**Non - [Metallic Materials](https://mail.google.com/mail/u/5/#m_-8153304748177029390_RANGE!A1) Prof. Subhasish Basu Majumder Department of Materials Science Centre Indian Institute of Technology, Kharagpur**

> **Module – 01 Polymer materials Lecture – 04 Processing of polymers**

Welcome back to the course of Non-Metallic Materials this is the 4th lecture of the module name polymeric materials. And I will discussed; discuss in this lecture the Processing aspect of the polymers.

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So, in continuation to the last lecture, where we are talking about the mechanical property the deformation aspect of the polymeric material; we will start with the deformation of elastomer the rubbery material. Then we will introduce the vulcanization concept of this type of material, then crystallization melting and glass transition temperature of the polymer material will be described.

And what are the factors that actually affect the temperature of melting and glass transition temperature that we will review. And finally, the synthesis and processing aspect of the polymers will be covered.

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So, you can see that; the during the deformation in the unload state, the elastomer is amorphous and composes the cross-linked structure molecular chain they are highly twisted, somewhere it is kinked, coil formation is there. So, elastic deformation upon application of the tensile load is basically, due to partial uncoiling that you can see it is straighten up. So, some kind of uncoiling is taking place and twisting also is taking place and it is straightening so, it straighten up.

So, this is happening when you are applying a stress in the elastomers. So, once this is actually ordered the entropy increases if the chain returns to its original kinked position because, that is a disordered structure. So, when the temperature is increased and modulus of elasticity is also increased with increasing temperature. So, in that respect it is just opposite what we find in case of metal.

So, elastomers are basically they are amorphous and molecular chains are naturally coiled or kinked or twisted. So, the chain bond rotations are relatively free and ready to respond or to the applied force. So, the onset of plastic deformation that must be delayed, while this deformation takes place and this crosslinks basically act as an anchor to prevent the chain slippage.

And usually the cross link is done by a process called vulcanization which I will be taking shortly. And, ideally the elastomer must be above its glass transition temperature below the glass transition temperature actually this is brittle.

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So, the process of vulcanization is nothing but cross linking of this elastomer as you can see that; you take the rubber molecule and then you react it with sulfur. So, the crosslink main chain sites are carbon atoms were doubly bonded before vulcanization and after vulcanization, it is singly bonded.

So, usually if you see the stress, strain curve of a vulcanized and un-vulcanized rubber you can see that; the strength is suddenly increased in case of the vulcanized rubber usually, very small part of sulphur is added about 1 to 5 parts of sulfur in 100 parts of rubber. So, if you calculate back roughly 1 crosslink about 10-20 repeat units. So, it hardens the rubber and reduces its extensibility. So, since they are heavily cross-linked, elastomeric materials are thermosetting in nature.

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So, crystallization of the polymer actually occurs from its molten state by nucleation and growth process. So, when it is cooled through the melting temperature this random molecules they are ordered and in the chain-folded layers.

Here I have; I earlier I described in one of my earlier lectures that, this is the nucleation site and this is the lamellar region, where this chain-folded layers, this polymers are ordered region. And in this region this spherulite's the so, called spherulite they grows and this region are amorphous in between this lamellar growth region this is amorphous.

So, if you plot this fraction crystallized at various cooling temperatures, then you will find that, it is a sigmoidal kind of curve and fractional crystallization is usually plotted in logarithmic time scale and it follows a typical Avrami equation. So, y equal to 1 minus exponential of minus K t is the time and n is the Avrami coefficient this is used for other material as well, the similar kind of thing is also followed here.

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Now, the melting corresponds to the transformation of a solid material of ordered structure of aligned molecules chained to a viscous liquid with random structure. So, during melting it takes place and usually it is having a range of temperature not a specific melting point. And, that depends on the history of the polymer especially the temperature at which it was crystallized. Usually, thicker the lamellar the chain I showed that the folded regions higher is the melting temperature.

If you increase the lamellar thickness by induced by annealing just below the melting temperature so, you raise the temperature just below the melting temperature you soak it for elongated period of time.

So, the lamellar thickness is increased, presence of impurity for example, that decrease the melting temperature increase of the heating rate at elevated the melting temperature. Annealing also raise the temperature by decreasing the vacancy and other imperfection of the polymer crystals and increase the crystallite thickness in the process.

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So, if you consider the specific volume versus temperature plot of a amorphous polymer and a semi crystalline polymer which is much different than the crystalline solid. So, specific volume is nothing, but the reciprocal of density right the v by m is the reciprocal of the density. So, in case of a purely crystalline material you see that there is a specific melting temperature and the specific volume is dramatically reduced here and the slope is reduced at the solid state.

If you go for a crystalline material therefore, there is a discontinuous change of the specific volume at the melting temperature. For totally amorphous material it is continuous, but it experiences a slight decrease in slope see the slope is change there is no dramatic change in the specific volume. And for semi-crystalline polymer both melting and glass transition temperature it occurs.

But, here it is when whenever the slope changes the slight change in slope takes place and there is no dramatic drop in the specific volume. So, this particular temperature is known as a glass transition temperature. So, that is in between when we are talking about a semi-crystalline solid material. So, with the host lot of polymer material the glass transition temperature and melting temperature this is listed for your comparison.

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Now, the melting temperature this is affected by the chain polymer chain stiffness, which basically is controlled by the easiness of rotation about the chemical bonds along with the chain has a pronounced effect to control the melting temperature.

So, if double bonds are present or aromatic groups are present that lowers this chain flexibility and melting temperature is increased. Similarly, if you have a bulky side group that also restricts the chain rotation and it raises the melting point, if polar groups are present for example, if chloride or hydroxyl or cyanide groups are present that leads to significant intermolecular bonding force and it raises the melting point.

Increase of the molecular weight also raises the melting temperature, if there is heavily branched that also affect the melting point of a polymer the side branches introduces defect into the crystalline part and that, basically lowers the melting temperature. And as an example you can see that; high density poly ethylene is having a melting temperature about 137 degree Celsius which is higher than LDPE, which has some kind of branching.

So, if the branching is there the melting temperature is reduced. So, if you compare the earlier slide the polypropylene versus PVC then you will find; polypropylene is having a higher melting temperature as compared to PVC as far as the bulky side group is concerned that restricts the rotations. So, if you compare polypropylene with polyethylene the melting temperature of the former is higher as compared to polyethylene and it works well.

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So, similar kind of factors whatever is described that is also valid for glass transition temperature; so, if you progressively see that bulky side group T g increases, polar group if it is there T g increases, double bonds if it is present or aromatic bond if it is present in the backbone that tends to stiffen the polymer chains and that increase the T g. Increase in the molecular weight tend to raise the glass transition temperature.

So, it goes more or less similar with melting point criteria whatever I described and high density of crosslink, molecular motion is virtually it is seized and long range molecular motion is prevented, to the degree that polymer do not experience any T g. So, this view graph it shows that the variation of this temperature this both this temperature with the molecular weight.

And, depending on the molecular weight and melting temperature transition behavior we can define where the mobile liquid region or viscous liquid or rubbery region or tough plastic region that can be defined; usually, T g that lies in between 0.5 to 0.8 of the melting point and this is measured in Kelvin.

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So, polymer are synthesized and processed there are three distinct kind of steps. The first one is of course, polymerization which briefly I introduced in my first lecture; and the properties of the polymers are modified by inclusion of different types of additive material and once you are ready with the polymer, then the desired shape is given by various types of forming process.

So, we already introduced this polymer this kind of polymerization reaction, which is termed as addition polymerization. So, addition polymerization there is first a initiator is involved. So, R this dot this is a active initiator. So, it acts as a catalyst for ethylene to make this polyethylene structure. So, this is the initiation part and then it propagates and finally, it is terminated.

So, these three steps are quite distinct. So, the propagation actually involves the linear growth of the polymer. Now, the termination part can be this two types. In the first type this two active end propagates chain may link. So, here this R is there one active group and another active group somehow they met and then these two are basically blocked. So, your polymer polymerization is terminated.

And second one is this growing molecules they react to form a double bond so, double chain as has been shown by this green panel and then also the termination of the polymer is possible. So, this addition polymerization this having three steps, three distinct steps of initiation propagation and termination.

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Another type is a condensation polymerization, then example is given that ethylene glycol is one part and it is terephthalic acid it is reacting for polymerization. And it basically forms polyester polyethylene tetraphthalate which is PET that is the reaction between ethylene glycol and terephthalic acid. And this is a stepwise process successfully successively, it is repeated and it produces a linear molecule. And reaction time for condensation are usually a bit longer than additional polymerization.

And these thermosetting polyesters and phenol-formaldehyde, the nylons, and polycarbonates they are actually produced by this condensation polymerization, where water is coming out due to this reaction it is unlike this chain addition. And this also includes the tri-functional or higher functional monomers capable to form a cross-linked structure network polymer polymeric structure that is also possible.

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So, these two are the main mechanism of polymerization additionally, you may would like to add foreign substances we call its additive is intentionally introduced in the polymer to make it more serviceable. So, these are called filler materials or sometimes plasticizers are used, sometimes coloring agents are also used and sometimes fire retardant materials are used.

So, popular fillers include wood flour, the saw dust, and sand or glass, sometimes clay limestone's are also used a finer particle about 10 nanometer of microscopic dimensions. And this can be considered as a composite material because foreign materials are being added with the polymer. So, fillers make the polymeric material inexpensive.

Plasticizers usually they are liquid with low vapor pressure that lowers the T g and the ambient condition the polymer may be used in the application that requires some degree of ductility. So, thin sheet making or tubing etcetera if it is done then this plasticizer is useful. Eventually they increase the interchange distance with a reduction of secondary intermolecular bonding so, that gives some kind of plasticity to form the film structure of the polymers.

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Stabilizer they are basically used certain polymers they deteriorates when you have UV radiation or when it is exposed to oxygen ambient. So, this stabilizer these are used in the polymer that either absorbs the UV radiation or either consume the oxygen's to prevent this kind of deterioration of the polymer.

Sometimes colorants are used two types are popular, one is dye type which actually dissolves in the polymer another is the pigment types, that is also a filler material which does not dissolve, but remain as a separate phase. Certain flame retardants are used because most of the polymer they are flammable.

So, the combustion process this is inhibited by the use of this flame retardants. So, these are the filler materials I mean the secondary materials that is used during polymer processing once the polymerization takes place.

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After that there comes the forming techniques of the plastic. So, the in general consideration whether it is thermoplastic or thermosetting, this if it is thermoplastic, then what is the softening temperature, what is the atmospheric stability of this polymer and also whether it is a simplified shape that you are trying to make or it is a complicated shape.

So, thermoplastics if amorphous they formed above their glass transition temperature above melting temperature if semi-crystalline, if it is amorphous then glass transition temperature, beyond glass transition temperature or if it is semi-crystalline then above melting temperature the applied pressure is maintained during cooling so, that the shape is maintained and thermoplastics are recyclable. So, you can reuse the plastic made article.

Fabrication of thermosetting polymers they basically we use two step process; the first one is a linear polymer is having liquid having a lower molecular weight is prepared and in second stage it is cured.

So, curing is carried out in a mold having a desired shape. During curing a cross-linked network structure forms and after curing the thermosets are difficult to recycle so, it is chemically inert and can be used at relatively high temperature. So, these two types of plastic have their relative advantage and disadvantages.

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Now, for compression molding, I mean you can use both of them as you can see it is just a some type of press where you can simultaneously heat this also. So, the preform in the form of a either a mix or a cold pressed pellet, that is used. So, first you need to preheat it, so that reduce the molding time and then you just press it from the shape and then keep it hot and then cool it down and take it up.

So, this is an inexpensive process, it has a variety variation which is transfer molding the solid ingredients is first melt here and heat in a heated container and then the molten material is injected into the mold chamber as has been shown. So, the pressure distribution is more uniform and usually that transfer molding is used with thermosetting polymers and usually that is useful when the shape is quite complex.

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Injection molding is also used in case of thermoplastic polymer as well as thermosetting polymers in case of; thermo plastic polymer the cycling time is quite less. So, the charge as you can see is pushed here there is a ram and is a hot zone here. So, you first push it. So, it the pressure is pushed here and the polymer goes to the mold unless it is solidified.

So, cycling time is very high in case of a thermoplast for thermoset curing takes place when the material is under pressure in the heated mold and it has a longer processing time. And sometimes the reaction it is termed as the reaction injection molding; reaction injection molding is commonly used for materials such as polyurethane. So, it is a simple processing of the polymeric material.

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Extrusion is another technique a mechanical screw is here that propels through the chamber and where pelletized material is used initially, from the polymer it is pelletized and they form a viscous fluid extrusion takes place in the molten mass here is pushed through a die orifice.

And solidification takes place here and this is this can be expedite by blowing with a water spray to make it cooling cooled mass and usually it is adopted for tubes or sheets etcetera. One variation is blow molding similar to that is used for glass bottles. So, this viscous mass is blown with air to form the shape or like metal you have casting you can cast the polymer also.



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Usually polymer films are also used because for the polymer bag which is now banned in most of the places, but it has a huge market. So, this is extruded here as you can see and then simultaneously it is blown with air. So, this air bubble they form a sheet something like this and there is a guided roller it rolls on top of it and forms a sheet of polymer.

So, a positive gas pressure is maintained inside this tube and by drawing the film in the axial direction it emerges from the die and the material expands around this trapped like a balloon and you get a continuous roll of polymer films.

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So, in this particular lecture, we talked about the deformation of the elastomer: and large extension is possible for amorphous and lightly cross-linked elastomer and deformation corresponds to the un kinking or uncoiling of the cross chains, crosslinking is basically achieved during vulcanization. Many elastomers and called copolymers are considered for this purpose.

And then crystallization, melting and glass transition phenomena we have introduced, and we talked about the melting and glass transition temperature for certain polymeric materials. And, then we have introduced the factors which influence melting and glass transition temperatures.

And finally, polymer processing was introduced its having three steps; one is the polymerization, two types of polymerization we have described; one is the decision polymerization and addition polymerization. Then the effect of the additives are introduced and finally, certain popular forming techniques of the plastics and that we have described.

Thank you for your attention.