

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

Lecture-64
Adhesives and Paints

Hello, welcome to the course on polymers. In this course, we are looking at various aspects related to macromolecules. We have focused quite a lot on concepts and properties of these polymeric systems, but we have also looked significantly at sustainability aspects, and we are looking at the applications as well and since in this week we are discussing interaction of polymers with other materials. One of the most important application in which macromolecular systems are very common are adhesives and paints, which by definition, are substances which interact with other substances. So, adhesives says us something which bond different materials together and paints, of course coat different materials. And so what is involved in these type of products?

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The slide is titled "Adhesives" and features the NPTEL logo in the top left corner. The main heading is "Failure of a joint (steel-aluminium)". Below this, there are two diagrams of a joint. The left diagram shows a joint with a green checkmark and is labeled "Cohesive failure". The right diagram shows a joint with a yellow highlight and is labeled "Adhesive failure". To the right of these diagrams, there are handwritten green notes: "Surface" and "Covalent bonds ionic bond". Below the diagrams, the text "Mechanisms of adhesion" is followed by a bulleted list:

- Mechanical bonding: surface roughness
- Secondary interactions: van der Waals, hydrogen bonding, ...
- Chemical adhesion: reaction of adhesive with reactive groups on surface

In the bottom left corner, there is a small video inset of a man speaking. At the bottom of the slide, there is a footer that reads "For accessing this content for free (no charge), visit | npftel.ac.in" and a Creative Commons license icon.

So, as our focus remains on uses what we will do is we will look at both of these adhesives and paints as products and look at some of the things that we have discussed in terms of concept of properties of polymers, how are they brought into design of these kind of systems. So, adhesive basically is something which bonds one substrate with another substrate. And so the adhesive layer basically is put between 2 substrate and we use glues and gums and so

many other different types of materials. Key thing here is the 2 substances which are being joined need not be the same material. So, paper can be stuck on walls. Metal can be stuck with ceramic; so many different types of joints are possible. So, all different types of materials can be bonded using adhesives. And why is this required? Because, rather than fabricating and using mechanical fastening or processes which can be very expensive, what we could do is, we do not have to worry about what material are we making things out of.

Once those components are made, you can use a third substance, which in this case is macromolecular adhesive, you can then bond any of those substances. So, therefore applications are everywhere in transport, in electronics, in packaging. So, various places we can use the idea of adhesive bonding. And generally, if you look at structural adhesives, they are playing a structural role, and therefore they are a load bearing. And they are the strength of the adhesive joint based on these structural adhesives is extremely good. And we can also have flexible adhesives and sealants which play the role of not only holding materials together, but they are not structural materials but they do play a role of sealing where leakage cannot happen from one side to the other side. So, therefore these flexibility adhesives play a role of vibration isolation sealant, as well as holding the overall components together.

So, the key thing related to these adhesives, is the fact that when we are bonding 2 surfaces with an adhesion. Here, for example, there is a steel and aluminium joint which is bonded using this black looking polyurethane adhesive. And then you can see the steel side and the aluminium side. So, what has been done in this case, if you take, let us say steel and you take aluminium and then in between you put the adhesive and you make a bond like that. And then what you do is you pull it apart, to see you know what happens, how does it fail? And if you then look at these 2 surfaces if let us say there is a lot of adhesive here and lot of adhesive here. Then, what you have is a cohesive failure. So, it is adhesion was good, and because the adhesive failed the joint failed. But you could also have the adhesive failure in which case the adhesive did not really bond with the surface.

So, in this case you can see that the bonding with aluminium was not very good because you can see exposed aluminium. You can also see several places where there is exposed steel, so even bonding with steel was not good. So, ideally what you want is a process where the full strength of the adhesion is encountered by adhesive failure itself. So, generally, how this can be ensured is when the adhesion with the surfaces has to be very good.

So, there has to be several mechanisms of adhesion which have to come together for us to give very good adhesive strength of the overall joint. So, you can have let us say mechanical bonding, which is induced because of surface roughness, because the aluminium surface let

us say is very rough and whatever is the macromolecular adhesives, it can go and basically interact with the metal surface in all of these rough protrusions and valleys which are there on a metal surface. On the other hand, if we have a metallic surface which is very smooth, then the macromolecule will have less area to interact and the number of points where the physical bonding may be there is much less. So, this is the something like mechanical interlocking between 2 materials. And of course, the interaction between the metal atoms and the macromolecule has to be very good in this case.

If let us say we take 2 different polymer composites and want to join them. Then in that case the macromolecule of the 2 pieces which are going to be joined and the macromolecules of adhesive, they need to interact with each other using Vander Waals or other secondary interactions as the case may be. And then of course we can also have chemical addition, where this can form covalent bonds or ionic bonds. So, that there is an adhesion actually reacts with whatever the active groups present on the surface. So, depending on the type of adhesives, each of these mechanisms or multiple such mechanisms can be there in case of a single adhesive.

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The slide is titled "Adhesives" and is part of an NPTEL presentation. It is divided into several sections:

- Failure of a joint (steel-aluminium):** Shows two photographs of joint failures. The first is labeled "Cohesive failure" and the second is labeled "Adhesive failure".
- Mechanisms of adhesion:**
 - Mechanical bonding: surface roughness
 - Secondary interactions: van der Waals, hydrogen bonding, ...
 - Chemical adhesion: reaction of adhesive with reactive groups on surface
- Adhesive formulations:**
 - Prepolymer or monomer → crosslinking : urethanes and epoxies
 - Polymers : poly (vinyl alcohol), poly (ethylene vinyl acetate)
 - Pressure sensitive adhesives
 - self-sticking labels, double-sided tapes, ...
 - triblock copolymers : poly (styrene isoprene styrene) or poly(styrene butadiene styrene)
 - acrylates

A small inset video shows a man speaking, and the NPTEL logo is visible in the top left corner.

And so generally adhesive formulations have a pre polymer or a monomer. And then we have cross-linking going on, because when we need to apply the adhesive we need sufficient flow behavior. But in the final part, the adhesive needs to be strong, such that it itself has good strength. At the same time, it needs to also form very good bond with the both the surfaces which it is trying to bond. And so, with the liquid state with a pre polymer or a monomer state, it is easier to do this. So, urethanes and crosslink epoxies are quite commonly used as adhesives. We also have polymers such as PVA and polyvinyl acetate, ethylene vinyl acetate

which are very good adhesives, some of these can also work as pressure sensitive adhesives, where a lot of these sticky notes and double sided tapes where you remove the backing material and then immediately it can bond.

We also have triblock copolymers, which are styrene isoprene styrene or styrene butadiene styrene which can act as very good adhesives. What you can see in many of these cases is a good distribution of polar and nonpolar entities. And these distributions of polar and nonpolar entities ensure that there is always sufficient number of points at which these macromolecules can form good interaction with the substrate which it is trying to bind.

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The slide is titled "Paints: materials and phenomena" and features the NPTEL logo in the top left corner. It contains a list of bullet points and a diagram illustrating the process of paint adhesion.

- Paint - an example of adhesive that binds on the surface being painted!
- Components of paints and coatings:
 - Polymers (binders), pigments, solvents, additives
 - Example polymers - Acrylics, epoxies, polyurethanes, polyesters
- Role of polymers
 - binding pigment particles
 - ensuring the adhesion to substrate
 - providing weather resistance, which includes UV and chemical resistance
 - forming a water protective barrier coating

The diagram on the right shows a cross-section of a substrate with a layer of paint. The paint layer consists of a network of polymer chains (represented by green and purple dots) that are bonded to the substrate. A blue arrow labeled "Polymer" points to the polymer chains. A black arrow labeled "Adhesion" points to the interface between the polymer and the substrate. A handwritten note "polymer film" is written next to the paint layer. Below the diagram, there are three bullet points:

- Solvent-polymer phase behaviour
- Flow and spreading
- Polymer particle coalescence

Now, let us look at the other example of a product where again the interaction with the other substrate is crucial is paint, paint is nothing but actually an adhesive, which is binding on the surface being painted. So, when we apply your paint we want the paint to stick to the surface on which we are applying it. So, therefore there is adhesion also involved, and at the same time we want the outer surface of the adhesive to give color or any other feature that we want from an aesthetic point of view. We also can do paints and coatings for protecting in terms of anti corrosion protection or in terms of scratchproof protection and so on. So, paints and coatings can play several roles in addition to being aesthetically giving pleasing surfaces. So, general components of paints and coatings are polymers, which are actually the adhesives and therefore they are called the binders.

They also bind the pigment particles together, because quite often paints and coatings may also have colors and pigment particles. So, they have to be held together. And that is the job of polymer. So, pigments can be there, solvents, and additives can be there to make sure that all these multi phase system of polymers, particles is remained stable. It is well distributed

and the viscosity is nice. In the sense that when we are trying to apply the paint, it can be applied easily, but as soon as we stop applying it wherever we have applied it paint stays there. So, rheological response of paints is also very crucial in terms of determining its overall performance, and again macromolecule plays a very significant role in determining the rheology of such paint systems.

Effectively what we have is depicted here initially we start with the paint formulation, in which we have these polymer particles. And we also have the pigment particles. And then the solvent, which is depicted in blue here has to disappear. So, that when we go to a final paint formulation, the solvent is no longer there the pigment particles get distributed very nicely and the polymer forms of film. And this polymer film will do 2 jobs, it will make sure that the pigments are well distributed and it gives aesthetically pleasing, or scratchproof surface or whatever is the functionality on one side and on the other side, it gives good addition to the substrate. So, therefore polymers are quite crucial in this application and general examples of polymers which are used in case of paints or acrylics, epoxies, polyurethanes, polyesters so many similar polymers again because adhesion is a very important component of paints. And so role of polymers in summary is to bind pigment particles, make sure that there is adhesion to the substrate. It can provide the weather resistance and which includes UV and chemical resistance, and it can form also water protective barrier coating. And so, in such a system where you are going from a multi phase polymer particle solvent system to finally a polymer particle system a lot of interesting thermodynamic questions related to miscibility of solvent polymer systems are involved.


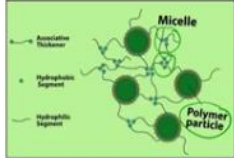
In terms of variability and interface between the spreading paint and the substrate, or how the viscosity and rheology of this paint is, these are also very important. And finally, how do this green polymer particle come together and then finally lead to a very uniform film? So, polymer particle coalescence and formation of a film. These are all very fundamental phenomena which happened during a painting process. Fascinating isn't it, I mean when we think of it we just think we are applying a paint and then it just forms a very nice film. But if you look at it from the point of view of thermodynamics and kinetics of the processes which are happening lot of role of macromolecules phenomena in terms of performance of a paint system.

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Paints

Water based paints: associative thickeners

Hydrophobically modified ethoxylated urethanes (HEUR)

- Amphiliphic polymer
- Association of hydrophobic blocks - sticky ends
- Formation of micelles
- Adsorption on hydrophobic polymer particles
- Bridging between associative polymers, and between a polymer particle and another particle

To leave you with an excellent again example of how interactions are manipulated to devise an excellent paint. There is a lot of emphasis on water based paint. So, that when solvent evaporates, it does not have an environmental impact. So, the emulsion paints many times you might have heard and then they will say water based emulsions, and so whatever is evaporating in this case is just water. And so, water based paints are using these days what are called associative thickness. So, as the name suggests thickness, they modify the viscosity and rheology of the material, and they do this by associating. And what do we mean by that? So, what we have these are basically urethanes, but they are ethoxylated. So, there is all these urethane linkages, but there are several ethoxy groups also. And because of these kind of variated groups on them the ends of these macromolecules become sticky. So, what you have effectively is a macro molecule which is like this. It has a hydrophobic modification, at the end. And then, overall, it may be hydrophilic because of these R_1 and R_2 groups. And because of this, if you put another molecule of this together, the green and green part would like to come together. So, therefore there is an association between hydrophobic parts. This can also be called sticky polymers and they have polymers with sticky ends so the ends which are sticky with like to stick with each other. And so, if you look at closely what is the system in the end is you have a polymer particle. And then you have complex structure which is formed by these sticky polymers.

So, they can form micellar like structure, they can bond with the polymer particle. And by doing this, they are forming a 3 dimensional network, and we have of course discussed in case of polymers how formation of a 3 dimensional network leads to very complex behavior. And you can of course always reach a gel or more solid like property. So, in this case also thickening action and rheology modification happens because of this network formation.

The interesting thing here is this network is being formed based on physical bonding stickiness of hydrophobic parts of macromolecules. So, generally these are associated with thickness are amphiphilic polymers, because they have this green hydrophobic part and the black hydrophilic part and the association of hydrophobic blocks leads to what are called the sticky ends.

And then these could lead to micelles, they could adsorbed on the polymer particles and they act as bridges and the form the 3 dimensional network. So, you can read more about these paints, which include these hydrophobically modified sticky polymers. So, with this we come to close our discussion on adhesives and paints, which are very modern examples in terms of how we manipulate interactions at the macromolecular scale to achieve superior performance. So with that we will close, thank you.