Polymers: Concepts, Properties, Uses and Sustainability Prof. Abhijit P Deshpande Department of Chemical Engineering Indian Institute of Technology-Madras

Week 9 Polymer Processing and Recycling Techniques

> Lecture-68 Polymer processing I

(Refer Slide Time: 00:13)



Hello, our exploration of polymers continues, and in this week we are looking at processing and recycling techniques. We have looked at polymerizations and relevance of polymerization in the context of polymeric materials. In this week and the lecture specifically, we will start looking at processing operations and continue this for a few lectures. In this particular lecture our focus will be on concepts.

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We will take a look at what do we mean by processing of polymers and what are the different types of operations that are involved when we say we are processing the polymers. And given that in processing deformation is critical and shaping is involved flow behavior of polymeric material is of paramount importance. So, we will see what is the relationship between flow behavior and polymer processing operations to begin with? Based on some of our discussion related to processing, we will recognize that flow behavior is very important. And rheology which is the study of flow behavior of polymers is also extremely important and we will have few lectures discussion on rheology as well.

(Refer Slide Time: 01:29)



So, when we say processing of polymeric materials, of course we are looking at processing of a homopolymer or copolymer or a blend or a composite, right. All of these will have to be processed to get a final part. And so, generally what we have are set of operations, which are based on the requirements at hand. So, we could have mixing involved especially if we have blends and composites. We could have a mixing in case of homopolymer because of additives which are involved. And so, plasticization for example is an example of an additive where we add the plasticizer to improve the flow ability of the material or also modify the performance later on. Generally especially in case of thermoplastics, we will have to increase the temperature, so that we can melt the thermoplastic polymer.

In case of other materials such as thermostat and rubber processing again temperature will have to be maintained. From the point of view of maintaining the flow behavior as well as carrying out a reaction because higher the temperature, higher will be the rate of reaction. So, temperature is always a variable of interest during processing operations, either from melting point of view or from reactions point of view. And so of course, whether melting and reactions are happening, we will always have flow involved. And so, pumping actions, pressure generation, pulling and pushing operations, rolling operations. So, all of these ensure that material gets pushed, material gets pumped and flow happens. And then we will have to make sure that the plasticized flowing, reacting, polymeric material gets shaped by either enclosing the material in a mould.

Or if it is free flowing like a film then stretching it to get a thinner and thinner film, so that we get the final thickness that we want or roll it, so that again we can manipulate. So, generally we have these tools which are called moulds or dyes. Moulds basically encase the overall polymeric material while dye is an opening through which the material is passed. So, you can recognize immediately for making fiber dye will be involved.

Because the polymer melt or a polymer solution will have to be pushed through an opening and then cylindrical jet of fluid will come out. And that can be then stretched and we can obtain the fiber of a given diameter. And of course the final stage is vitrification, solidification, crystallization, so all of the processes by which we will get the final state of the polymer. And so, this is the overall set of operations.

Extrusion is a very common processing technique where we do mixing, we also do compounding and also the shaping in terms of using dyes along with extrusion. So, some common term that you will hear is in terms of an extrusion dye. So, exclusion can be used for both mixing and shaping operations simultaneously. So, even wire coating for example, right, when wire which is a metal, let us say copper on that we have polymer insulation.

So, this is also done through a wire coating operation which involves extrusion, in which the wire itself is pulled and the polymer then can flow on the top of it. So, what we have basically is a wire, thin wire which is being pulled. And on top of that because of extrusion, we have basically the polymer material and this polymer material basically starts thinning out and then eventually we get a fine coating. So, the rate of pulling off the wire itself will determine how much polymer is getting deposited, of course the rate of pumping off the polymer also determines it. So, you can see that if you want to analyze the polymer processing operation and come up with the control, where you decide, what will be the final thickness of insulation that you want, you will have to understand the flow behavior of polymeric system.

Injection moulding is the workhorse as far as polymers are concerned because of it is time, you can make a injection moulded part in one second. So, whether it is toys or whether it is fabricated parts in automotives, a sector. All of the places household objects, we have lots and lots of injection moulded products. The moulds can be of very complex shape and in a single shot, we can generate product which is very complex in shape but very quickly.

Compression moulding is a technique which is slower and it is used for largely flat or somewhat less complicated shapes. Film blowing, again is a big operation and that is based on the amount of films that are around us. And in fact, so this also is a major reason for us to talk about single use plastics and sustainability. Because it is an operation in which you can produce films at an extremely rapid rate and the film properties can be controlled very precisely.

Because we can control the processing operation and flow and what we will see is the extensional flow behavior of polymeric material so well. That we can get these films at very large quantities with excellently controlled properties and therefore they are very inexpensive. And they can be used in single use where that is use and throw kind of applications. And so, that is we will look at that during extensional flow.

Blow moulding is again a very popular technique where bottles, shapes such as bottles are. So, as the name suggests, so you can see that many of these are suggesting the way in which it is carried out also. So, injection moulding, there is an injector which is used in case of blow moulding, blowing is happening along with the mould. Of course then we have the coating and calendaring operations which involve a set of rollers on which polymeric fluid is coated or calendared onto a set of substrate.

Roll mills are used in rubber processing, so this does the role of mixing as well as shaping the rubber before it can be finally made into the part. Rotational moulding is a very common technique to make tanks. Especially in India, we see the water tanks for overhead storage and most of them are made use in this rotational moulding as a technique. Again it is a technique within reasonable amount of time you can make the cylindrical tanks.

And thermoforming is similar in some sense to compression moulding but thermoforming is an idea borrowed from metallic processing where we can take a sheet and then just do a quick stamping of it and shape it. While compression moulding involves quite often reactions and therefore it takes more amount of time where thermoforming is quicker.

(Refer Slide Time: 09:16)



So, this is a broad survey of these polymeric processing techniques and in each of them polymer is flowing. It could be a three polymer, it could be a resin, it could be a final polymer, it could be with different additives such as plasticizer, it could also be with fillers and fibers. So, therefore the flow behavior of polymeric systems is extremely important. And this is highlighted in this question here where one way to look at the flow behavior is to look at what happens to the material when we apply a rate on it and we wait for the steady state.

So, this is basically data where it is called a steady and it is also called shear, steady shear. Steady because we apply our stress, wait for shear rate to become constant and then measure both stress and rate. Or we apply a constant strain rate, wait for the stress to reach steady value and then measure the both stress and strain rate and then we can plot. And, so for a Newtonian fluid, we know that stress is proportional to shear rate and of course the proportionality constant is viscosity.

So, this graph here is basically for Newtonian fluid. And this is part of any polymer processing discussion, these kinds of graphs where we have different types of fluids like dilate and bingham plastic, pseudo plastic. And so, can you just spend some time and try to think of what is the meaning of each of these terms and why do these graph signify and the reason for doing so is flow behavior will depend on how is material responding to stress?

And each and every processing operation involves different amount of shear rate. Injection moulding involves very high shear rates, compression moulding involves less shear rate. So, therefore the same polymeric material may behave one way in injection moulding will behave completely differently in case of compression moulding. Because the stress in the material is not directly proportional to shear rate like Newtonian fluid, it is a complicated function.

You can see that in some cases there is an increase, some cases there is a decrease, some case there is a direct jump. So, each of these shows very different behavior and we need to characterize this, if we have to study flow behavior of a polymeric system in the context of polymer processing.



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This is just to highlight also that even if you talk of the same family of polymers, in this case let us say polyester. But if you have the polyester in the form of a liquid crystalline polymer or the normal polyester which is a flexible macromolecule, the viscosity versus shear rate can be very different for the 2 cases. And what I also want you to think of is how to go back and forth between these two graphs. Stress versus rate and the other case viscosity versus rate and of course we define viscosity as stress divided by shear rate. So, if you were to plot the red data on this graph, how would it look like or if you were to plot the blue data on this graph, how does it look like and so there is a significant difference especially in terms of low shear rate behavior. For the blue the aromatic or liquid crystalline polymer it appears that viscosity increases and continues to increase and may even go to infinity, when we go to lower and lower shear rate.

While the polyester the viscosity at low shear rate seems to become constant, so this is a constant value of viscosity for polyester. So, very different behavior and wherever there are low shear rates this can be very crucial. So, liquid crystalline polymer wherever shear rate is very low viscosity will be extremely high, velocities there can become very low and we can have a stagnation point. While in case of polyester viscosity will not go beyond a certain upper limit. So, you can see that if you have to analyze a polymer processing operation, avoid a stagnant place. Because stagnant place implies that polymer will just circulate there and it is not really moving. And in a processing operation, we make the material flow and fill into a cavity, mould or we will pass it through a die, so our objective is to have all of the polymeric material move or flow.

And so, generally to analyze the overall response, the flow behavior depends on viscosity. However that is not the complete picture because polymeric materials have a certain elasticity. We have these segments which can stretch and recover, stretching and recovering is nothing but elasticity. So, therefore even in a molten state, even when pre polymer is there and molecular weight or molar mass may not be very high, the segments have a tendency to stretch and recoil, stretch and come back.

And therefore polymers are in the fluid state, quite elastic and therefore they viscoelastic materials. It also depends strongly on what type of flow and what is the geometry of flow. Because polymeric fluids given the ability to stretch and recoil, the exhibit very different behavior if they have been going through a very gradually changing geometry or a sudden contraction or a sudden change in geometry. Because what happens is polymer on average has a

certain conformation as soon as you change the geometry, it is possible that it can acquire other conformation. And the going back and forth between these conformations is elasticity. So, therefore how this happens determines the overall flow behavior of polymeric materials? So, generally strain rate, past history of deformation all of these influence the current state in the material.

And this is what we saw during viscoelastic models also, we saw that whether it is Maxwell model or standard linear solid model, current state of stress determines on past history of deformation that the material has undergone. Or other way to say it is the current state of stress depends on not just current values of strain and strain rates but it may depend on stress rate and variety of other rate quantities.

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So, generally this is of great interest because processing determines the properties and all of this is influenced based on molar mass. So, when we want a certain property we may require a certain molar mass but if we want ease of processing we may require another molar mass. So, for example the fluidity or the distortion resistance of the material increases whenever molar mass is decreasing, when molar mass is low it is easy for the polymer to flow.

However many of the properties of the polymers will go down if the molar mass is lower, so there is some optimum always. So, whenever we think in terms of development of a polymeric product. So, far in our discussion we have only talked about properties and how properties can be optimized; how properties can be maximized? But the success of polymer product will also depend on whether we can make the polymer product.

And in other words can we process it and so, processing may require a different set of properties. Or as a scientist, and an engineer we will have to then think of new ways of processing, so that we can achieve the desired product. So, therefore in general the processing structure properties that we discuss have to be taken together. One industrial way of measuring the flow ability is called melt flow index. This is a simple technique in which we apply a mass on polymer melt, and this is so there is a basically piston which is pushing the melt. And given standard mass measure we just measure what is the amount of melt that comes out in a given amount of time. And so, this is a very standard way in which if you look at industrial grades of polymers MFI will be mentioned and this is inversely related to viscosity.

I hope you can see why I am saying that because at a given mass if more amount of polymer comes out, well flow index is higher. But since more amount of polymer is coming out, it implies that viscosity is lower that is why flow rate is high and more amount of polymer comes out. So, that is why molar mass and the melt flow index are inversely related to each other, when molar mass increases, the melt flow index will be lower.

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And so, when we are looking at all this flow behavior and different characteristics, what are the dimensionless groupings which are of importance? Of course Deborah number which talks about the experimental timescale and the material timescale, we have discussed this several times, so

this is important. Specifically for flow we also have the Weissenberg number which is based on the strain rate of the polymer processing operation.

Because in polymer processing we will definitely be flowing the polymeric material and for example, if we have a screw and a barrel in case of an extruder, the screw is pushing the polymer and so the velocity next to screw will be very high. But outer barrel, the velocity of the polymer will be zero because the barrel is stationary. So, then the strain rate determines the rate at which the pushing is happening. And so, that timescale associated with strain rate and the timescale associated with material decides what will be the behavior? Reynolds number is of course the comparison of the inertial to the viscous forces in the material. And the ratio of Weissenberg number and Reynolds number can also give us another way to look at how much is the elasticity in the polymeric materials? So, any polymer processing operation generally we tend to look at you know what is the magnitude of these numbers. And that gives us certain idea about how to analyze those polymer processing operations?

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So, with this we will close lecture on the polymer processing operations introduction. The GATE question that you saw, hopefully you would be able to decide based on the textbook definitions of a shear thinning material which is called pseudo plastic, shear thickening material which is called dialect. And in each case the stress and strain rate are not proportional to each other.

In case of shear thinning the stress increases but increases proportionally less so, or less than proportional. While in case of shear thickening or dilatant material stress increases more rapidly than proportional. And of course whenever there is a discontinuous jump at lower strain rates, we have an yield stress kind of a material. And bingham plastic and there are other models which describe that behavior. So, with this we will close the lecture, thank you.