Polymers Processing and Recycling Techniques
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology - Madras

Lecture – 77
PolCoPUS: Conversion of Polymers

Hello welcome to our discussions related to polymers processing and recycling techniques and while we are discussing all the options which are available in terms of polymer processing and recycling, one of the options that we have discussed at times is conversion of these polymers to something else, maybe to monomers or maybe to a low molar mass liquid or to low molar mass gases or maybe just combust it, incinerate or burning of these polymers.

So, all of these options are also available which need not necessarily take us back to the polymers themselves and so in this lecture we will look at these different options that are available for conversion of polymers and a lot of this discussion is relevant because of our emphasis on sustainability.

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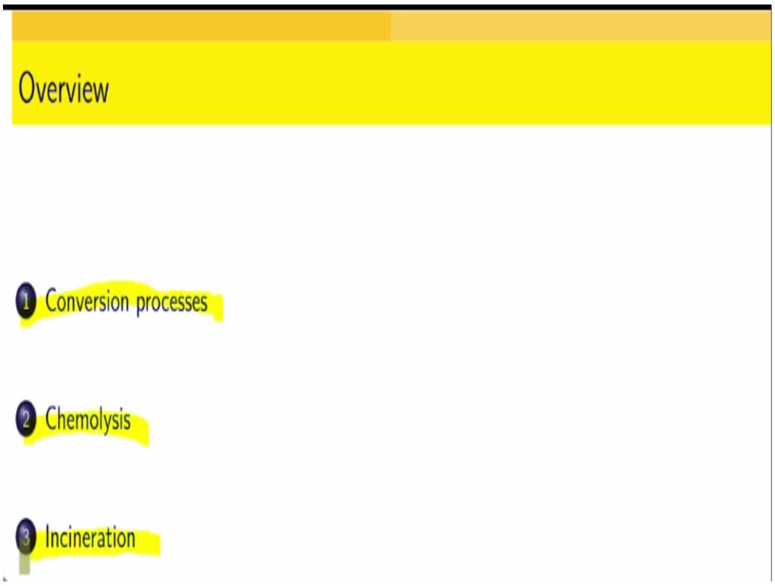

So, we will review quickly what are the different conversion processes which are possible and then we look at chemolysis in a bit more detail and especially given that polyethylene terephthalate is the most researched polymer in the context of recycling, we will look at what are the different conversion processes that have been also thought about for PET and of course the last option that I mentioned in terms of combustion of polymers and in this case the goal is to also obtain energy from such a process.

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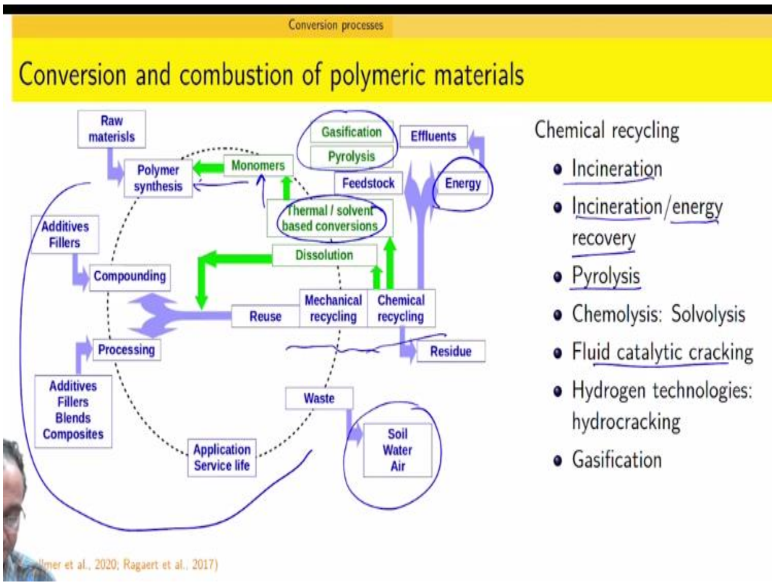

So we have seen this cyclic diagram before and we know that the current paradigm sort of largely works only half way where we do not really have a cyclic process. Also we are worried that lot of waste ends up going to the environment and therefore can we start focusing on these processes which are mechanical and chemical recycling and we saw already that you could basically have conversions in which you can get monomers.

And they could again possibly be fed into polymer synthesis or also they could be used as feedstocks for some other chemical manufacturer which are valuable. Similarly, we could do pyrolysis and gasification to obtain other set of low molar mass liquids and gases which could be again used as fuels or as feedstocks and the last option is related to incineration. And so, we have incineration alone which basically just gets rid of the large amount of waste and reduce it to much smaller quantity of noncombustible in overall plastic mass.

So, there is some char formation, there may be some inorganic additives, so all of that will remain as the waste material post an incineration process. Of course, we will really do this given the overall sustainability issues associated with incineration alone, at least there is some amount of energy recovery that is done with all incineration process these days or we have lysis which is breaking of bonds so macromolecular bonds are broken so that either we will get low molar mass liquids or gases.

There are several techniques in terms of how this can be done; how can the bonds be broken to obtain a target product at the end.

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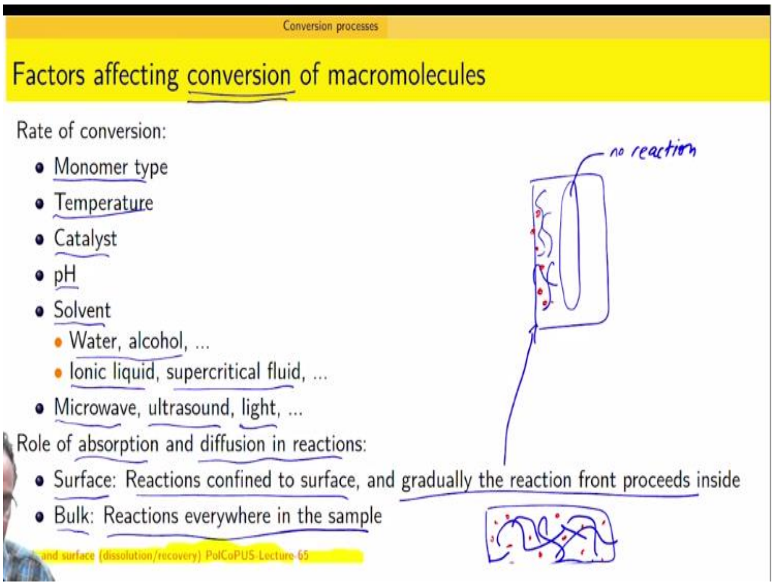

So what are these factors which influence this conversion or breakdown of macromolecules and of course it is the monomer type itself because the monomer decides what are the functional groups, what are the bonds that are available. So in terms of our ability to break bonds, a lot of it is determined based on what is the monomer type and the temperature at which the breakdown is being attempted.

The presence of catalyst, acidic or basic environment, what is the pH that is there and also the presence of solvent because many macromolecules will have very close interactions with solvent and solvent macromolecular interactions will lead to a different electronic environment based on which reactivity can be enhanced or suppressed. So therefore, presence of solvent is very crucial in terms of influencing the conversion of these macromolecules.

And in addition to using solvents in which these macromolecules are soluble such as water and alcohol, we also are researching a lot about the use of what are called green solvents in a sense. Because many of these solvents are easy to recover post the manipulation of macromolecular molar mass and then therefore they are easy to reuse within the same industrial reaction and therefore they are called more green solvents and so these are examples of ionic liquids or supercritical fluids.

Supercritical fluids also bring in of course additional difference in terms of the temperature and pressure which are involved and because of supercritical fluid and temperature pressure involved, the solubility of again polymers may change when we look at supercritical fluid as opposed to other solvents. Over and above, we try to enhance this rate of conversion by impinging on the material different types of radiations.

For example, it could be microwave radiations, it could be an ultrasound wave which is used to need to cavitation and therefore nanometer size pockets or micrometer size pockets of very high temperature. We could also have light radiation falling and therefore photo induced reactions which can take place. So, this is all the set of variables which are available to us for us to look at effective conversion.

Remember we are thinking in terms of an overall sustainability and cyclicity of this and this conversion has to be relatively economic, it has to be relatively less energy intensive for it to become a sustainable process from a life cycle point of view. So therefore, as many factors that can be used to do this effectively is what is the goal of researchers and many of these have not been yet realized where we are not really closing the circle in terms of circular economy of plastics.

But there is lot of effort over the last 10 years or so to achieve this in various different macromolecular systems. Now, one of the complications of reactions with polymers themselves is the fact that the catalyst or the solvent which is useful in terms of the macromolecular cessation, the breakdown of the chain have to reach macromolecules and so the absorption of these smaller molecules onto plastic or polymeric system and their diffusion within the macromolecular mass it can be quite often the rate limiting step.

So for example when we look at overall reactions involving these polymeric materials, whether composites or homo polymer or a blend system, we could have reactions which are being carried out on the surface or bulk. So if diffusion limitations are there or absorption limitations are there, then what happens is reactions are confined to the surface. So if you have a macromolecular film or a molten macromolecular sheet, then what happens is the macromolecules which are closer to the surface are the only ones that are seeing the reactants.

Which could be catalyst or solvent and enhancing the cessation processes in these macromolecules while bulk of the macromolecule there is no reaction. So this is an example of basically reaction first happens at the surface and then gradually proceeds inside, but if there are no diffusional limitations, then in this case the overall macromolecular melt or macromolecular film can be there and basically the reaction enhancing compounds can be there everywhere and so chain cessation reactions can happen everywhere.

So this we also discussed when we were discussing the bulk and surface dissolution and recovery. We saw that overall context of sustainability, dissolution and recovery of polymer is a very good option in addition to mechanical recycling and in fact compared to mechanical recycling this may prove to be better because the degradation in macromolecular system is not as much.

So in this case also, dissolution and recovery is again determined based on these diffusional limitations. So only sometimes the surface of the polymeric film will dissolve first and then slowly it will go in, the front will move in as we speak.

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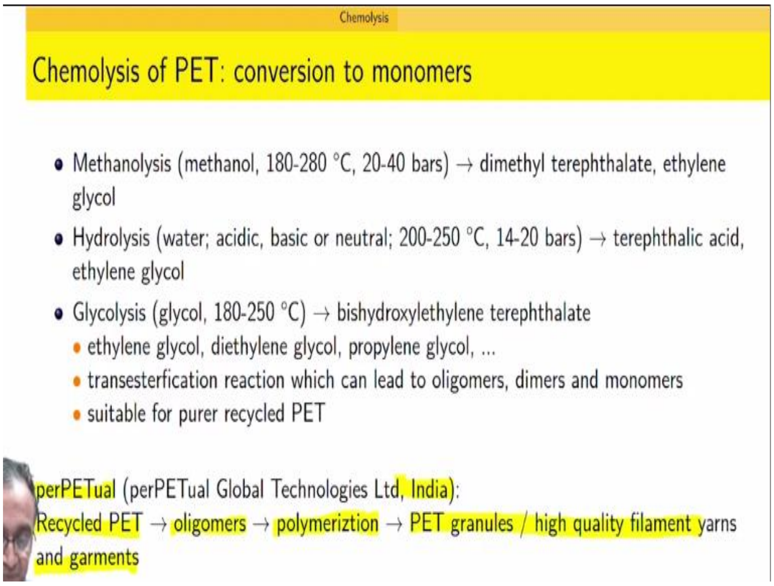

So, one of the examples of conversion processes is breakdown of polymeric chains and so therefore this is called chemolysis and basically use of different chemical substances to carry out lysis or chain precision reactions in polyethylene terephthalate and the idea is to convert and get back the monomers. So, for example if we use methanolysis, methanol is the solvent, high temperature and pressure is used and we can get DMT or dimethyl terephthalate and EG ethylene glycol through this kind of a process.

Other reactions are also known where water is used and of course different pH can be used and again very high temperature and pressures are required, but one can get terephthalic acid and ethylene glycol so this kind of process. So, you can see that depending on solvent and temperature, pressure conditions, one could lead to different types of monomers and therefore depending on the cost of monomers and depending on the overall economics of this process and overall sustainability of the process, several options can be explored.

We also have the use of glycols whether it is ethylene glycol or diethylene glycol or propylene glycol in reactions which are glycolysis, and again in this we can obtain another value added chemical and therefore you can also see that temperature is still very high and this can lead to also a set of products, you can have a monomer, you can have a dimer, or you can have an oligomer and therefore this can be very useful process.

However, glycolysis is generally known to be better in the absence of impurities. So the effectiveness of many of these reaction processes depends on you know if there are scavenger molecules, then they will preferentially react with the catalysts and so on. So therefore, side reactions and products which are obtained due to these side reactions can cause issues related to the efficiency of the process.

One example related to PET recycling is in fact in operation and this is just one of several examples where there is a brand name called perPETual and it is a company based out of India where the recycled polyethylene terephthalate is converted into oligomers and then polymerization can be done again to get a very high-quality yarn. So, this is an example of the upcycling that we have discussed quite a bit. So it is a combination of recycling, chemical conversion and finally processing again to get and achieve circularity in the application of PET.

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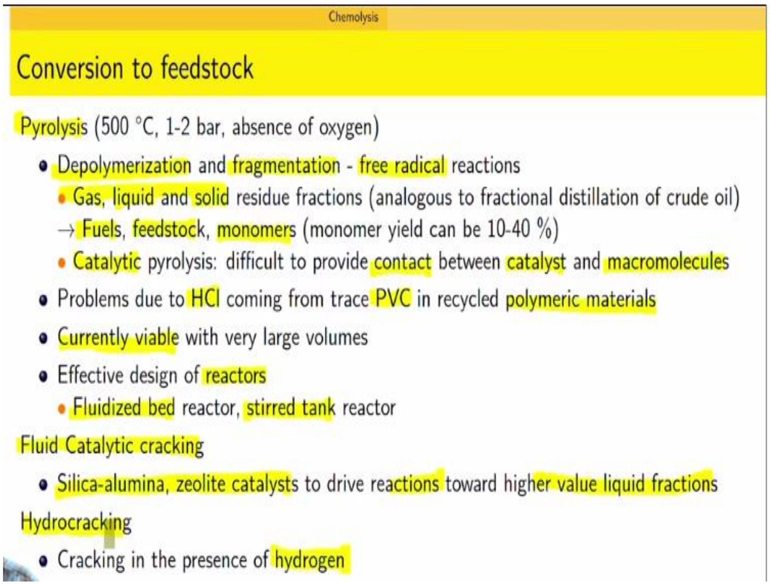

Now one important way of converting is to get feedstocks which then can be used in other applications. So for example if pyrolysis is carried out we can do depolymerization and some amount of fragmentation and this largely happens using free radical reactions and we can basically get all the fractions. We can get gas fraction, liquid fraction and solid fraction. This is somewhat analogous to crude oil refining.

When we get crude oil from a petroleum field, we do basically a fractional distillation and from tar which is a very high molar mass to petrol and diesel and kerosene all of which are middle fractions to gases butylene, propylene, ethylene and ethane, methane, all of these are obtained from a process of petroleum refining. So similarly, you could obtain a variety of molar masses material and so you could get fuels, you could get feedstocks which can be converted to some other chemicals or monomers which can be again polymerized back.

Sometimes to control this, we can do catalytic or pyrolysis. However, as I talked about the contact between catalyst and macromolecule is a crucial aspect because catalyst diffusion into a macromolecular melt or a macromolecular film is not very easy. There is of course combination of problems due to impurities, so if hydrochloric acid is there which is part of the overall waste stream then that could lead to side reactions.

And that will change the overall product composition in terms of the gas, liquid and solid residues that we obtain. This is currently viable but for extremely large feed stocks and large feedstocks which are clean and purer without PVC that kind of purity is not really available. So, we do not have various examples of these though there is lot of research going on in terms of achieving this. A lot of work is also going on in terms of industrial application of this in a very efficient reactor.

Given that we have to do this on a very large scale, we need very efficient reactors which can make sure that the temperature is maintained, the mass transfer of reactants in products happens effectively. So things like stirred tank reactor or fluidized bed reactor which are useful reactors for other types of conversion processes can then be adopted for the polymer pyrolysis kind of reactions.

So, for example fluid catalytic cracking which is a standard operation in any petroleum refining plant to maximize petrol and aviation fuel, the two most sort of sought after fuels from the crude oil, fluid catalytic cracking is used. So can that be adopted for pyrolysis of polymers? So there we can use catalyst to drive reactions towards higher value liquid fractions just the way it is done for petroleum refining or we could have presence of hydrogen also leading to hydrocracking and that again changes the product composition.

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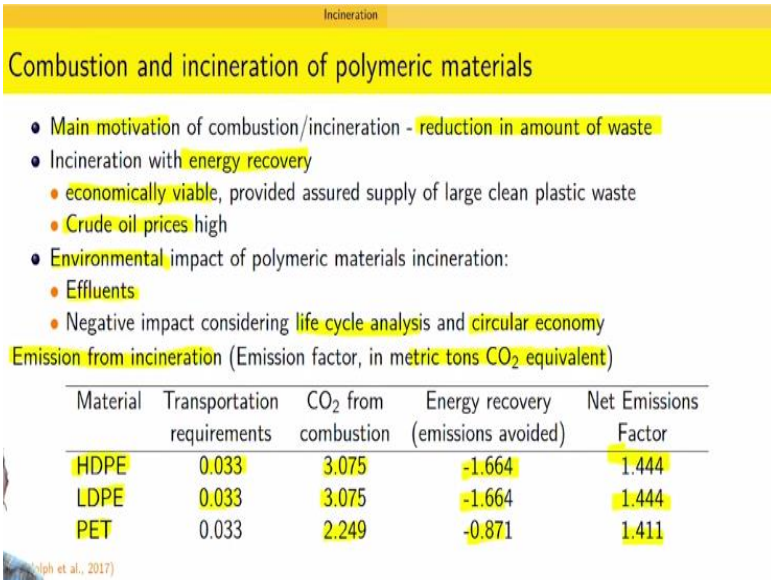

The final option which is available in terms of all these conversion processes is combustion or conversion of polymers into carbon dioxide and water with the hydrocarbons which are present there and of course if we have heteroatoms like sulphur or nitrogen and chlorine, then we have also added issues related to sulphur dioxide, nitrogen oxides and then chlorinated compounds coming in and that is why incineration of polymeric materials is a challenge.

This is done predominantly because it basically you can reduce the amount of waste and waste incineration has been practiced for municipal waste also. So municipal waste combined with plastic waste has been used for incineration. However, off late we have started doing more and more energy recovery. So, given that the large waste is there and it has to be reduced in volume.

And if let us say the other sources of energy are relatively costly, then this can be economically viable. However, there are significant impacts and as I mentioned already about effluents. We can also think in terms of overall circularity, in this case the effluents even if its carbon dioxide and water are not going to come back as part of process and from a greenhouse gas emissions point of view this is a big negative.

So then can something be done and incineration be reduced is one of the questions which is leading to all these efforts related to mechanical and chemical recycling of polymeric materials. Just to highlight the fact, this is data from the literature which talks about emission from incineration process in terms of the amount of CO_2 equivalent. So, there is always a transportation requirement and of course there will be CO_2 which will be emitted from the combustion process.

But there is also an energy recovery because we are burning these hydrocarbons, we can recover some of the energy back, but unfortunately there is a net emission of carbon dioxide through any such incineration process. So, from a greenhouse gas emissions point of view, incineration is not encouraged.

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PolCoPUS-Lecture-65 (2020).

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So, with this we have taken a panoramic view of all types of conversion processes and these also need to be kept in mind while we think better and more suitable ways of mechanical and chemical recycling to enhance the sustainability of polymeric materials. Thank you.