Polymers Processing and Recycling Techniques
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Lecture – 81
Absorption and Leaching

Hi everybody, we are looking at concepts, uses, properties and sustainability of polymeric systems in this course and while we are discussing polymer processing and recycling techniques, we have several times talked about usage of solvents and catalysts to look at how to recover monomers or other small molecular systems from polymers or during the service life how small molecules can interact with these polymers so that their recycling becomes a challenging aspect. So overall in terms of handle and process these polymers and from their sustainability point of view, the absorption and leaching in these polymeric systems is extremely important.

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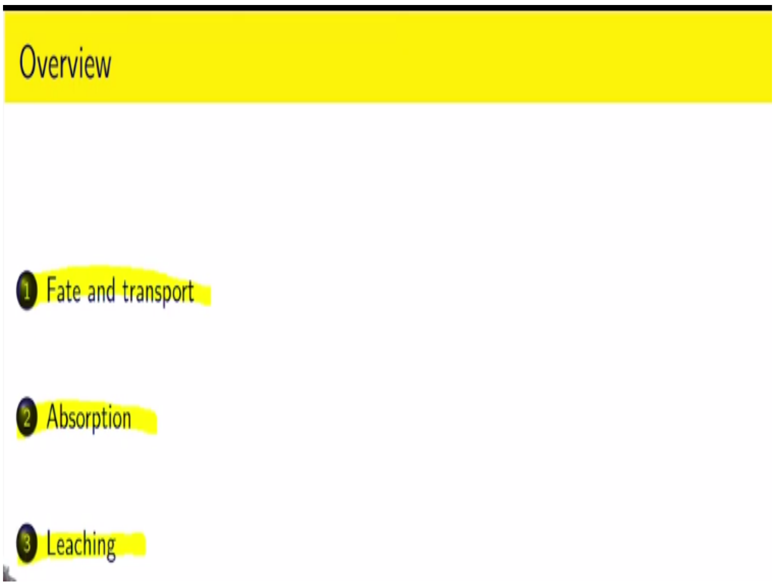

So by keeping our focus on sustainability, let's discuss what are the issues associated with fate and transport of small molecules along with the polymeric materials and the phenomena which determines this fate and transport is absorption and leaching. Absorption where small molecules from other polymeric systems or surrounding phases come into polymer or leaching where small molecules from a polymeric system go to other polymeric systems or other solid systems or liquid and gaseous systems.

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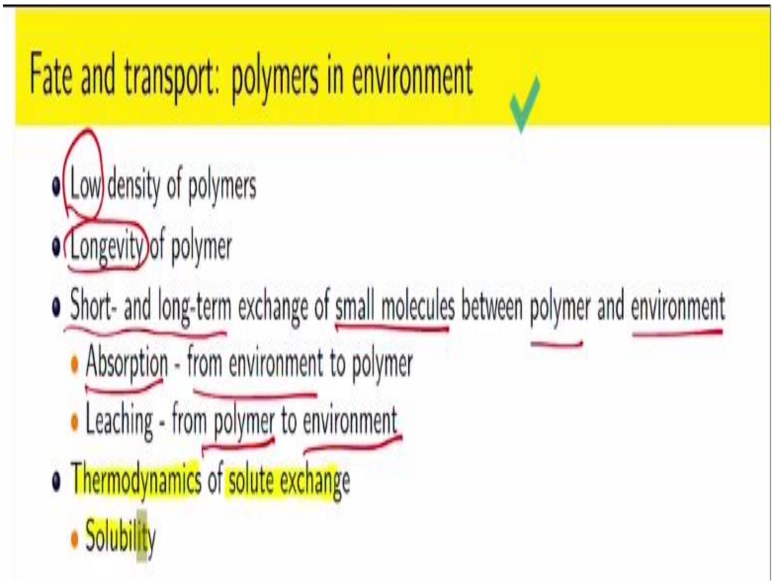

So, let’s look at this fate and transport from the point of view of polymers in the environment. Basically, one of the key features is the density of polymers being low and when we say low it is in comparison to dust, soil, clay and various other things which are also there in our water bodies for example. So what happens is deposition of plastic objects is not very easy because the density is low and so they tend to float and they tend to travel long distance. Of course, also we know that the presence of these polymers in environment is over a long time because of lack of biodegradation, lack of degradation of these materials. So given that they can get carried over a very long distance due to their low density and given that they are around in the environment for very long distance, we have to worry about not just the short term exchange but even the long term exchange of small molecules between polymer and the environment and that’s the reason the polymer itself being there in the environment is cause of concern, but given that polymer is exchanging molecules with the environment, we have to also worry about what are these molecules being exchanged between polymers and the environment.

So for example, absorption is where the small molecules are going from environment to the polymer, from water to polymer or from oil to polymer or from air to polymer and conversely, we also have small molecules going from polymer to the environment and all of this is happening over a long distance and over long time. Now why could this be important? Let’s say we have a polymer which is floating in a river body, and the river water is generally clean and therefore there may be some exchange, polymers may have some plasticizer, it may gain get into the river and that is one cause of concern that we have.

Now let's say when this river flows down and then it encounters a polluting stream which is coming from some other industry and there are some ingredients, chemical and pharmaceutical and die industry and so some pollutants which are coming from there and now the river water becomes polluting and during this period the plastic material which is floating can exchange and absorb some of the small molecules which are part of the polluted water and now again the plastic is continuing to flow and again it encounters a reasonably clean water but the polymer itself still has those small molecules which were picked up from the waste water. So therefore, you can see that how plastics are closely interacting with the surrounding and their state will be very different compared to what's the state of the environment, but given that they are around for a long time and longer distances they can exchange and have an impact which is not just related to polymers alone but how these polymers interact with the environment.

So, therefore this thermodynamics of solute exchange, you know, whether the die molecule which is a pollutant in the river will it come to polymer? The plasticizer molecule which is there in the polymer, will it go to water? Similarly, some molecule which is let's say dissolved in water can come to plastic, then it gets absorbed in plastic, then will it also again leach out and go to some other place soil or will it get evaporated and get exchanged with air or water vapor?

So all of these are questions where we have to look at what is the solubility of these small molecules in polymeric systems. If let's say solubility is not there or zero, then we do not have to worry about. The solutes will not get exchange with polymers, but remember polymers are certain type of hydrocarbons or with heteroatoms like oxygen and nitrogen, so they have wide ranging possibilities of interactions. There is of course Van der Waals interactions, there is possible to have hydrogen bonding. So polymers come in all types of interactions and similarly these small molecules also come in all types of interactions possible. Generally, we will find some small molecules which can always interact with these polymers and so some amount of solubility of small molecules will always be there. What's of more concern for us is if some small molecules which have been identified as toxic molecules, then we have to try to see if polymers are acting as reservoirs of these small molecules, so that they absorb these small molecules because they are soluble in polymer and then they are carried along with the polymer itself. So, this is something where role of polymers will have to be examined. So solute exchange and solubility is one of the important terms that we have to worry about.

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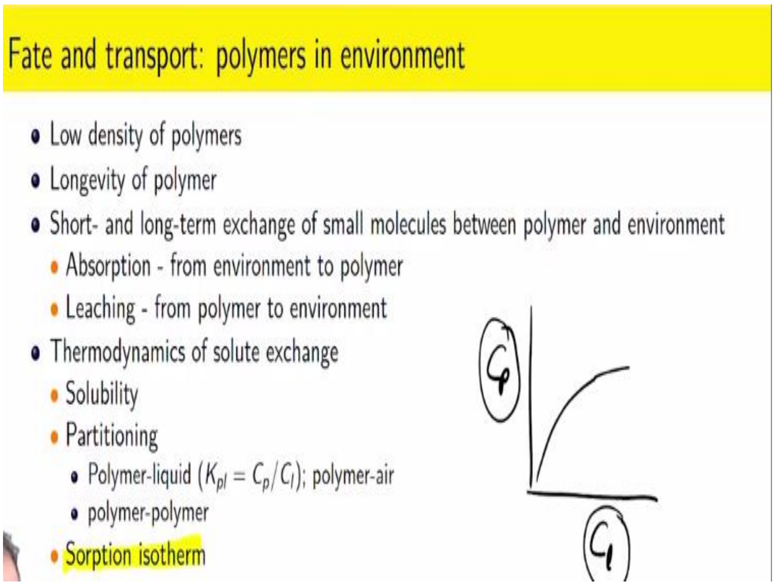

The other important thing is, even if let's say solubility is high in polymers, if it is not getting to the surrounding phases, if it is not getting transferred to water or air, then again it is something at least it is getting confined to the polymer phase. So, the partitioning between different phases is something we have to worry about. Here it could be polymer and water and partitioning is generally thought of as concentration in polymer phase to the partitioning related to concentration in another phase. The ratio of these two tells us what is the so-called carrying capacity of one phase with respect to the other or how does a solute get partitioned between the two phases. So if let's say we start with the solute in liquid phase, it will go to polymer phase if Cp is very high. If Cp= 0, then it will remain in the liquid phase itself and it is therefore not getting partitioned between liquid phase and polymer phase.

So each solute will come up, will have a characteristic partitioning coefficient. Depending on the concentrations in the liquid phase and the polymer phase or the air vapor phase and the polymer phase or between even two polymer phases because we have multilayer films polymer materials which are blends, so we have possibilities where polymer-polymer exchange is also possible. So partitioning of a solute between these two phases is equally important.

Finally we need to understand from the point of view of if concentration changes in the surrounding phases, how much is getting absorbed in the polymer and generally this is talked about in terms of sorption isotherm where what we say is we will look at a polymer which is getting exposed to various concentrations in the liquid phase let's say and at equilibrium what is the concentration that is absorbed in the polymer itself. Generally, you will have various types of absorption isotherms, so that whenever you increase the concentration in the liquid phase the amount which is absorbed in the polymer will also increase, but there are various different forms in which these isotherms can be, but this is an important indicator of how solute exchange is happening between polymer and the other phases.

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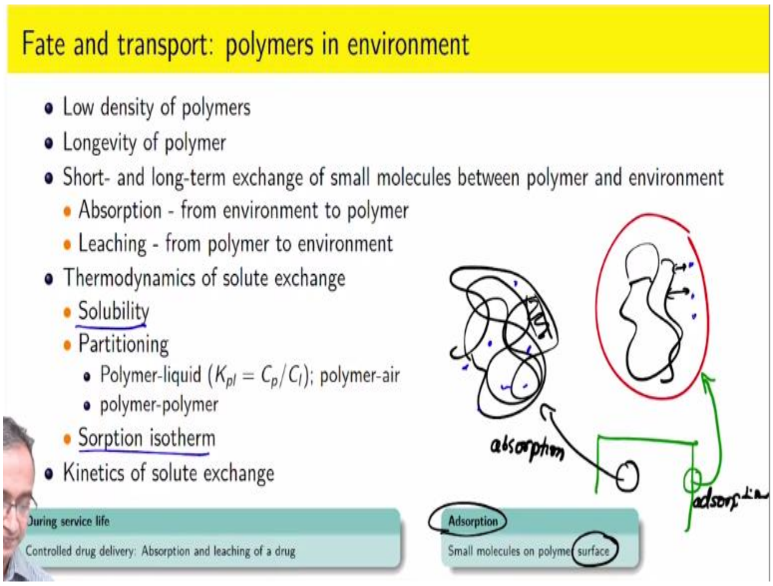

One important question which is related to the fate and transport is dependent on the kinetics, how fast or slow is this exchange happening. And this exchange between polymers and surrounding is in fact exploited in an application. So if you have a controlled drug delivery application, what we do is we make let's say a gel particle or a basically what is called a drug delivery vehicle and in this drug delivery vehicle we have to absorb the drug molecule and then we ingest it. When it goes to whichever part of our body where it is supposed to go and act, let's say, it goes to the stomach and then leaching happens. So that the small molecules first has to be absorbed in this drug delivery vehicle, then it is carried to let's say our stomach and then it is leached out to the surrounding or it is released. By manipulating the rate of release we can have what is called a controlled drug delivery.

Those of you who have looked at let's say even simple medicine like antacid, you can see that some antacids are to be taken more frequently while there is an antacid which is controlled drug delivery which can be taken lot less frequently because it goes in our stomach and releases the antacid active ingredient over a longer period of time. Otherwise as soon as tablet dissolves in our stomach, whole the drug molecule gets released and then of course it cannot do its job, so therefore it goes out of the system. But if we have a controlled release, then we can have sustained release and overall drug action for a longer duration of time, so that's the idea of controlled drug delivery. So you can see you can exploit polymeric vehicles to achieve this controlled drug delivery and for controlled drug delivery polymeric systems are very important application. So here also absorption is involved to put the drug in the delivery vehicle and then leaching is involved and drug which is the solute in this case is getting exchanged between surrounding and the polymer system.

Another thing to keep in mind is when we say absorption, it is in the bulk. So we have the polymeric system and of course it's an entangled mass or it may also have some crystalline portion, but what we are talking is in terms of a solute which is there everywhere in the polymeric system and how this solute is getting absorbed, how much quantity of it will get absorbed, when we change the surrounding concentration will more get absorbed, all of these are questions that we have discussed. Additionally, there is a possibility that when we have a macromolecular system like this and what happens is only the molecules are there on the surface. So this picture that I have drawn here is basically a zoomed version of a polymer film and we look at this small portion and this is how it looks like, while the earlier picture that I had drawn was in the bulk. This is absorption, where molecule is everywhere and this is called adsorption. We might have to worry about both of these when we are looking at small molecule exchange. Sometimes the small molecules may only adsorb and may not absorb, but they are still getting carried along with the polymer molecule by being on the surface.

So remember that adsorption as a phenomena is related to surfaces and for example this sorption isotherm, similarly we also have adsorption isotherm, but again the exchange is between the two phases but solutes rather than going inside the polymer system are only confined to the surface and this is possible because they interact very closely with the macromolecules on the surface of the macromolecules.

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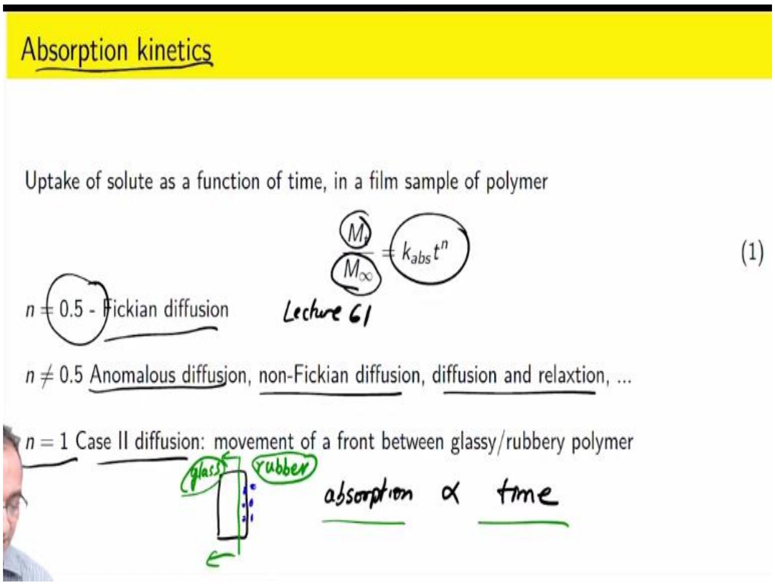

So, let’s close this lecture by discussing little bit about kinetics. A generic expression that you can talk about kinetics is where the uptake or the amount of small molecule which has gone inside the polymer phase at time t, related to whatever is the maximum amount that can go in, is basically function of time. And if you see that it is proportional to square root of time, then we have the Fick’s law of diffusion as we discussed in lecture 61. But quite often in polymers because of the molecular relaxation, because of the glass to rubber transition that happens when small molecule comes in and it has to plasticize before diffusion can happen, so because of all of these things n is not 0.5 and those times we call it either a non-Fickian diffusion, anomalous or phenomena where both diffusion and relaxation of macromolecular chains are happening.

One specific case which is observed quite a lot in case of polymer where this absorption is linearly proportional to time, so the absorption amount is proportional to time and this is called the case 2 diffusion and this is generally a discussion where we also looked at when we use let’s say solvents to recover the polymer, when we use dissolution to recover the polymer. In all of these cases, what happens is there is a polymer which is in the glassy state and when the small molecules start coming, they will get absorbed and then they plasticize and so what happens is in the material there is a front. So this side of a front, the behavior is rubber like where macromolecular segmental flexibility is there, while on the other side there is glassy state and the diffusion coefficient is very less in the glassy state, while diffusion coefficient is reasonably high in the case of rubbery state.

So there is a front which keeps on moving as these small molecules keep on coming in, they get absorbed, they modify the macromolecular flexibility and therefore this front keeps on moving. So in this case, the amount of absorption that can happen is proportional to time.

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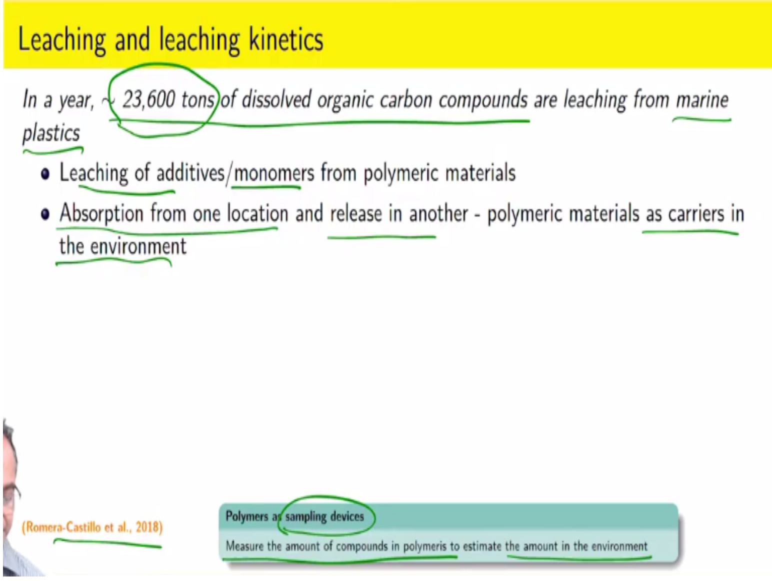

So with this, we will now look at leaching which is the reverse where the solute get exchanged and one of the reasons why leaching is very important from an environmental impact point of view is for example the number of dissolved organic compounds which are there in polymer and the amount which are getting leached with the plastics which are there in marine environment. So you can see there is a huge impact in terms of not just the number of these compounds but also the amount of these compounds, and so leaching of additives and monomers which are there in polymeric materials to surrounding is an important point for us to remember. What we can also have is absorption from one location and then leaching or release in another. So polymeric materials as I discussed earlier can act as transporters of cargo, in this case the cargo is the small molecules. So their impact is felt in lot more ways than just whatever they contain themselves.

One of course way in which we can use therefore polymers is to look at the state of the environment. Polymers can be used as a sampling device to figure out where all what molecules are there by looking at the small molecules which are present in it. We can think of this polymer as a sampler. Sampler is something which collects sample.

So if I take a polymer samples and examine what are the small molecules in it, I can then get to know whatever may be the small molecules in the liquid surrounding in the environment or the vapor or the air surrounding in the environment. So therefore, we can measure the amounts of compounds in polymers to estimate the amounts in the environment, so therefore it becomes an effective sampler.

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So with this, we close this lecture which is related to exchange of small molecules in polymers and is very important from the point of view of the environmental impact of polymeric systems. Thank you.