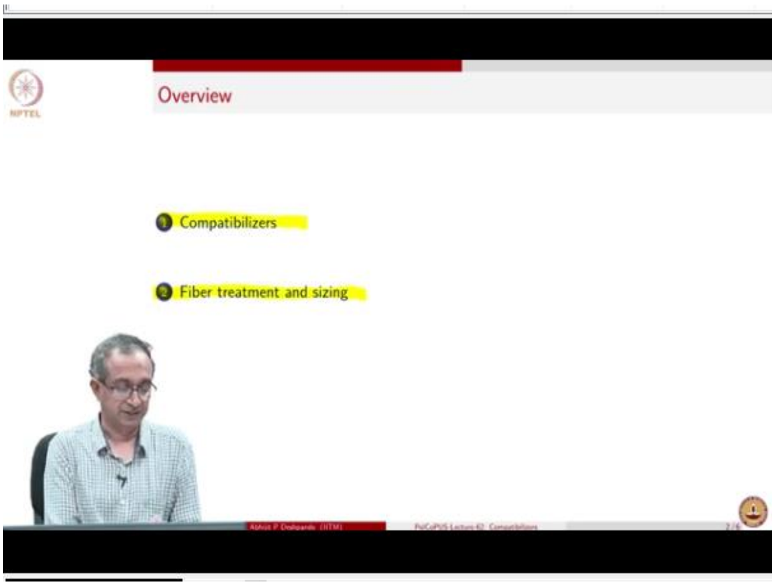

Overview

1. Compatibilizers
2. Fiber treatment and sizing

We will look at what are the different types of compatibilizers and also we will see this compatibilizer in case of composite materials.

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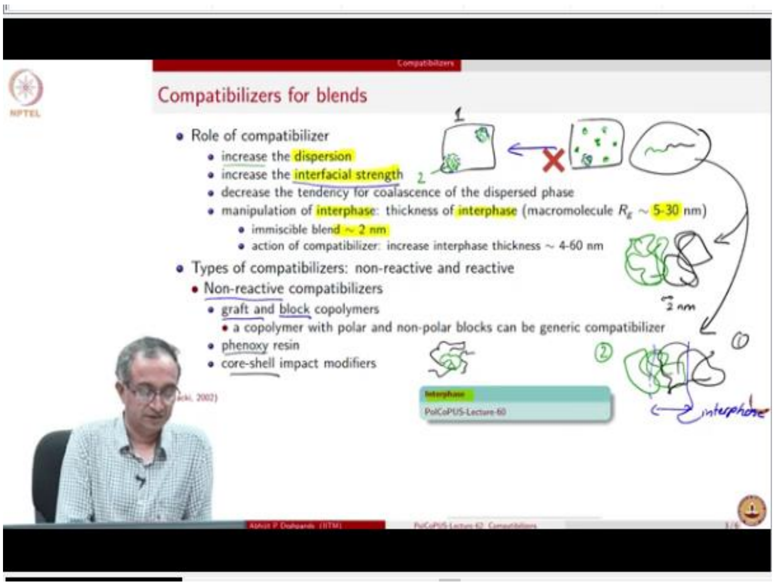

Compatibilizers

Compatibilizers for blends

- Role of compatibilizer
  - increase the dispersion
  - increase the interfacial strength
  - decrease the tendency for coalascence of the dispersed phase
  - manipulation of interphase: thickness of interphase (macromolecule $R_g \sim 5\text{-}30$ nm)
    - immiscible blend ~ 2 nm
    - action of compatibilizer: increase interphase thickness ~ 4-60 nm
- Types of compatibilizers: non-reactive and reactive
  - Non-reactive compatibilizers
    - graft and block copolymers
      - a copolymer with polar and non-polar blocks can be generic compatibilizer
    - phenoxy resin
    - core-shell impact modifiers

cki, 2002)

Interphase

PolCoPUS-Lecture-60

So, compatibilizers for blends as far as they are concerned their main role is to increase the dispersion. So, if 2 macromolecules are not miscible, if 2 polymer systems are not miscible, then the tendency will be for them to form layered materials. But what we want quite often is dispersion of one component in another and therefore when we say increase the dispersion what we imply is that the both the polymers are as well mixed as possible. So, for example if we are talking about a polymer which is represented by the black where let us say the all the macromolecules are and in that we have now domain of the second macromolecule which is depicted in green here. So, if this is the kind of distribution then there are lots of pockets where there is only polymer 1 while what we would like is actually the polymer 1 and 2 to be as well mixed as possible.

Since these are immiscible polymers they are not going to macromolecularly mix. So, therefore if we want to increase the dispersion what we mean by that is when we have a situation where we will have lots of smaller domains of the second macromolecule in the first macromolecule and so we increase the dispersion to obtain good homogenized system where properties may be better. We can also increase the interfacial strength because there is an interface which is involved here and we would like at the interface properties to be not the weakest. Generally interface is a surface of heterogeneity, on one side is one macromolecule, on the other side is other macromolecule. So, will it be the weakest link in this overall material system? So, can we increase the interfacial strength?

And then even if let us say we have done this dispersion and we have got good domains which are distributed everywhere there is a possibility that the different distributed domains can coalesce, they can come together and again come. So, this is something which we would like to avoid. So, that it should not go back to larger domains. So, whatever is the control domain we want the material should stay in that particular size domains.

So, these are all the features where we are trying to manipulate the overall distribution of one component in the other and trying to enhance the interfacial strength. Generally this involves manipulation of the interface and we have discussed about this interface in 60th lecture where we were discussing macromolecules at interfaces. So, the thickness of interface generally is about 2 nanometers between 2 immiscible phases or immiscible macromolecular systems. Now if you look at the size of the macromolecule itself that is sufficiently large. So, the interface then if it is only 2 nanometer it implies that there is a very stark boundary between the 2 macromolecules. But if the interface region is larger then what happens is that implies that the 2 macromolecules are interacting favorably with each other. So, that there is a gradual transition between molecule 1 and molecule 2. So, just to depict this what we are trying to say is that if we have let us say micromolecule 1 and then there is another macromolecule if you have an interface which is very small let us say 2 nanometer then there is hardly any interaction between these 2 macromolecules. But we could have a system where we have some amount of inter penetration between these 2 different molecules.

So, on one side is of course polymer which is 2 and on the other side is polymer 1 but what we also have is an inter phase region which is significantly large, where both the molecules are there and this interface needs to be maximized if we want good interactions between these 2 macromolecules and so the type of species which can play this role belong to both reactive and non-reactive category.

So, let us just look at non-reactive compatibilizers first, block copolymers or graft copolymers are quite popular. What that does is, if you if I make a block copolymer which looks something like this. So, I have a green macromolecule of block and then I have the black. So, you can see that if I add this molecule in such a mixture then what I can do is, this green macromolecule part will be in the green polymer domain and the black part will be in the black domain. So, effectively now I have a molecule which is connecting both of the domains and this will naturally lead to an increase in interfacial strength. There are some other materials also like phenoxy resins which are useful. We can also make the polymer particles which are from the point of view of core and shell. So, for example we could have a core where the green macromolecules are and the surrounding is the black micromolecules.

So, when we add such a substance then what we will have is a mixture where we are compatibilizing based on the black macromolecules which are available on the surface of such impact modifier particle.

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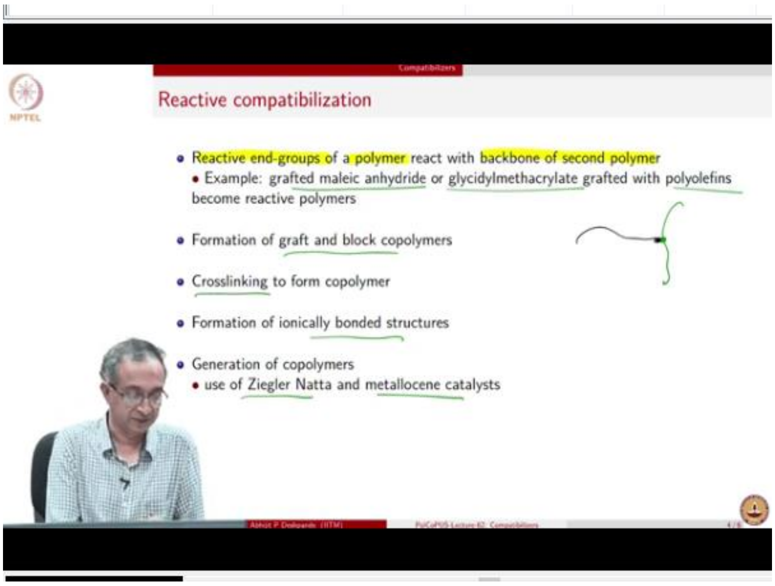
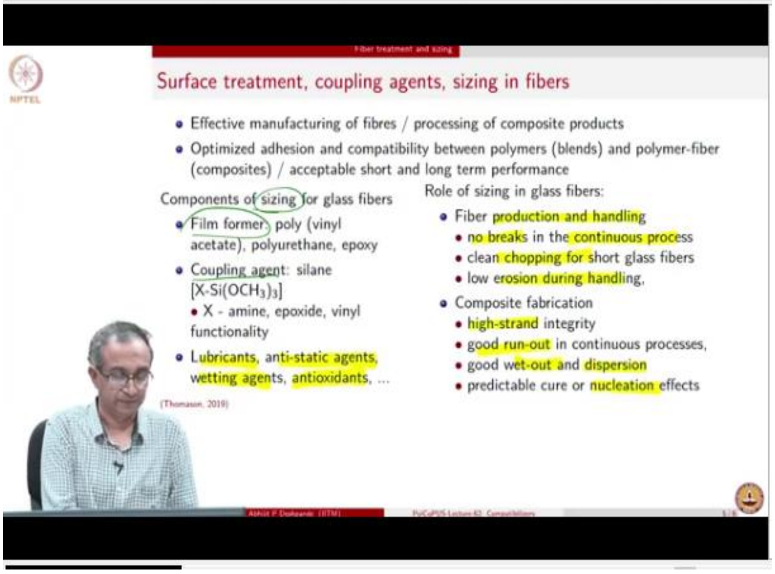


Reactive compatibilization

- Reactive end-groups of a polymer react with backbone of second polymer
  - Example: grafted maleic anhydride or glycidylmethacrylate grafted with polyolefins become reactive polymers
- Formation of graft and block copolymers
- Crosslinking to form copolymer
- Formation of ionically bonded structures
- Generation of copolymers
  - use of Ziegler Natta and metallocene catalysts

Reactive compatibilizer on the other hand reacts with one or both of the macromolecules. So, for example a macromolecule can have reactive end groups and that can react with backbone of a second polymer. So, then what we are doing is we are connecting. So, a macromolecule its end group is reacting to the backbone of another molecule and so this way we establish connections between different macromolecular systems. And grafted maleic anhydride or GMA as it is called glycidyl methacrylate are quite common examples for polyolefinic systems. Again graft and block copolymers if they can be formed by reactions then they will act very well as a set of compatibilizer which are reactive. We could also just form cross linking or we can also induced ionically bonded systems, generally we could also have use some catalyst and then generate some copolymers by having a block of 1 polymer react with block of another polymer. So, these are all reactive schemes by which we can improve the compatibility between the 2 macromolecular system. **(Refer Slide Time: 08:32)**



Fiber treatment and sizing

Surface treatment, coupling agents, sizing in fibers

- Effective manufacturing of fibres / processing of composite products
- Optimized adhesion and compatibility between polymers (blends) and polymer-fiber (composites) / acceptable short and long term performance

Components of sizing for glass fibers

- Film former: poly (vinyl acetate), polyurethane, epoxy
- Coupling agent: silane [$X\text{-}Si(OCH_3)_3$]
  - X - amine, epoxide, vinyl functionality
- Lubricants, anti-static agents, wetting agents, antioxidants, ...

(Thomason, 2019)

Role of sizing in glass fibers:

- Fiber production and handling
  - no breaks in the continuous process
  - clean chopping for short glass fibers
  - low erosion during handling,
- Composite fabrication
  - high-strand integrity
  - good run-out in continuous processes,
  - good wet-out and dispersion
  - predictable cure or nucleation effects

As far as composites is concerned we have now a fiber surface which could be glass or kevlar and then a matrix surface which could be epoxy or nylon or polyester or bismaleimide as we discussed related to the aerospace applications. So, we have plethora fibers available and lots of polymers which can be incorporated in a polymer composite. So, given that we are incorporating fiber and as we also discussed that the fiber size has to be smaller. So, that defects are minimized, but at the same time handleability of fibers is also an issue. So, generally few microns is what is used but along with the fibers what we do is surface treatment, we can add coupling agents or what is called sizing can be applied on the fibers.

And the overall goal of such idea is to improve adhesion and compatibility between polymer and the polymer fiber. So, that we have acceptable short term and long term performance. So, generally what does the sizing contain? So, it generally will contain a film former. So, that it can spread nicely on the fiber surface and then each spot on the fiber surface can interact with the polymer as soon as the polymer and the fiber surface come into contact with each other.

We can also add some coupling agent which reacts with the fiber and they have some compatible groups which will interact with the polymer and of course because the fibers are handled in large industrial settings generally we can also add several of these lubricants and antistatic agents, wetting agents to improve the performance of the fibrous systems.

And so the sizing plays an important role not only during fiber production itself it plays a role during composite manufacturing also. So, during fiber production itself basically if we have sized fiber then it does not break very often. So, there are no breakages when we use continuous process to wind these fibers and also when we do chopping and cutting for the various different applications the sizing has a very important role not just during composite manufacturing but it also has a role during fiber production itself. Because in the end these fibers are performing a very important role of reinforcing the overall polymeric composite and their performance is very crucial to the performance of composite. So, during fiber production we need to make sure that there are no breaks in the continuous process, whenever fiber is being manufactured if there is a breakage of fiber involved that will lead to loss of production time.

So, generally fiber production as handling is improved when we apply these sizings, where there is a nice film former, there is a coupling agent and there are lubrication and anti-static agents, then they perform the role of making sure that fiber does not break very easily. Many times we will use short glass fibers, in that case the chopping should be clean. So, that again the adhesion between the polymer and the fiber is good if there are such surfaces and also we can minimize the erosion during handling.

On the other side when we go to composite production then we need to make sure that when these fibers are woven together in yarn or they are used as single strands. So, they need to be well defined and also not have erosion and other properties. So, therefore high strand integrity is enforced if we apply sizing. We will have very nice production process where fibers can flow very easily because of these wetting agents and lubricants which are added. And these fibers which have to flow out of a spool and get wound on different other rollers and when they have to slide across different solid surfaces, all of that can be done and there will be a good run out. Also we want matrix, the polymer which is being mixed which could be a pre-polymer epoxy resin or it could be a thermoplastic melt, such as nylon, it needs to actually spread very nicely on the fiber. And so there is a good wet out, as we saw that contact angle, if the contact angle is very low that means liquid will spread over. So, in this case also sizing will ensure that polymer will spread over the fiber and so good wet out and dispersion are also very crucial and then one other important role that the foreign surfaces like fibers play is modify what is the nucleation spots available for phase separation to happen? So, crystallization in the presence of fiber where fibrous surface acts as nucleation points or nucleation density increases because fibers are there will lead to very different morphology compared to when the crystallization is done without the fibers themselves. So, therefore we would want the fiber to give predictable nucleation effect. Similarly the reactions that go on in polymer system can be affected due to presence of fiber, one because may be fibers have some reacting groups and they themselves also take part in reaction.

Or fibers could also change the diffusion coefficients of small molecule which are diffusing through the macromolecular network, because diffusing molecules will not be able to diffuse through fiber most of the time. So, they will have to go around the fibers or the thermal conductivity of the composite may change because of the presence of the fiber and therefore heat transfer and temperature distribution may change.

So, therefore in general whenever we add fiber we want excellent wetting of polymeric matrix on the fibers and whatever is the role fiber is playing during composite manufacturing we need to be able to do a good prediction of it in terms of what is the effect on curing process as well as on the crystallization process?

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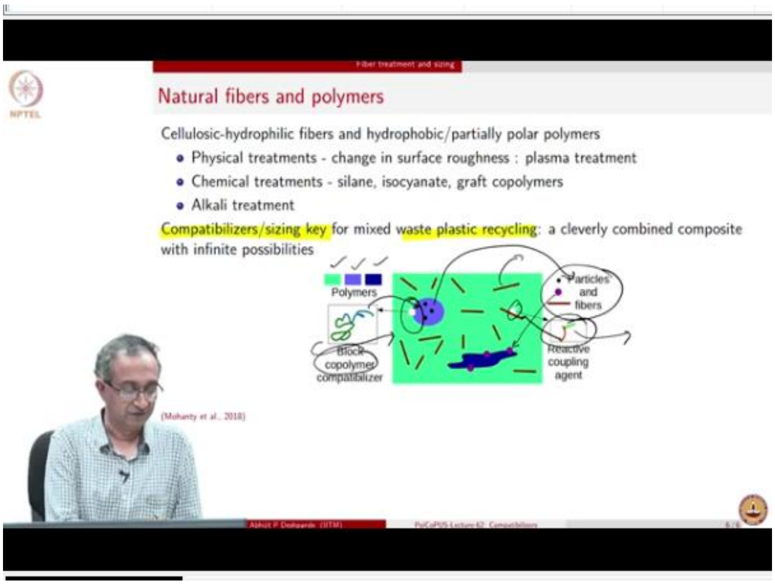

Natural fibers and polymers

Cellulosic-hydrophilic fibers and hydrophobic/partially polar polymers

- Physical treatments - change in surface roughness : plasma treatment
- Chemical treatments - silane, isocyanate, graft copolymers
- Alkali treatment

Compatibilizers/sizing key for mixed waste plastic recycling: a cleverly combined composite with infinite possibilities

So, one last issue that we will discuss in this lecture is related to what happens when we are using natural fibers and as we have seen that jute, sisal, coir, pineapple so many different types of natural fibers are being used in what are called bio composites these days and given that many of these natural fibers are hydroscopic as well as hydrophilic materials while many polymers are hydrocarbon materials and hydrophobic materials. So, how do we do compatibilization and sizing in case of such systems? So, generally as I said cellulosic hydrophilic polymers and hydrophobic partially polar polymers how do we compatibilize them? So, generally we can do physical treatment of the fiber which can change the surface roughness you can also do plasma treatment. So, all of these are basically influencing the surface of the natural fiber.

So, that better interaction between polymer matrix and natural fiber can occur. We can also modify the surface by again adding a coupling agent which could be either a copolymer or it could be a silane or we could also do alkali treatment because cellulose and lignin have different response to acid medium as well as alkali medium. So, by doing this alkali treatment we generate different functional groups on the cellulose fiber surface. And then therefore enhance the interaction between polymer matrix and the fiber. In general the idea of compatibilization is very important from a sustainability point of view also, because we have seen that mixed plastic waste is the major challenge to recycle because in terms of all these different components which are there if you have polypropylene, polyethylene, polyethylene terephthalate. All of them are not compatible with each other and so by adding suitable compatibilizers by adding suitable reinforcement can we devise a composite system and can this be done on a demand basis. So, can we start tailoring the amounts of each of these, start tailoring the compatibilizers and then achieve any given plastic waste we can devise a very good material which is recycled material.

So to give you this thought I will leave you with this description that you know compatibilization and sizing is a very key issue for waste plastic recycling and what do I mean by that? We could have let us say 3 different polymers. So, they are indicated by 3 different colors and so green is the continuous phase polymer and then the other 2 blue polymers are distributed. Now how do we ensure that the distribution is controlled and we get the required phase domains that we want for suitable performance of this particular composite? Now the polymers by themselves which are mixed with each other may not give us the correct performance. So, we may want to add some particles and fibers to enhance the properties. Now in this case for example fibers are being added to improve the properties in terms of the mechanical performance.

But the particles are being added to improve compatibility between different polymeric systems. So, in this case green and dark blue polymers they can be compatibilized using a particle. We could also have other sets of particles which are again acting as reinforcing material. So, these set of particles are again acting as reinforcement within the blue polymer and in all of these cases there are so many interfaces and so many compatibilization action which may be needed. So, for example if we look at this particular case we can add a block copolymer which has a green macromolecular segment which mixes well and then a blue macromolecular segments which mix as well. So, then the interface region will grow will become slightly more and interfacial strength will improve. Similarly given that the green macromolecules are always in contact with the fiber we could add a compatibilizer which is let us say a reactive compatibilizer. So, it has the green segment so that it can mix well with green and then it has another segment which can go and do a reaction it could be a ester group formation, it could be any of the different formulae amine could react with something. So, therefore we can have a reactive compatibilization where fiber and the green polymers are connected to each other through this reactive coupling agent.

So, if we have these it is like going to a supermarket or it is going to a large store and collecting all these different things putting them together and then getting a performance and so can this be done and if we can do this effectively, predictably on a large scale then it will be easy for us to recycle mixed waste plastic.

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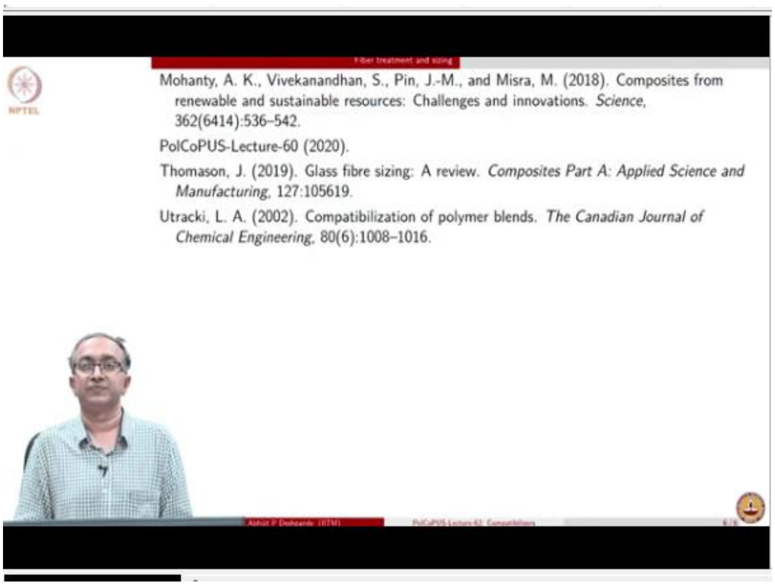

Fiber treatment and sizing

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So, with this thought we will close this lecture and I hope this gives you an idea that compatibilizers are very important as far as applications of polymeric systems go and in fact they are going to be proving even more important when we want to recycle more and more of waste plastics into useful products, thank you.