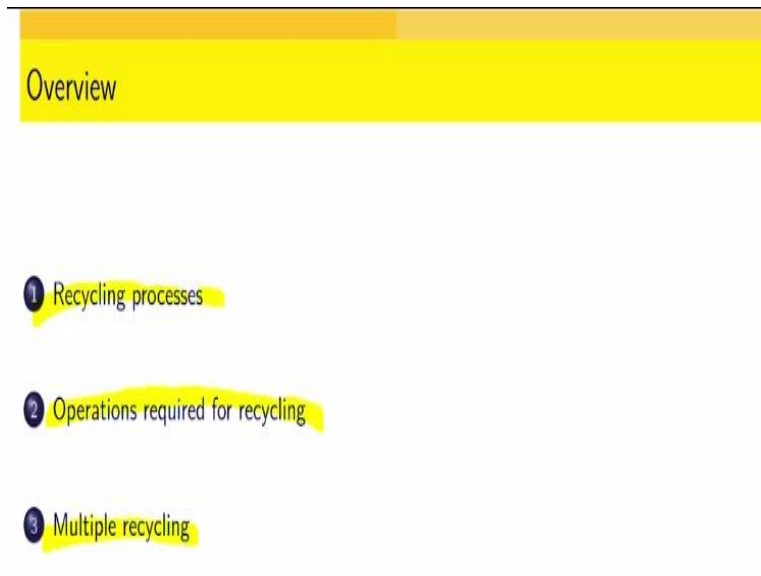


Polymers Processing and Recycling Techniques
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology - Madras

Lecture – 72
PolCoPUS: Processing for Recycling

Hello, welcome to the course on polymers in which we are focusing quite a bit on sustainability in addition to looking at the properties of polymers, the concepts behind many of these macromolecular systems and their applications and so many different walks of our life. We will continue our discussion related to polymer processing and recycling techniques and in this lecture the focus will be related to what are the challenges associated when we are looking at processing for specifically recycling many of the polymeric materials.

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We will do this by looking at some of the recycling processes and then which are the operations which are required before recycling can happen or for recycling to be enabled and one of the questions we will look at specifically from the point of view of the properties multiple recycling is a very good idea because then we can continue to use and reuse the same set of materials and we may be able to use them in one product and another product interchangeably.

But what happens to the material when we do multiple recycling, so that is something we will discuss that will give us in perspective on how mechanical recycling is always possible but may not be always desirable for all kinds of applications.

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Recycling processes

Recycling methods

- Primary recycling
 - Recycling polymeric materials in the same application
 - Closed loop recycling
- Secondary recycling
 - Recycling polymeric materials in alternate applications, which are less demanding
 - Open loop recycling
 - Downcycling
 - Upcycling
- Recovery and conversion
 - Monomers, oil, char, ...
 - Energy

So when we look at overall recycling methods and the processes which are available, we could classify them many different ways and many of these different classifications are available, different literature and different industries use slightly different terms to describe many of the processes that are followed. Primary and secondary implies what is being done, where is the polymer material waste coming from and where is it going.

So primary for example implies that we are recycling the polymeric material in the same application and this can be done in a in-house kind of an application. So let us say you have a car manufacturer who is making a plastic part out of a polymer and then during the processing operation itself there is some mould overflow or there are some cuttings. So all of these are waste materials, so they can be put back into the stream of polymeric materials and recycled.

So that is why this kind of a recycling is also called closed loop because the polymer is basically for a definite application and it is a waste arising out of that application and it is recycled back into the same application. On the other hand, we use the term secondary recycling or also open loop recycling where we recycle the polymeric material in alternate applications which sometimes are less demanding.

In that case, specifically we then call it downcycling because the polymer is being recycled, but in terms of value that is associated with its application it is going for an application where mechanical property requirement is little less, safety requirement is little less or electrical

conductivity is little less. So, therefore we are downcycling it, more and more in our research also in the way industries are looking at recycling.

We are exploring this option of upcycling where can we not improve the properties during recycling using clever strategies and what would these clever strategies be? Can we not incorporate some other polymer component, other filler component, can we not change the molar mass distribution of the polymer during recycling so that it is available for upcycling, can we not remove the set of contaminants which are available will then it be suitable for upcycling then.

So the idea behind upcycling is to use polymers in a wide ranging set of applications depending on what market requires or demand requires or the prioritization based on industries prioritize demand instead of being constrained that whenever you recycle a polymer material it will always be reduction of properties and therefore it will be down cycling. So if we are able to do upcycling effectively that will open a plethora of choices in terms of what to do with a recycled polymer.

Of course we can also carry out recovery or conversion in which case we can recover the polymer itself or we can recover the monomer or we can carry out partial reactions so that we convert the polymer into some lower mass fragments which becomes oil or we can carry out the pyrolysis so that it becomes char and that can be used and of course during many of these conversion or burning processes, combustion processes we could also recover energy. So this is a broad set of processes which are available

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Recycling methods

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| <ul style="list-style-type: none"> ● Primary recycling <ul style="list-style-type: none"> ● Recycling polymeric materials in the same application ● Closed loop recycling ● Secondary recycling <ul style="list-style-type: none"> ● Recycling polymeric materials in alternate applications, which are less demanding ● Open loop recycling <ul style="list-style-type: none"> ● Downcycling ● Upcycling ● Recovery and conversion <ul style="list-style-type: none"> ● Monomers, oil, char, ... ● Energy | <p>Targets in Indian National Resource Efficiency Policy</p> <ul style="list-style-type: none"> ● 100% recycling and reuse rate for PET by 2025 ● 100% recycling of PET and 75% recycling and reuse rate of other plastic packaging materials by 2030 ● Ban on disposal of recyclable waste (plastics, metals, glass, paper, cardboard and biodegradable waste) to landfills by 2025 |
|---|---|

Generally, there are guidelines to make sure that the waste polymeric materials going to landfills or generally ending up in soil or any other water bodies and all can be reduced. So for Indian National Resource policy which is a fairly recent document in fact tries to lay down this as something for a country to work for. So for example 100% recycling and reuse rate for polyethylene terephthalate, PET is used in bottles as you know.

So by 2025, can we make sure that no amount of, zero amount of PET goes to either a waste disposal site or ends up being disposed in a water body and so on, quite ambitious target is not it? But for such a target to be achieved, the recycling, reuse, recovery all these processes that we discussed have to become more and more effective. So for example, the other target is not just the 100% recycling of PET, but 75% recycle, reuse of other materials also by 2030.

So in 10 years from now can we not use basically and recycle 75% of the polymers which are used. Secondly, there is contemplation of complete ban on disposal of recyclable waste to landfills and these recycler wastes not only include plastics but other materials also. So by preventing it from going from landfill and this landfill could be open or closed depending on the kind of waste disposal site it is, but basically the idea is that whatever is biodegradable or whatever can be recycled should not end up going there.

So lot of these ambitious aspects have management and social behavior and variety of these challenges, but they also contain important scientific challenges and especially from the point of view of the nature of macromolecules and what kind of processes can we do with the macromolecules.

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Operations required for recycling

Operations before recycled polymer processing

- Separation / Sorting
 - Macro-separation: Sieving, optical sorting, density difference methods, magnetic / eddy-current based separation
 - Micro-separation, molecular separation
- Consolidation
- Cleaning
- Cutting, crushing, granulating and grinding
 - Machining required for virgin / recycled polymeric materials

GATE 2018

Match the following:

P. Plastic egg container	1. Injection moulding
Q. Water tank	2. Extrusion
R. Chair	3. Rotational moulding
S. Cable	4. Thermoforming

(A) P-3; Q-1; R-4; S-2 (B) P-4; Q-3; R-2; S-1
(C) P-2; Q-3; R-4; S-1 (D) P-4; Q-3; R-1; S-2

- Blending, mixing, homogenizing, ...
- Processing

So before effective recycling can be done, few sets of operations are essential and they basically are separation and sorting because polymer products come in very different shapes and sizes. For example, here these are 4 products a plastic egg container, a water tank, a chair and a cable and of course each of this is made using a very different processing operation. So there are 2 questions here. One is the fact that if you are trying to recycle them, then they will be very different sizes and shapes.

Secondly if we use waste plastic can injection moulding, extrusion, rotational moulding and thermoforming be used as effectively with the waste recycled plastic material as it was with the what is called the virgin plastic material. So just to highlight this, you can try looking at this question and variety of options, remember that processing technique is closely related to what is the overall shaping that is required and so for example a plastic container is pretty much a flat sheet with some openings.

So a technique which can quickly do a stamping kind of an operation and produce these inclusions in the plastic material which can hold eggs will be very useful. So for you to know little bit read about these techniques and based on the lectures that we discussed in related to polymer processing, you should be able to answer this question. Now the separation and sorting of all these different materials can be macro-separation which is basically separating caps from the bottles, bottles from the cans, bottles from the films, different types of films.

This is all macro-separation and of course this can be done manually but it can also be done

using engineering processes. For example, density difference could be used, you could use it based on sieve, lot of robotic sorting, trying to look at laser based or optical methods. We could also have techniques which are based on magnetic. For example, many times many of these films will also contain some metal foil.

So therefore, wide ranging set of choices are available. The challenge of course is the key idea in terms of selectivity, how effective? Can we get 99.99% of one polymer in one stream and another polymer in another stream by doing this kind of a process. We could also do a micro-separation or molecular separation in which case we can for example if we use a solvent and put all the polymers and then preferentially dissolve one of the solvents, then we are achieving molecular separation.

So it is not just a separation of a bottle which is a part from another bottle, so for example the shampoo bottles are very different materials, it is usually a co-polymer polypropylene polyethylene compared to water bottle which is PET. So these two separations of course is possible also, but molecular separation implies separation at the molecular scale and even blend which can be recycled this way by separating it first into two pure components and then putting it through again a processing operation.

Of course, when we say bottles and when we say chairs and plastic egg containers, these are all unwieldy shapes. They are that shape because they serve a purpose, the chair to sit on, a plastic egg, so these are very voluminous products. If you weigh each of these, of course the weight is total is less. So can we not consolidate them? So many crushing operations have to be performed or compression operations have to be performed for doing first of volume reduction before they can be handled effectively either for separation or for further processing.

Cleaning is an important aspect because during use, variety of these plastic products come in contact with various materials and before recycling can happen this is an important component and so that is why source segregation and effective collection of waste which is also tied to management and social behavior, which is a very important aspect of recycling, and whenever we discuss recycling in addition to the science and engineering of macromolecular materials, we always have the other side related to management and social behavior perspective.

And in terms of this consolidation and sorting, we can also have basically cutting down the bottles into smaller pieces in granulating, crushing or grinding and of course just like we require machining, we were cutting or drilling holes and many of these things are required for even parts which are made out of virgin plastic, these will also be required for recycled polymeric materials. So generally, these are the wide set of operations that are required even before the waste material can be used in an injection mould or any such processing operation.

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Operations required for recycling

Pre-processing and processing conditions for recycling

Mixture of polymers in any recycled collection, with range of processing temperatures:

Polymer	Temperature, °C
LDPE	160-260
PVC	180-210
PS	180-280
HDPE	200-300
PP	230-270
Nylon 6	230-280
Nylon 66	260-320
PC	280-320
PET	280-320

(Ragaert et al., 2017)

Therein lies the challenge associated with polymer recycling because you have wide ranging set of operations to be performed before you can actually recycle the polymer and sometimes this can throw the cost of the process to a very high value and therefore policy interventions and priority based on sustainability are required for us to start investing more and more in these processes which are sustainable from a long term perspective.

Once the polymer is ready for processing, there are still challenges when we have waste materials and generally, we saw that given that there is a mixture in recycle and there is too much cost and energy associated with very effective separation if we process them as a mixture, what will happen? And here we are looking at the temperature range which is used for each and every polymer, but you can see that from 160° Celsius to 320° Celsius.

There is a very wide temperature range over which these polymers are processed. So if I have a mixture of LDPE and PET, what temperature should it be processed or if I have a mixture of polystyrene and nylon what temperature should it be processed? Of course, when we

process them, the blending, the miscibility, the compatibilization of blends all those technical challenges are there from a macromolecular science point of view.

But just looking at the rheology and flow behavior and whether mixing and whether homogenization or whether good dispersion is possible that again depends on the temperature at which processing is done and generally if I use a very high temperature, degradation of some other polymer may set in. If I use a low temperature, some other polymer may not have reached the melting point at all and so there is a challenge in terms of how to process these materials at what temperature to process them.

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Multiple recycling

Property change due to recycling of a single material

- PET
 - 3 cycles: \bar{M}_w 38000 → 22000 kg/mol; Impact strength 25 → 20 J/m
 - Contamination by acid producing contaminants poly vinyl acetate (acetic acid), PVC (hydrochloric acid)
- HIPS
 - 30 cycles: Colour white → light yellow; Impact strength 90 → 75 J/m
- LDPE
 - 100 cycles: Viscosity 2000 → 13000 Pa s
- PC
 - 5 cycles: Modulus 750 → 680 MPa; Elongation at break 100 → 65 %

Effect of water; other contaminants - dyes, detergents, pesticides, ...?

(Radolph et al., 2017)

And even if let us say we end up processing these materials, mechanical recycling does have an issue related to degradation of properties. So here we look at some example of property changes when a single material itself is being reprocessed and by no means therefore recycling is a solution from an overall sustainability point of view. It is one of the solutions which is far better than disposal.

But however, there are many improvements needed within this mechanical recycling domain itself so that the property changes that happen can be reduced. For example, PET over a three times recycling can change its molecular weight, molar mass from 38,000 to 22,000. A lot of these are from specific reference which tries to review many of the effect of these recycling methods. Importantly, the impact strength also decreases.

So clearly then downcycling will have to be done because the polymer properties are getting

deteriorated as each recycling process. However, we know why does this molar mass reduce and part of the reason is also presence of hydrochloric acid or acetic acid. So if there is contamination by other polymers such as polyvinyl acetate or PVC, even if small amounts of these other plastics are there, then what we will have is these side reactions which lead to chain cessation and molar mass getting decreased.

So can we have an effective method of removing all of PVC and polyvinyl acetate which is not very expensive so that PET can be recycled in much more number of times. So you can see how if we keep sustainability in mind, there are various questions we can ask and seek answers to rather than just looking at mechanical recycling as the alone answer. High impact polystyrene which is also a very large amount of waste that is part of waste stream over 30 cycle, again there is a reduction in the impact strength.

And also the white color turns to yellow due to oxidation and other reactions which happen with each subsequent stage of cycling. Look at the case of low-density polyethylene, in this case over 100 cycles the viscosity goes up from 2000 to 13,000, so what do you think might have happened? In case of both PET and polystyrene, we spoke about the reduction in molar mass, but in case of LDPE cross linking can happen and that leads to an increase in molar mass and therefore increase in viscosity.

Which is again not desirable from the point of view of the usage of LDPE in a given application and polycarbonate if you look at again there is a reduction in modulus as well as elongation at break. So not only modulus decreases, even the strain at which failure happens also decreases. So therefore, when we recycle a single material itself, there is issues related to degradation of its behavior due to each subsequent stage of recycling.

Over and above this, we will always have some solvent, water let us say for example in case of nylon recycling or it may influence even other polymeric materials and then of course we have various other contaminants. These plastics come in contact with say various other chemicals because they are storing them or because they are being used in an environment where these other chemicals are there and how do they influence the polymer properties as it is being recycled.

And since recycling is necessarily a high temperature operation, many of the influences of

these chemicals may be quite high in terms of chain cessation or any other side reaction that we do not want to happen during processing. So you can see that sorting, separation, purification these are very important steps before mechanical recycling can become as promising as it can be. In the absence of other methods, this is still one of the most promising practices that we are following, but we need to do far better.

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GATE question on Slide Number 4 : Answer-D

The question related to different polymer processing techniques and a product I am sure you would have figured out that chair for example is injection moulded, water tanks are done using the rotational moulding operations and so on. So with this, we will close this lecture. Thank you.