

**Polymeric Materials of Different Kind**  
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**Lecture - 24**  
**States in Environment**

Hello, welcome to another lecture of polymers, in this lecture, we will look at the sustainability aspect by looking at what are the different interactions that polymers will have with the environment? In this week, we are looking at polymeric materials of different kinds, which are actually used in practical applications and each of the material during its manufacture during its service life and post service life interact with environment. And so, while we are looking at all these different kinds of polymeric materials, it is incumbent upon us to think overall about the sustainability issues also.

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Overview

- 1 Biogeochemical cycle
- 2 Different states of polymers

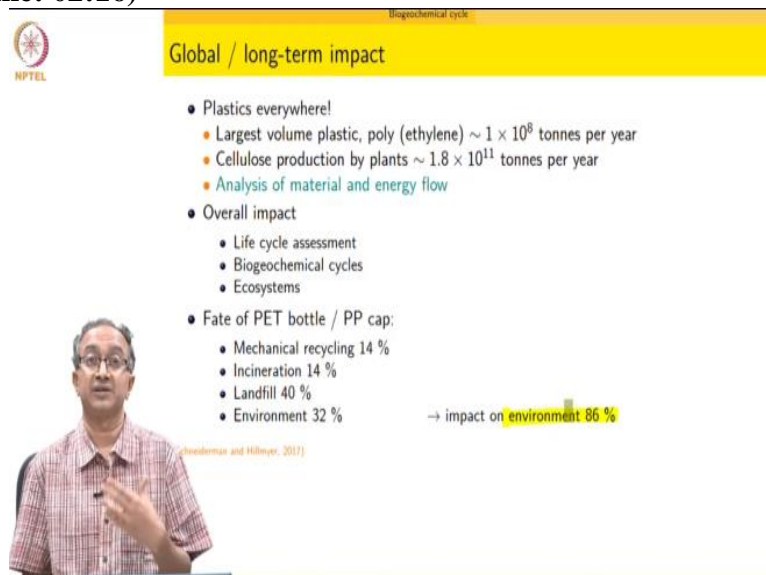
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And we will do this by looking at, briefly about the overall impact, long term impact and for example, that is looking at the biogeochemical cycles based on which we analyze the overall set of phenomena which are happening on earth? And how material and energy flow occurs across very different lengths and timescales from very local phenomena all the way till climate?

And so, analysis of such cycles, which is over scales of globe itself, and at the same time, timescales also; which is not just 1 year phenomena, but over decades. So, therefore, some of these impacts are measured in terms of long term and long range influence of some of the actions which we are doing at a very local scale, at a very short range of time. And the end of

the lecture, we will also just summarize given the vast possible impact of polymeric materials on a global scale, what are the different states in which the impact can be studied or understood.

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Biogeochemical cycle

Global / long-term impact

- Plastics everywhere!
  - Largest volume plastic, poly (ethylene)  $\sim 1 \times 10^8$  tonnes per year
  - Cellulose production by plants  $\sim 1.8 \times 10^{11}$  tonnes per year
  - Analysis of material and energy flow
- Overall impact
  - Life cycle assessment
  - Biogeochemical cycles
  - Ecosystems
- Fate of PET bottle / PP cap:
  - Mechanical recycling 14 %
  - Incineration 14 %
  - Landfill 40 %
  - Environment 32 %

→ impact on environment 86 %

Arredondo and Hillmyer, 2017

And so, let us start with the consideration of the overall impact that polymers will have. And generally we start with this perception that you know, plastics are everywhere. This is true also, because of the non biodegradability of polymers and the, whether it is a rubber tyre or a plastic bag, its visibility and its visibility in various different states of the environment and so, in terms of our perception.

The plastics being everywhere, is a very common feature and therefore, it has an extremely strong impact on the global and overall impact scale. If you look at the amounts involved, though, it just gives us a perspective in terms of what is the capability of these biogeochemical cycles to generate, handle and then finally, process and degrade macromolecular systems.

So for example, cellulose, which is a natural polymer, it is produced  $10^{11}$  tonnes per year, that is the amount of cellulose which gets generated, then it gets used, it has its service life in terms of providing structure to the plants and all the other functions that it can provide. And then eventually, it becomes biomass and then gets utilized and therefore, it again has an end of service life.

And the amounts which are involved is  $10^{11}$  and polyethylene, which is by far the largest volume plastic that we use is 3 orders of magnitude lower in terms of the quantities that are involved. So therefore, in terms of macromolecular, handling and macromolecular processing, the biogeochemical cycles have capability of very large amounts, but the key differences in the type of materials and therefore, what we really need to look at is the material and energy flow associated with each of these materials.

So that the quantity wise polyethylene will be lower, but in terms of its impact, how does it what are the energies, which are involved in its generation production and its end of service handling? What is the set of materials which are involved? What materials are being converted to polyethylene? When polyethylene finishes its service life, what materials does it go to?

So, this overall material and energy flow is what will determine whether the overall biogeochemical cycle is able to process these materials and clearly right now the answer is, no. Unlike cellulose, which we do not often worry about as a waste material which is accumulating and therefore is becoming a big problem, even though it is in  $10^{11}$  tonnes per year, 3 orders of magnitude higher than polyethylene.

So to force us to think of issues which are related to how do you analyze materials which we are bringing in into the biogeochemical cycles, we start looking at concepts such as lifecycle assessment, in terms of its production, in terms of its service life, in terms of its end of life, what is the, so rather than just looking at the cost of the material purely from the point of view of when we are selling it, we look at the overall life cycle.

We can also look at the influence of the materials on the biogeochemical cycles or also look at it from an ecosystem perspective. And actually, each of these is a subject in itself. So for our course purposes, we will not really go into details of all of these, but from time to time, I will give you some pointers towards how thinking associated with these very important concepts are involved as far as sustainability of polymeric systems is concerned.

So for example, if you just look at let us say, PET bottle and PET bottle, which is used for water or soda, and this is actually one of the item which is recycled quite reasonably, the, it is one of the highest recycled product as well as material. And the bottle itself is polyethylene

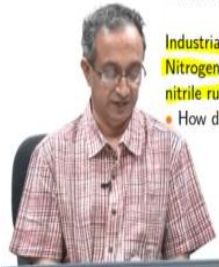

terephthalate, while the cap is polypropylene, and if you look at the recycling of it, and it is about 14%. And what happens to the remaining material, some of it gets incinerated in terms of either energy generation or waste handling.

A lot of it ends up going to the soil in the form of landfill. Many of these landfills are of course protected in the sense that they have a lining, they have a barrier so that many of the materials which are in landfill may not be able to interact with surrounding soil and water. But there are of course, many places where landfills may not have such protection. And secondly, there may be breaches of the protection depending on the age of such landfills.

And then we also have directly in the environment in this actually, the idea that plastics are everywhere is related a lot to this 32% being insight. And it is a large amount of material which is either floating on rivers or oceans, or it is there in the channels. So these are all associated with water bodies, but they are also there in the soil or when we dig to plant a new plant, some plastic pieces may come out. So therefore they are there everywhere, because they are not been disposed properly or they have not been recycled.

So if you look at really the amount of best possible recycling material, we still have about 86% of the polymer which is directly interacting without it being serviced. And so a lot of PET PP of the, in the form of bottle is interacting with the environment. And so the question is, how is it influencing it in the long term? And these are the kinds of questions now we are trying to grapple more and more as polymer scientists.

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**Biogeochemical cycle**

Common cycles which are monitored:

- Carbon
- Nitrogen
- Oxygen
- Water
- Sulfur

• How do polymeric materials and products influence / contribute / take part in the cycles?

Industrial products: fibers, plastics, rubbers, resins, dyes, paints  
Nitrogen containing polymers: Nylon, Polyurethanes, poly (acrylonitrile) (SAN and ABS), nitrile rubber, ...

• How do these contribute to nitrogen flux and species types?

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And trying to come up with an answer related to can we use it in a more sustainable way? And of course, as I have highlighted in the 9th lecture related to polymerization, depolymerization can we also think of new ways of generating new polymers. So let us continue looking at the biogeochemical cycle and from school onwards, we learn about the cycle such as carbon cycle and water cycle and in study of these cycles, we look at basically how carbon gets transformed from one species to another species?

And how material flow and energy flow happens when all these different species get transformed with respect to each other? And generally, it is a cyclic process, so that generation and eventual returning back to the same form is involved. So, cyclic processes are an important aspect of this analysis. And that is how the overall dynamic equilibrium of global scale processes are maintained due to these cycles and there is a periodicity associated with many of these transformation processes.

The and therefore, now we can ask the question as to how do polymeric materials, the synthetic polymers that we have are using more and more over the last 5, 6 decades. How do they influence or how do they contribute or how do they take part in these cycles? And once we say they interact with these cycles are do they become part of the cycle. So, are they in fact, at few points in the cycle they intervene, but they are not really part of the cycle.

So, these whether it is carbon or water cycle is part of a cyclic process and these polymers and material products, do they just intervene and then take part and then again come out so, that they are not really part of the cycle. So, this is something which then implies that the sustainability of the materials is compromised. So, generally if we look at the industrial products, we can classify them in terms of these various products and if, we focus specifically on nitrogen.

So, the nitrogen cycle and ask this question, you know, how do polymeric materials influence in nitrogen cycle? So, we can identify these industrial products and we know that many of them will have nitrogen. So, whether it is CONH of polyamide or CHCN in case of acrylonitrile, the cyanide group and polyacrylonitrile is important with copolymer styrene acrylonitrile or in terms of acrylonitrile butadiene styrene ABS system and so, we have polymers rubbers, which are all contain nitrogen.

So, how do these contribute to the material flux? And how do these contribute to the type of species of nitrogen which are present. So, in biomass as part of biogeochemical cycle nitrogen cycling is of course, there and nitrogen is also part of the air system. So, therefore, it is there in air, water, soil, biomass. So, we therefore, quantify all of the processes which are happening with respect to nitrogen by looking at this nitrogen biogeochemical cycle. So, the question is how do these chemicals incorporate? And this is something which we are still trying to understand and trying to do quantification.

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The slide, titled "Nitrogen cycle with industrial chemicals", lists the following nitrogen sources:

- Natural**
  - Biological nitrogen fixation
  - Lightening
- Anthropogenic**
  - Cultivated biological nitrogen fixation (~140 Tg per year; teragram per year (2008 data))
  - Fossil fuels (~25 Tg per year)
  - Industrial nitrogen fixation (~25 Tg per year)

So, here just for example, initial sets of quantifications which are based on about 12 year old data, because it is these are all very challenging questions to answer because, we will have to estimate these based on other sets of data which are available. So, if you look at the way nitrogen gets transformed, and so, the sources by which nitrogen changes are related to natural or based on the activities which are specific to the progress and development that has happened and the industrialization that has happened with related to human activity.

So, in natural level, we of course, have the nitrogen fixation by plants and also some of the species of nitrogen reactions will happen in the presence of lightning in case of atmospheric transformations. So, when these transformations of nitrogen are there they are part of the nitrogen biogeochemical cycle, but when we look at the anthropogenic sources, we have cultivation because of food requirements, very large amount of crops being grown and that leads to reasonably high amounts of nitrogen fixation.

If you look at compared to that, we have fossil fuel usage, which is something again is part of the biogeochemical cycle, but the rate at which the production of this happens is much, much slower compared to its current usage in terms of how we use petrol or coal or any of these fossil fuels. So, the nitrogen transformation based on that is 25. And this is done in its since it is naturally very large quantity tera gram per year is the unit in which many of these fluxes and amounts are talked about.

And what is important to notice is also that the industrial nitrogen, which is where polymers and many other products of course, fertilizer for example, is also an industrial product, which does contain nitrogen. So the polymers are part of this group and we really have to see as to how does this industrial nitrogen fixation interact with the nitrogen cycle? And what influences does it have if we have to understand the overall sustainability of many of the polymers which contain nitrogen.

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The slide is titled "States in environment" and is part of a presentation on "Common states of polymers". It features a list of bullet points:

- Water
  - Macro-plastics and micro-plastics
  - Dissolved or amphiphilic polymers
  - Density of plastics is similar to water → long distance transport possible
- Soil
  - Macro-plastics and micro-plastics
- Air
  - Micro-plastics

Below the list, a yellow box contains the text: "Exchange / mass transfer of small molecules : polymers ↔ environment".

The slide also includes the NPTEL logo in the top left corner and a small inset image of a man in a checkered shirt in the bottom left corner. At the bottom, there is a footer with the text "Abhis P. Deshpande (IITM) PolGPIUS Lecture 24: States in environment 6 / 7".

So, generally, when we look at the states, which are present given that if we have to understand the impact of plastic materials and rubber materials and any other polymeric materials on the environment, we need to see how they are integrated in the overall biogeochemical cycles? And what states they are in? So, for example, in water, we can have the overall bottle itself floating.

So, the macroplastics but we can also have very small fragments and microscopic size all the way till 4 micron, 2 micron or even smaller nanometer size plastic fragments. And so, they are present in water, we could also have the polymers if they are soluble in water then they

could be dissolved in water, we could also have them forming some micelles and few other structures, if they are polymers which have a little bit of hydrophilic groups and hydrophobic groups.

So, therefore, they may be present as bulk materials or as a dispersion or they may be also present as dissolved materials. And one of the problems associated with plastic transport in these global contexts is the fact that density of plastic is similar to water, we will see that many of the crystalline polymer will have density of 1.2, 1.3 and many of the amorphous polymers will have densities of 0.9 and so, on.

So, everything is very close to water, what that implies is, there is a very good tendency of polymers plastic materials to go along with water flow. So, wherever water can flow and go it can easily carry the plastic around. We have seen this in terms of soil and alluvial soil for example, in delta region, so, those are also carried and density of those is much higher, but only during flooding and only during when flow rates are very high then rivers are able to carry these particles.

But if we if gentle flow is there non-flooding conditions are there polymers because of their density difference being smaller with respect to water, they can actually get transported over extremely long distances. So, therefore, their impact can be long range and long timescales. Now, looking at of course, the influence on soil also so, again we can have the overall plastic itself interacting with soil or we can have fragments of those macromolecular samples as micron sized particles or nanometer sized particles.

And many of the smaller particles can become airborne also, we can have aerosols and of course, we know that there are aerosols which originated from trees and bioaerosols, we can also have aerosols which come from the industrial materials such as plastics. The other key thing to remember in when we are looking at this from a global impact point of view is polymers which we use as an inert material for our day to day application and we think it is non corrosive.

And so, many different advantages it has however, when we consider long term and given that it comes in contact with so, many different types of inorganic and organic molecules, when it is interacting with the environment, there is a very strong exchange or mass transfer



of species between polymers and environment. So, for example, a plastic film which is just lying let us say in air can absorb some of the organic species which are present in air which let us say come from pollution from vehicles, inversely also when we think of this plastic.

And we make certain applications of it in terms of geotextiles or we use it in the in the form of modification in roads, it will interact with the surrounding chemicals petrochemicals associated with the asphalt it may interact with rain water. So, there is always an exchange between the polymeric materials and the surrounding environment. And again at the timescale, which we are interested in, let us say for a PET bottle life, which is maybe 6 months to a year, this exchange will be very less and therefore, we are not worried about it.

But once this bottle is going to be present in the environment, whether it is water soil or contacting with air for 25 years, then the exchange of molecules can be significant. And given that we are talking about long distances possible, so, we basically have influence of plastics being quite significant on the environment, especially if we consider in the context of these biogeochemical cycles. So, therefore, when we look at the design and application of these polymeric materials and their overall lifecycle analysis, some of this impact needs to be factored in for us to really start looking at naval use of these polymers.

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Different states of polymers

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Schneiderman, D. K. and Hillmyer, M. A. (2017). 50th anniversary perspective: There is a great future in sustainable polymers. *Macromolecules*, 50(10):3733–3749.



So, with this, we will close this lecture and we will continue looking at the different types of polymeric materials which are present in this week as we go along. Thank you.