Introduction to Polymer Science

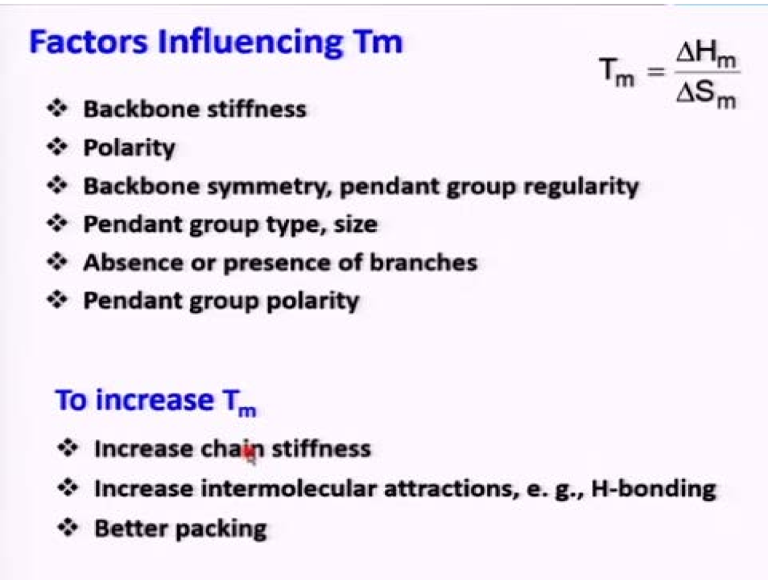
Prof. Dibakar Dhara
Department of Chemistry
Indian Institute of Technology – Kharagpur

Module No # 08
Lecture No # 37

Thermo Properties: Factors Influencing T_m, Determination of T_g and T_m, Other Thermal Properties, Thermochemical Properties

Welcome back, in this lecture I will continue my discussion on thermal properties of polymers.

(Refer Slide Time: 00:33)



Factors Influencing Tm

$$T_m = \frac{\Delta H_m}{\Delta S_m}$$

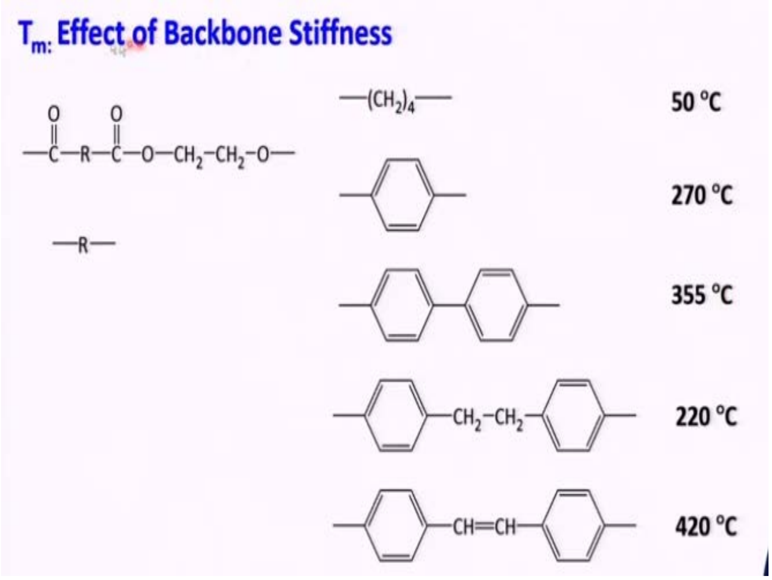
- Backbone stiffness
- Polarity
- Backbone symmetry, pendant group regularity
- Pendant group type, size
- Absence or presence of branches
- Pendant group polarity

To increase T_m

- Increase chain stiffness
- Increase intermolecular attractions, e. g., H-bonding
- Better packing

In the last slide of last lecture, we discussed the different factors which can influence the value of T_m e.g. increase in chain stiffness and with increase in intermolecular attraction between polymer chains and simple, symmetric structures which enable better packing increase the T_m, because these factors actually help in crystallization process.

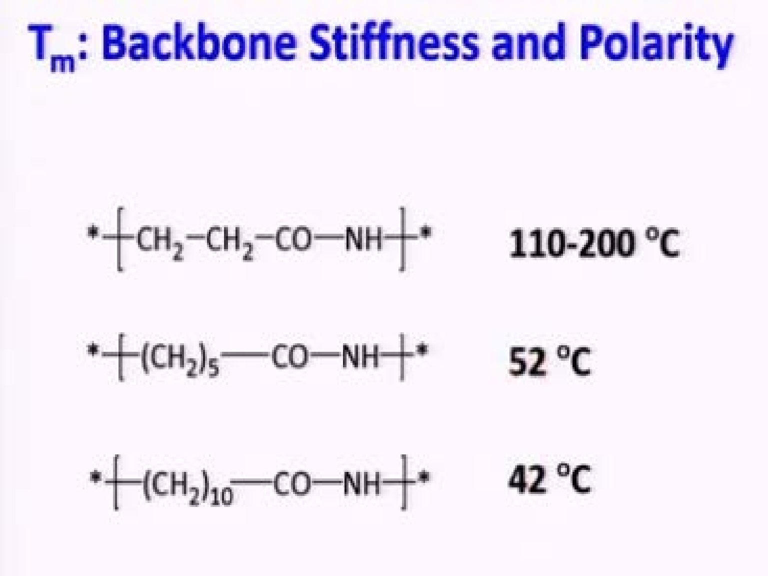
(Refer Slide Time: 01:14)



$T_{m:}$ Effect of Backbone Stiffness

Now I will give you examples., for in this case, let us compare the value of T_m by varying R as shown in the slide. If you compare between an aliphatic chain and an aromatic group obviously the latter is much stiffer, because single bond rotations is not possible in this case. Hence, stiffness goes up drastically, as a result T_m will also go up. If you go down the list, increase in the stiffness is even higher, you should expect that T_m would be even higher. When we are introducing more and more flexible groups, the T_m should come down. If we go from single bond to double bond, then we introducing more rigidity, more stiffness due to restricted rotation. So, T_m goes up significantly if you look at the numbers shown in the slide.

(Refer Slide Time: 02:58)

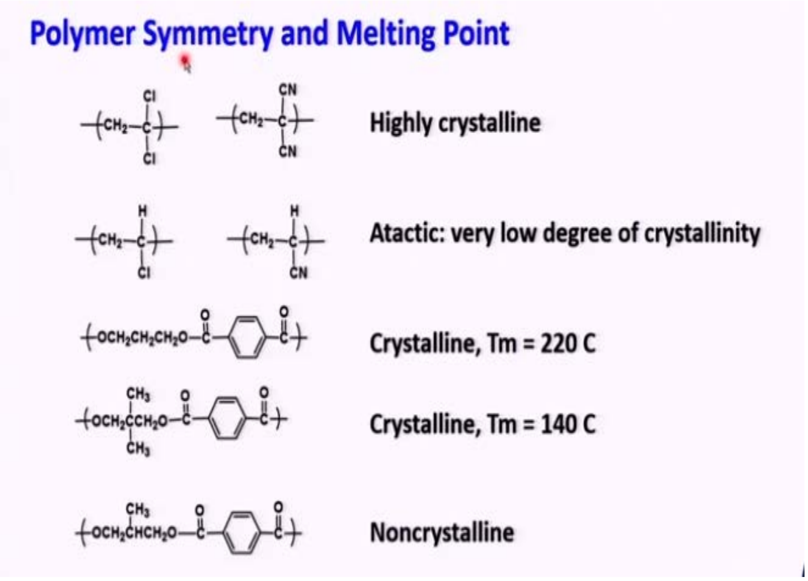


T_m: Backbone Stiffness and Polarity

$*\!-\!\left[CH_2-CH_2-CO-NH\right]\!-\!*$	**110-200 °C**
$*\!-\!\left[(CH_2)_5-CO-NH\right]\!-\!*$	**52 °C**
$*\!-\!\left[(CH_2)_{10}-CO-NH\right]\!-\!*$	**42 °C**

In this example we will basically combine two factors, backbone stiffness and polarity. If you compare between amide group and a C-C bond, obviously C-C bond will be more flexible because this single bond rotation is much more feasible in this case. If you observed carefully, as we increase the number of - CH_2 groups, the chains become more flexible or less rigid. Similarly, as we increase the number of - CH_2 groups, we are also decreasing the weight fraction of the functional group, e.g. the -$CONH_2$ group as shown in the slide. This group actually increases the intermolecular attraction because of hydrogen bonding present between the amide groups. Hence, by increasing the -CH_2 groups, we are also decreasing the polarity and intermolecular attraction between the polymer chains, hence, the T_m should be expected to go down, as is apparent from the values shown.

(Refer Slide Time: 04:41)



Polymer Symmetry and Melting Point

Highly crystalline

Atactic: very low degree of crystallinity

Crystalline, Tm = 220 C

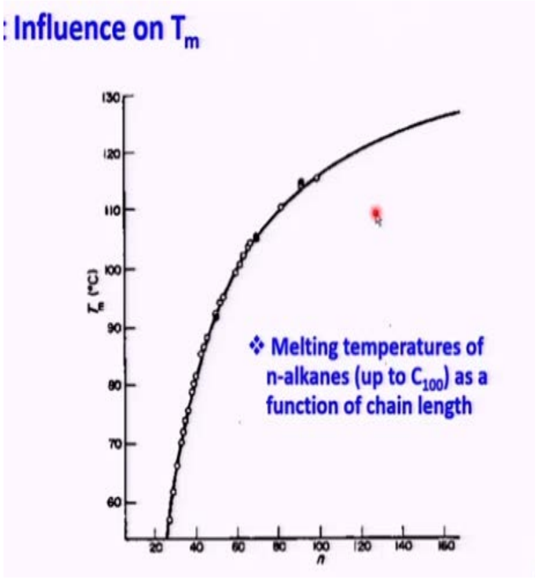
Crystalline, Tm = 140 C

Noncrystalline

Similarly, if we compare symmetry and melting point, we can see that if the molecule is more symmetric, then it is the highly crystalline. When the symmetry is lost, e.g. when one substituent is H and another is Cl, or CN and H, or for atactic polymers, then it has a very low degree of crytallinity. If they are isotactic, then there is a possibility that it will have crystallinity.

For molecules with more symmetry and simpler structures, the feasibility to undergo crystallization is much more and the T_m for this is much higher. So stiffness increases the T_m, the intermolecular attraction increases T_m, and molecular symmetry, regular structure also increases T_m for polymer chains.

(Refer Slide Time: 06:16)

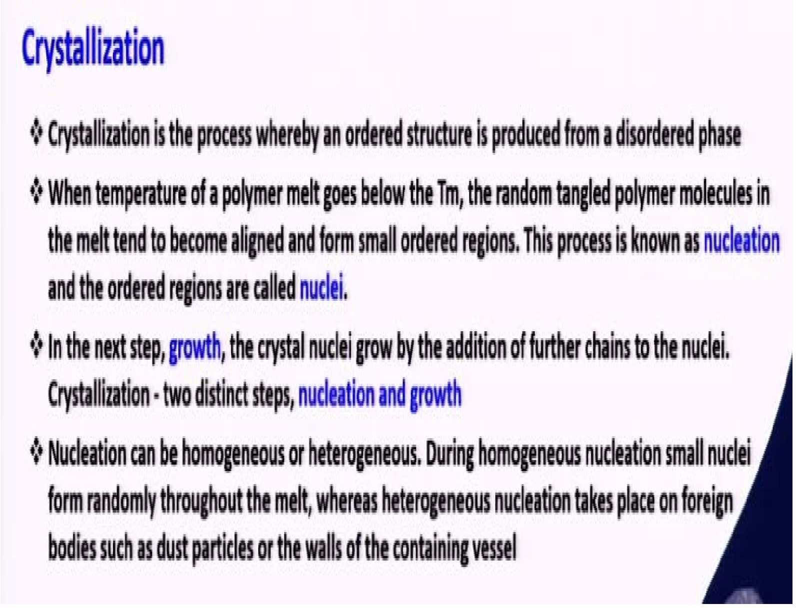


: Influence on T_m

- Melting temperatures of n-alkanes (up to C_{100}) as a function of chain length

Molecular weight also influences T_m but beyond a certain molecular weight it tends to level off. The data shown is for n alkanes up to C_{100}. You can see that after about n say 80 or something, it kind of levels off. Generally, the types of molecular weight we use in commercial application for the synthetic polymers, the molecular weights are quite high. So, the dependence of molecular weight, the dependence of T_m on molecular weight in that range becomes less important.

(Refer Slide Time: 07:12)

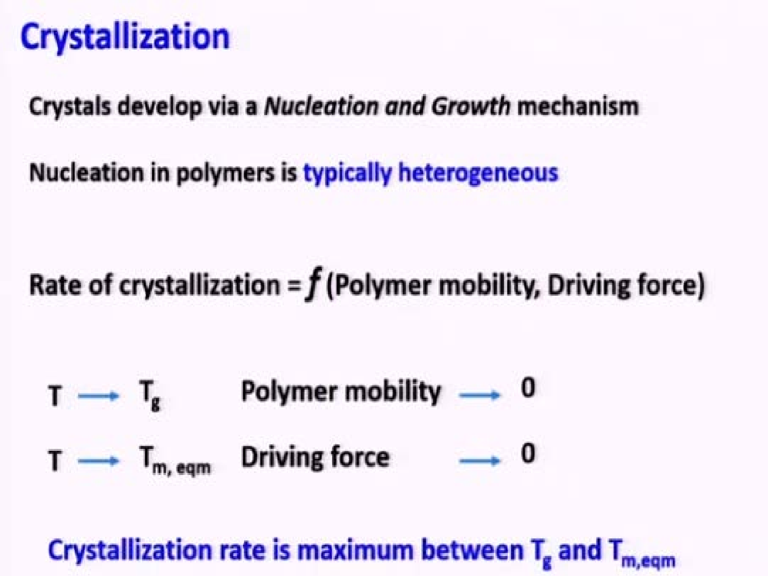


Crystallization

- Crystallization is the process whereby an ordered structure is produced from a disordered phase
- When temperature of a polymer melt goes below the Tm, the random tangled polymer molecules in the melt tend to become aligned and form small ordered regions. This process is known as nucleation and the ordered regions are called nuclei.
- In the next step, growth, the crystal nuclei grow by the addition of further chains to the nuclei. Crystallization - two distinct steps, nucleation and growth
- Nucleation can be homogeneous or heterogeneous. During homogeneous nucleation small nuclei form randomly throughout the melt, whereas heterogeneous nucleation takes place on foreign bodies such as dust particles or the walls of the containing vessel

Now we will discuss the crystallization process. Crystallization is the process whereby an ordered structure is produced from a disordered phase. Disordered phase could be from polymer melt or a polymer solution, most cases of course we deal with polymer melt. We will talk about crystallization process from polymer melt. When the temperature of polymer melt goes below the T_m, the random tangled polymer molecules in the melt tend to become aligned and forms small ordered regions. This formation of small ordered regions is the process called nucleation and the ordered regions are called nuclei. The process of forming these small ordered regions is called nucleation and the ordered regions are actually called nuclei. Now once this happens then growth happens in the next steps when more and more polymer chains come and form crystal on the nuclei. Crystallization has two distinct steps - one is nucleation where formation of nuclei, and next is growth. Nucleation can be homogeneous or heterogeneous, in case of homogenous nucleation, small nuclei form randomly throughout the melt. Whereas heterogeneous nucleation takes place on foreign bodies, such as dust particle or walls of container. Sometimes, we deliberately add some external agents which are called nucleating agents which basically act as the point where nucleation can take place. Since polymer crystallization happens mostly through heterogeneous nucleation and not through homogenous nucleation, the substance which are added to induce crystallinity or to induce nucleation process is called nucleating agent.

(Refer Slide Time: 09:58)



Crystallization

Crystals develop via a *Nucleation and Growth* mechanism

Nucleation in polymers is typically heterogeneous

Rate of crystallization = f (Polymer mobility, Driving force)

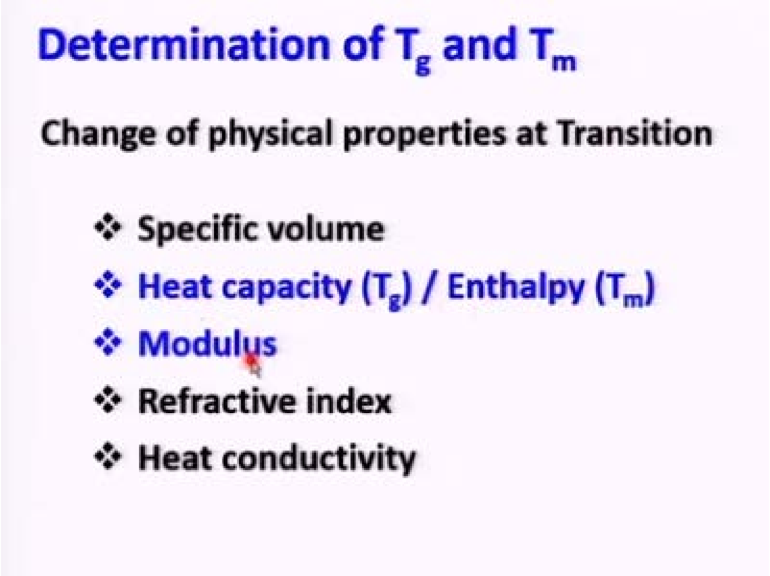
$T \longrightarrow T_g$ Polymer mobility $\longrightarrow 0$

$T \longrightarrow T_{m,\,eqm}$ Driving force $\longrightarrow 0$

Crystallization rate is maximum between T_g and $T_{m,eqm}$

Crystal develops via nucleation and growth mechanism as we discussed in the last slide and as I discussed also, the nucleation in polymers are generally heterogeneous, and we had nucleating agents to induce nucleation in polymers. Now, rate of crystallization in polymer samples depend on polymer mobility as well as driving force. Now if, we take a polymer sample and then heat it slowly then above T_g it has sufficient mobility but the temperature goes towards T_m then the driving force will become lower and lower. So, when the temperature is around T_g the polymer mobility becomes zero if we increase the temperature above T_g then we slowly start to induce polymer mobility. When the temperature is close to melting point, equilibrium melting point then driving force also will become zero. But if we decrease the temperature below the equilibrium melting point then obviously the tendency to crystallize will be much higher because the temperature of the experiment is below the equilibrium melting point. Hence, if we increase the temperature above T_g, it helps in crystallization and if we decrease the temperature below T_m it also helps in crystallization. So, there is an intermediate temperature where it is maximum, crystallization is maximum between T_g and T_m. There is a particular temperature where generally crystallization happens if we start to anneal a polymers sample and that temperature is called T_c or crystallization temperature.

(Refer Slide Time: 12:27)



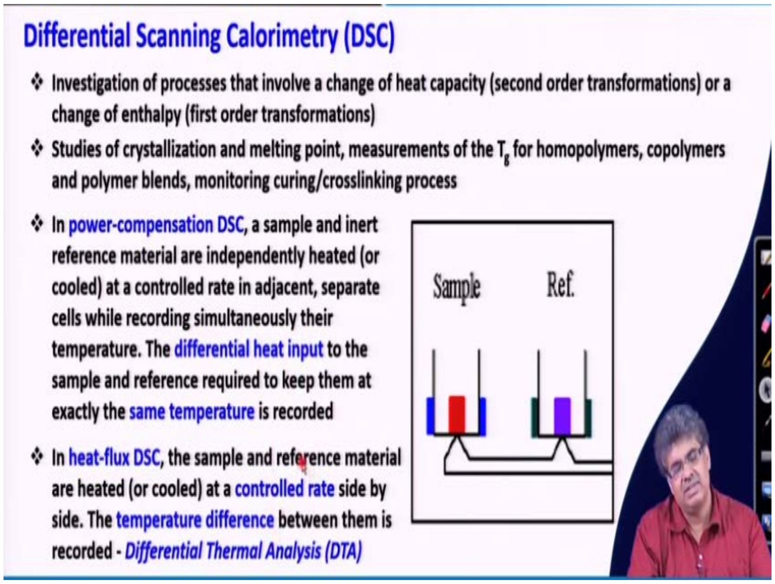
Determination of T_g and T_m

Change of physical properties at Transition

- Specific volume
- Heat capacity (T_g) / Enthalpy (T_m)
- Modulus
- Refractive index
- Heat conductivity

We now discuss the determination of the values of glass transition and melting point of a polymer sample. For that, we need to probe the physical properties at transition. There are several physical properties which undergo drastic change or discontinuous change at this transition. For example, heat capacity changes discontinuously in case of T_g and enthalpy changes in case of T_m. Specific volume or density also changes in these transitions, modulus or the mechanical properties also change, refractive index and conductivity also change. So, we can utilize or we can follow any of these properties as the function of temperature to find out or to determine the glass transition temperature and melting point. But generally, very two common methods which are used to determine T_g and T_m are differential scanning calorimetry, which basically utilizes the discontinuous change is in either heat capacity of enthalpy with respect to temperature. Other mechanical property, temperature dependent mechanical property where modulus is followed or probed or monitored with respect to temperature as the function of temperature to find out T_g and T_m. Let me discuss this differential scanning calorimetry first in details and later on, I will discuss about this property in later lecture.

(Refer Slide Time: 14:30)



Differential Scanning Calorimetry (DSC)

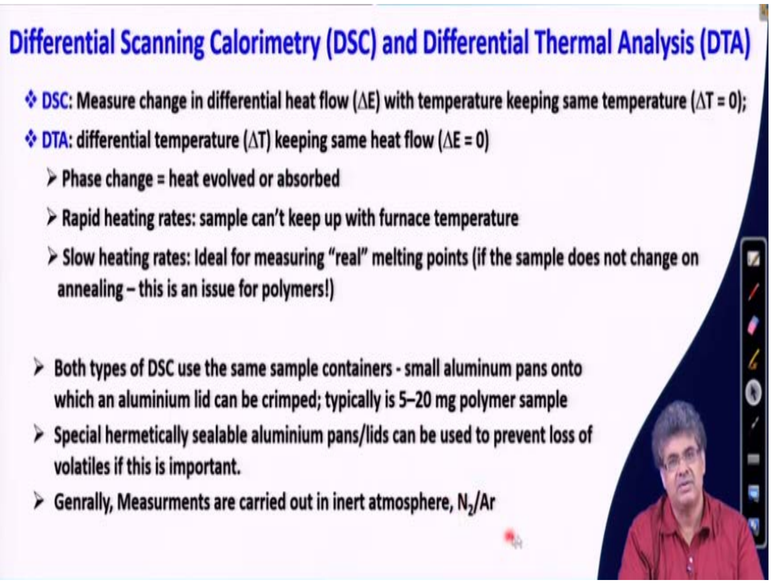
- Investigation of processes that involve a change of heat capacity (second order transformations) or a change of enthalpy (first order transformations)
- Studies of crystallization and melting point, measurements of the T_g for homopolymers, copolymers and polymer blends, monitoring curing/crosslinking process
- In power-compensation DSC, a sample and inert reference material are independently heated (or cooled) at a controlled rate in adjacent, separate cells while recording simultaneously their temperature. The differential heat input to the sample and reference required to keep them at exactly the same temperature is recorded
- In heat-flux DSC, the sample and reference material are heated (or cooled) at a controlled rate side by side. The temperature difference between them is recorded - *Differential Thermal Analysis (DTA)*

In differential scanning calorimetry, in short DSC is used to investigate the process that involves changes in heat capacity, second order transition like T_g or a change in enthalpy, and first order transitions like melting. Studies of crystallization and melting point measurement, T_g for homo-polymers, copolymers, polymer blends can be done using DSC method. We can also monitor other chemical events like curing, crosslinking and some degradation or some reactions happen that can be also monitored by using different calorimetry.

Any process which basically heat release or absorption by a system, can be followed using DSC. DSC is actually of two types, one is power compensation DSC. In this case, one sample and one inert reference material is used where inert means it does not undergo any phase change or transition in the temperature range where we will do the experiment. In case of power compensation DSC, these two, sample and reference material are heated up maintaining a fixed temperature. In this case, same temperature is maintained and the differential heat input to maintain this same temperature between sample and reference is plotted as a function of temperature. In case a transition happens, which will require either more heat to be supplied if there is endothermic process, or some heat evolution by the system in case of exothermic process and there will be less requirement for heat supply from outside to maintain the temperature.

This is followed in case of power compensation DSC or in simple DSC. There is another DSC, which is called heat flux DSC, where both the sample and reference are heated at a controlled rates. They are heated at same rate at by supplying same amount of energy but the difference in the temperature between sample and reference are plotted as a function of temperature. In case of any exothermic or endothermic events happening, there will be deviation of this temperature and difference between reference and the sample. This method is generally also referred as differential thermo analysis or DTA. We can also say both these methods as differential calorimetry as well.

(Refer Slide Time: 18:25)



Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA)

- **DSC**: Measure change in differential heat flow (ΔE) with temperature keeping same temperature ($\Delta T = 0$);
- **DTA**: differential temperature (ΔT) keeping same heat flow ($\Delta E = 0$)
  - Phase change = heat evolved or absorbed
  - Rapid heating rates: sample can't keep up with furnace temperature
  - Slow heating rates: Ideal for measuring "real" melting points (if the sample does not change on annealing – this is an issue for polymers!)

- Both types of DSC use the same sample containers - small aluminum pans onto which an aluminium lid can be crimped; typically is 5–20 mg polymer sample
- Special hermetically sealable aluminium pans/lids can be used to prevent loss of volatiles if this is important.
- Genrally, Measurments are carried out in inert atmosphere, N_2/Ar

DSC measure changes in differential heat flow with temperature keeping same temperature of both sample and the reference. In case of DTA, the heat flow is same, Δ is same but the differential temperature or ΔT is monitored as a function of temperature. In case of phase change there could be heat evolved or adsorbed depending on it is exothermic process or endothermic process.

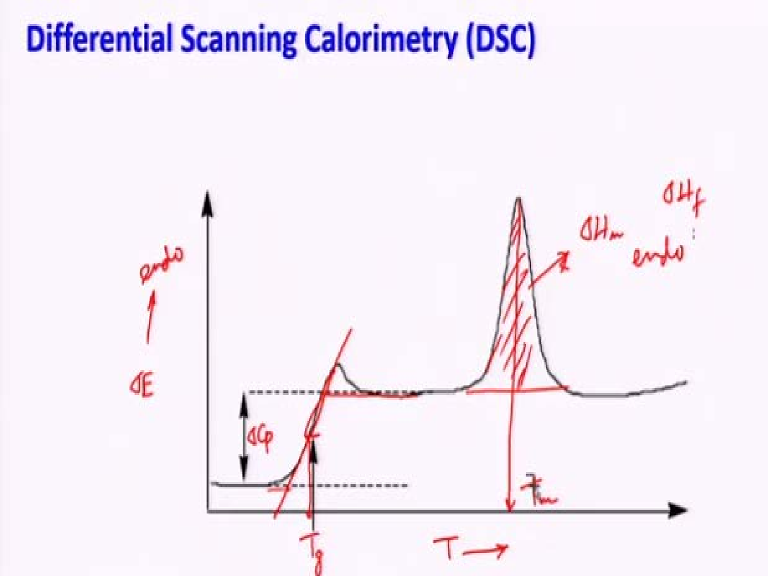
One thing also need to be noticed, if you supply heat from outside rapidly, then the sample may not actually follow this heat flow because the sample might require little longer time to actually overlap the heat flow or basically capture the heat properly. If the heating rate is high, then sample cannot keep up with the furnace temperature, so there could be an error in that measurement.

But if we do slow heating then we can actually have a proper measurement, but there is risk also in slow heating. If the sample is prone to crystallization, then on slow heating it might crystallize above T_g. As a result, the nature of the sample might change so the values which we will get that may not be reflecting the values for the original sample we started with. That is why, basically a balance is maintained, a moderate heating rate is applied in DSC or DTA.

Both these types of DSC, i.e. DTA or DSC, generally require small aluminum pans as sample container. Aluminum pans are used on which aluminum lid can be crimped so that nothing goes out during the measurement process. Typically, 5 to 20 mg polymer samples are used. Sometimes if the sample is volatile or liquid, then we use special hermetically sealable aluminum pans or lids that actually prevent loss of volatiles which are important.

Generally, the measurements are carried out at inert atmosphere like in presence of nitrogen or argon to prevent oxidative degradation of the polymer molecules in presence of air which complicates the measurements of T_g and T_m. Generally, unless it is specifically required, we do the measurement under inert atmosphere of nitrogen and argon.

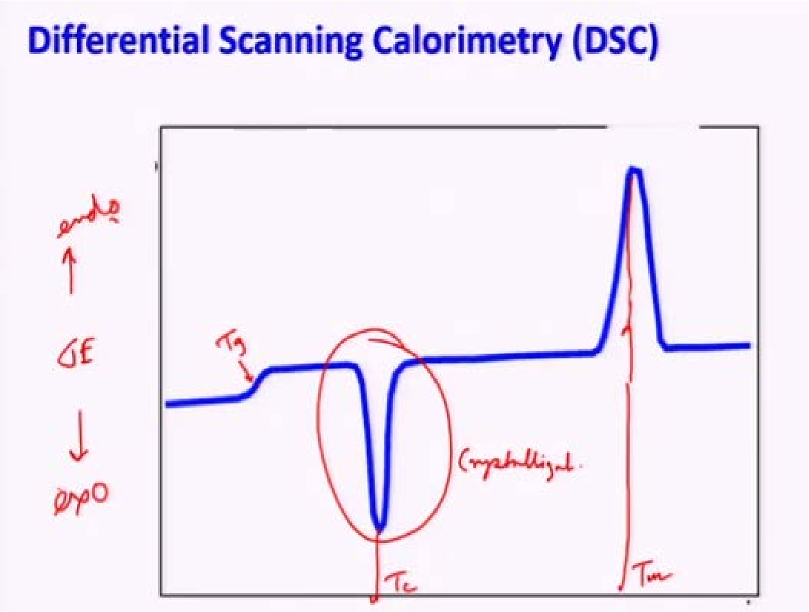
(Refer Slide Time: 22:01)



Differential Scanning Calorimetry (DSC)

This is what ideal DSC curves look like, if we plot the energy supplied and this is the temperature, and in this case, we are plotting this side endo. So, at T_g, the heat capacity of polymer samples changes so glass state will have lower C_p than the rubber state which generally have higher C_p. There will be a change in the C_p value of the glass and the midpoint of this transition is the value of T_g that is generally considered. This difference is ΔC_p, the difference in the heat capacities. The melting process is generally endothermic so we have a peak towards endo direction. The area under this curve will give us the value of $\Delta H_{melting}$ or $\Delta H_{freezing}$ whatever you call. This value, generally the peak value, which is considered as the melting point of the polymer. So, from the single experiment we can get, if the sample is semi-crystalline, we can get T_g and T_m.

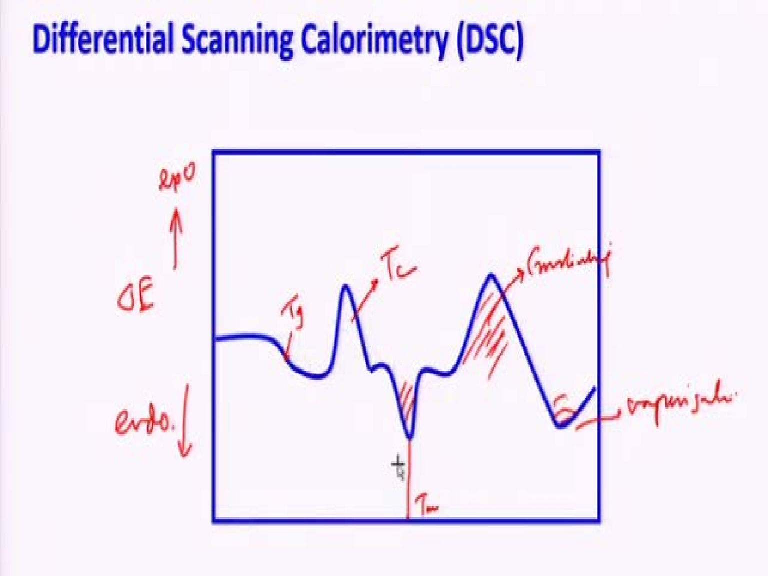
(Refer Slide Time: 24:36)



Differential Scanning Calorimetry (DSC)

If you do the heating very slowly and the sample is proven to crystallization, then it might happen that above T_g the sample might start getting crystallizing and you can get an exothermic peak for that. Crystallization is exothermic process, so you can get exothermic peak and the corresponding temperature we can call crystallization temperature or T_c. Once the crystallization happens if we heat further we will get the T_m for the crystal domains.

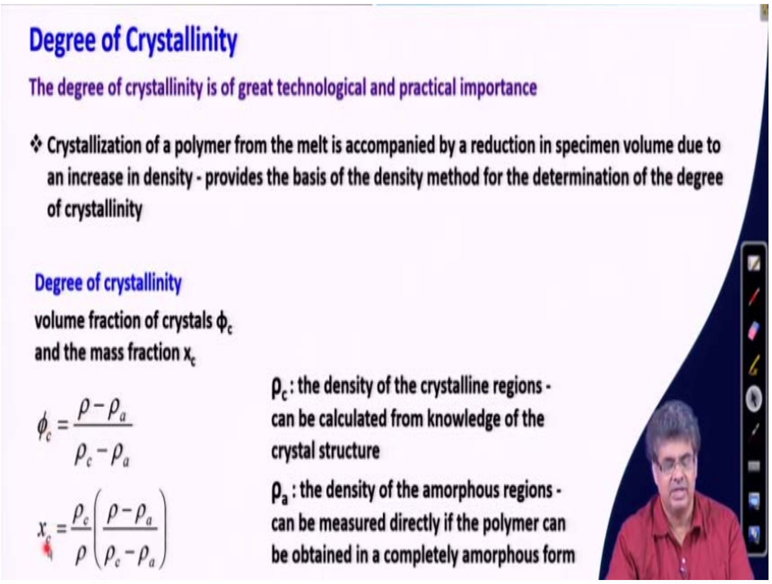
(Refer Slide Time: 26:34)



Differential Scanning Calorimetry (DSC)

We can also use DSC for getting the information about other events like crosslinking and there may be evaporation or vaporization of polymer. Sometime if there is some reaction happening which is either endothermic or exothermic that can be also observed using DSC. DSC is mostly used to determine T_g, T_c and T_m, but if the polymer sample undergoes other thermal events like crosslinking or vaporization or other reactions, that can be also monitored or probed by DSC provided those events do not overlap with either, T_g, T_m or T_c.

(Refer Slide Time: 28:24)



Degree of Crystallinity

The degree of crystallinity is of great technological and practical importance

- Crystallization of a polymer from the melt is accompanied by a reduction in specimen volume due to an increase in density - provides the basis of the density method for the determination of the degree of crystallinity

Degree of crystallinity

volume fraction of crystals ϕ_c
and the mass fraction x_c

$$\phi_c = \frac{\rho - \rho_a}{\rho_c - \rho_a}$$

$$x_c = \frac{\rho_c}{\rho}\left(\frac{\rho - \rho_a}{\rho_c - \rho_a}\right)$$

ρ_c : the density of the crystalline regions - can be calculated from knowledge of the crystal structure

ρ_a : the density of the amorphous regions - can be measured directly if the polymer can be obtained in a completely amorphous form

Now we will move to degree of crystallinity which is basically extent of crystallinity in a semi-crystalline sample. It is of great technological and practical importance, crystallization of polymers from melt is accompanied by reduction in specific volume due to an increase in density, and this provides the basis of density measurements for determination of degree of crystallinity.

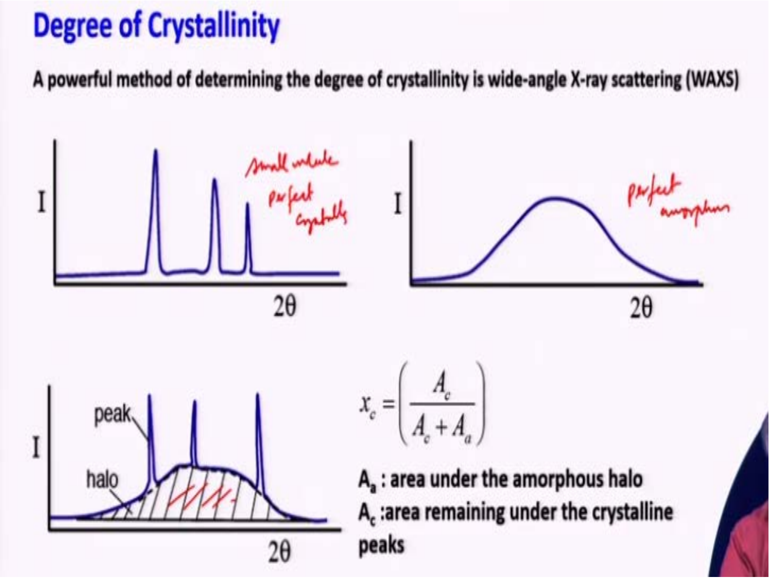
$$\Phi_c = \frac{\rho - \rho_a}{\rho_c - \rho_a}$$

$$x_c = \frac{\rho_c}{\rho}\left(\frac{\rho - \rho_a}{\rho_c - \rho_a}\right)$$

If we know basically density of 100% crystalline polymer then using that information and a 100% amorphous polymer, we can get the extent of crystallinity for a semi-crystalline sample. Degree of crystallinity is generally represented by volume fractions of crystals or mass fractions of crystals, and they are expressed by these simple equations where this ρ is the corresponding density. So ρ_c is the density of a 100% crystalline polymer and ρ_a is the density of 100% amorphous polymer and this row is the crystallinity of the actual sample or the same crystalline polymer whose degree of crystallinity we are going to determine. We can get this information like we can get the density of amorphous polymer easily if we quench cool the polymer sample from melt then we can actually get a 100% amorphous polymer whose density we can measure.

For 100% crystalline polymer is not possible, so for that we can use some model or theoretical studies to find that out. From the crystal structure we can find out the density value or value of ρ_c and ρ_a can be obtained from experiment and ρ can be also obtained from experiment. So from that we can get this value of ϕ_c and x_c.

(Refer Slide Time: 30:58)



Degree of Crystallinity

A powerful method of determining the degree of crystallinity is wide-angle X-ray scattering (WAXS)

$$x_c = \left(\frac{A_c}{A_c + A_a}\right)$$

A_a : area under the amorphous halo

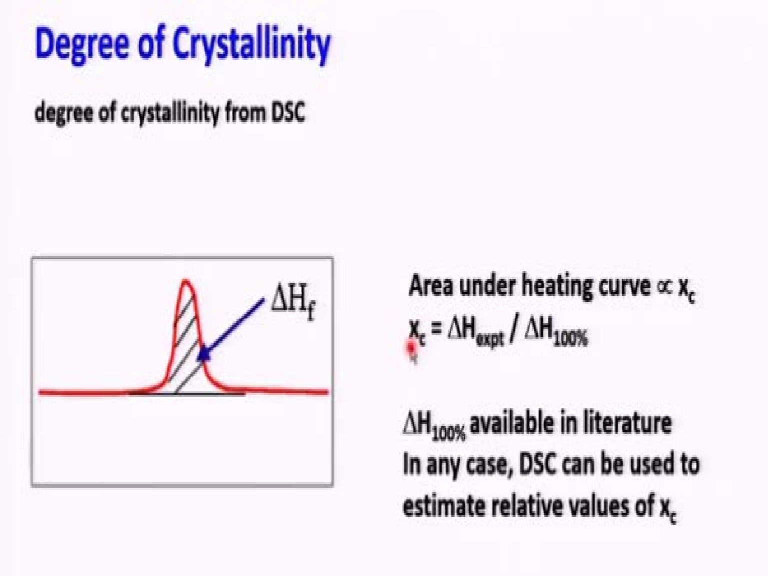
A_c :area remaining under the crystalline peaks

The other methods to determine crystallinity is wide angle X-ray scattering and this is generally for small molecule crystallite where we have a sharp crystalline peak. A small molecule perfect crystal is taken and also a 100% amorphous sample. For a semi crystalline polymer, we can get a mixture of crystalline peaks and amorphous halo as shown here.

$$x_c = \left(\frac{A_c}{A_c + A_a}\right)$$

From the ratio of the area under this crystalline peaks and this amorphous region, we can actually get the degree of crystallinity, which is given by the area under crystalline peaks and divided by the area under the crystalline peaks plus the area under the amorphous halo, which will give the weight fraction of crystallinity or degree of crystallinity.

(Refer Slide Time: 32:22)



Degree of Crystallinity

degree of crystallinity from DSC

Area under heating curve ∝ x_c

$x_c = \Delta H_{expt} / \Delta H_{100\%}$

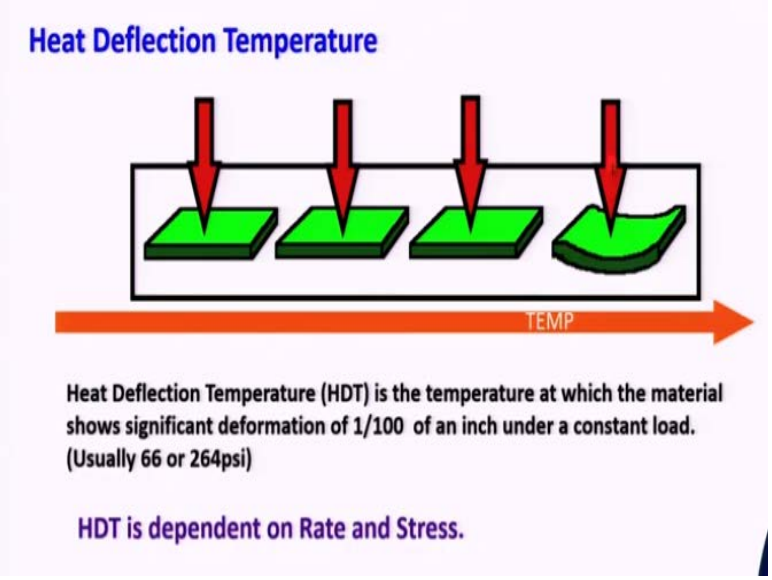
$\Delta H_{100\%}$ available in literature

In any case, DSC can be used to estimate relative values of x_c

We can also use the DSC. From DSC, from the area under the curve we can get the value of enthalpy of melting for that particular sample, and if we know or we can calculate the enthalpy of melting for the pure 100% crystalline polymer from the knowledge of crystal structure. Then, from the ratio we can get the value of degree of crystallinity. This is very important because degree of crystallinity actually determines to a large extent the properties of semi-crystalline polymers.

$$x_c = \Delta H_{expt}/\Delta H_{100\%}$$

(Refer Slide Time: 33:17)



Heat Deflection Temperature

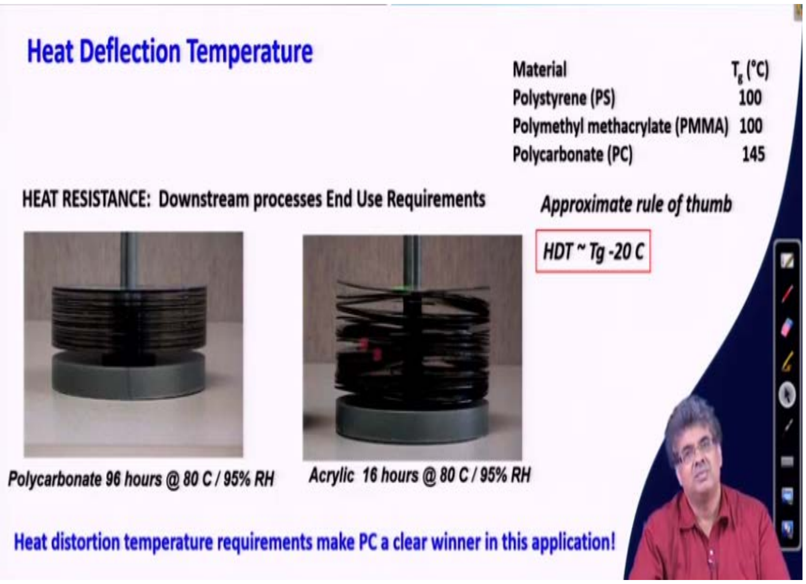
Heat Deflection Temperature (HDT) is the temperature at which the material shows significant deformation of 1/100 of an inch under a constant load. (Usually 66 or 264psi)

HDT is dependent on Rate and Stress.

There other transition temperatures, which are more of from a practical aspect like heat deflection temperature. This is from a practical point of view, that in an application we do not measure T_g or T_m. If we use a polymer under some load, then till what temperature it can sustain the load that is more important than the T_g or T_m value for the inherent polymer. Of course in that case the temperature till which it can sustain the load will depend on the load itself.

If the load is higher, the temperature will be lower in that case, so heat deflection temperature or HTD is the temperature at which the material show significant deformation of about 1 / 100 of an inch under constant load. The load is usually 66 or 264 psi as I described, HDT is dependent on the rate and the stress at which this load is applied. This is more from a practical point of view as you can see from these pictures, as you increase, this is the load, constant load, as we increase the temperature, at some temperature the bending happens. This is the temperature we call heat deflection temperature and this will depend on the rate at which we are applying the stress and the amount of stress we are applying.

(Refer Slide Time: 35:08)



Heat Deflection Temperature

Material	T_g (°C)
Polystyrene (PS)	100
Polymethyl methacrylate (PMMA)	100
Polycarbonate (PC)	145

HEAT RESISTANCE: Downstream processes End Use Requirements

Approximate rule of thumb

HDT ~ Tg -20 C

Polycarbonate 96 hours @ 80 C / 95% RH

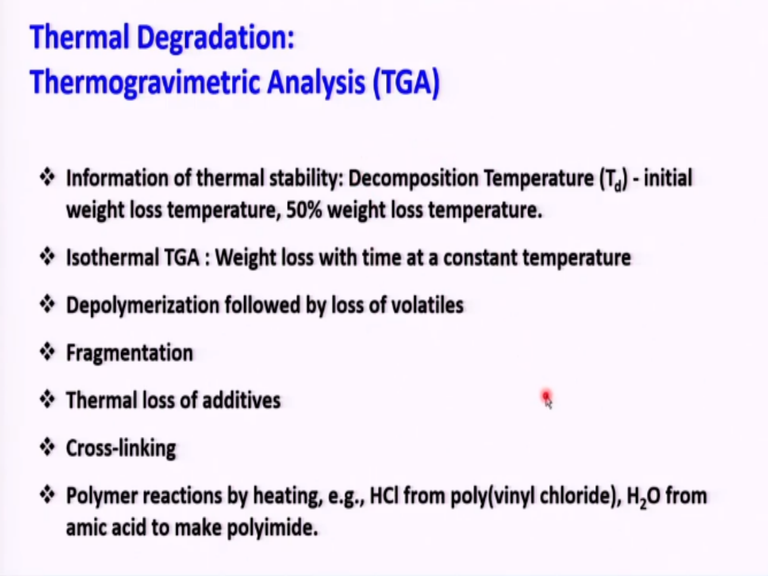
Acrylic 16 hours @ 80 C / 95% RH

Heat distortion temperature requirements make PC a clear winner in this application!

Practical example like, if we talk about DVDs or CDs made up of polymethyl methacrylate (T_g is about 100°C) and polycarbonate (T_g is 145 °C). Look at the experiment done. The PMMA CDs become bend and non-usable at 80 °C under the load of the CDs itself, whereas polycarbonate is unaffected at this temperature and this humidity. So basically we should know the value of T_g and T_m for a semi-crystalline polymer, but we should also keep in our mind what the final application is. Depending upon that we also need to generate or use some other thermal measurements like HDT and some others like vicat temperature.

What I am just trying to mention that not only knowing the value of T_g and T_m will be sufficient from a practical point of view, one should also do experiments which are closed to the application where the polymers are meant for.

(Refer Slide Time: 36:50)

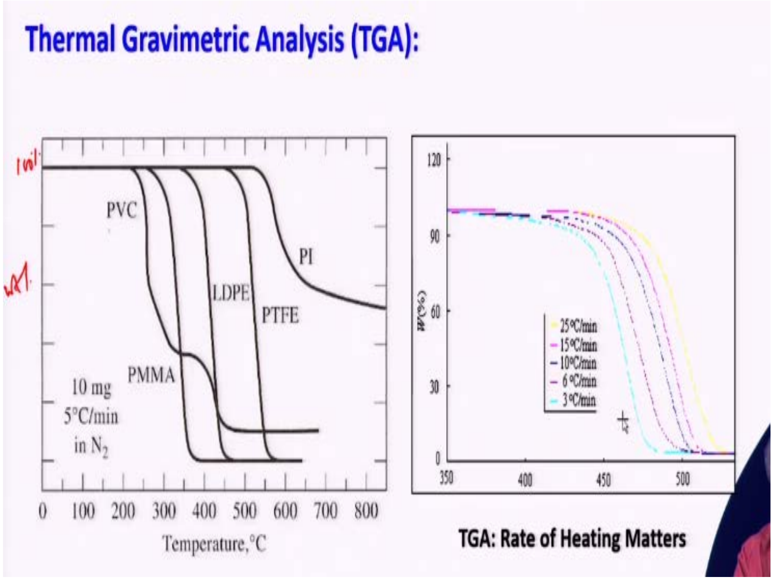


Thermal Degradation:
Thermogravimetric Analysis (TGA)

- Information of thermal stability: Decomposition Temperature (T_d) - initial weight loss temperature, 50% weight loss temperature.
- Isothermal TGA : Weight loss with time at a constant temperature
- Depolymerization followed by loss of volatiles
- Fragmentation
- Thermal loss of additives
- Cross-linking
- Polymer reactions by heating, e.g., HCl from poly(vinyl chloride), H_2O from amic acid to make polyimide.

Now I will discuss about thermal degradation, which is given by or determined by thermo-gravimetric analysis. As the name suggests it is a gravimetric analysis, polymer samples are heated and the weight of mass of the polymer is followed using a balance. Thermo-gravimetric analysis or TGA gives information about thermal stability. Generally the temperature from which it starts to lose its mass or weight, we call it decomposition temperature or initial weight loss temperature. We can also use another term, 50% weight loss temperature where in the temperature at which 50% weight loss happens. We can actually keep the sample at a particular high temperature and follow the weight loss with time at a constant temperature and we call that as an isothermal thermo-gravimetric analysis. We can follow de-polymerization process and loss of volatiles. We can follow fragmentation, thermal oxidation of additives, cross-linking or polymer reactions by thermo-gravimetric analysis. These are kind of indirect analysis, not direct analysis, to find the change in mass of the sample as the function of temperature. In this case also, generally inert atmosphere is used like nitrogen or argon, but if we want to find out oxidative stability of a polymer sample then we need to do this thermo-gravimetric analysis in air or in presence of oxygen.

(Refer Slide Time: 39:01)



Thermal Gravimetric Analysis (TGA):

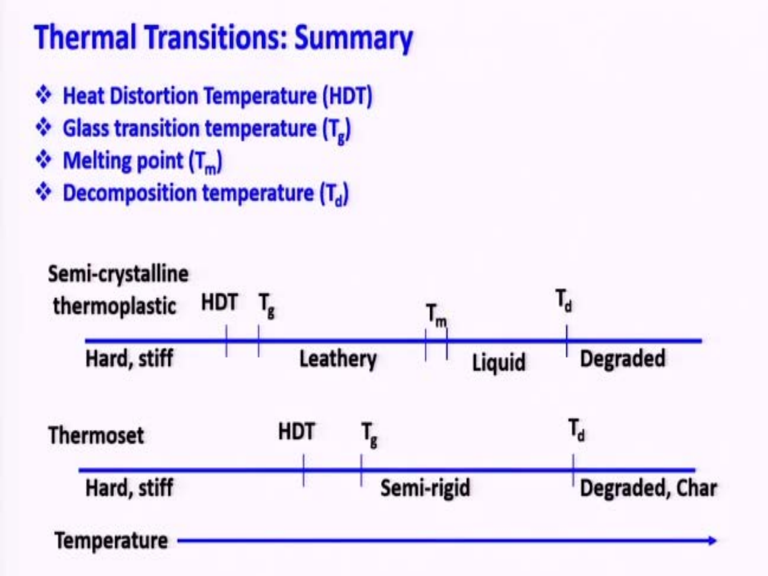
TGA: Rate of Heating Matters

An example of thermal stability of few polymers, PVC or polyvinyl chloride, PMMA, LDPE, PTFE, PI is given where weight percentage is plotted against temperature. At some temperature, the sample starts losing weight and it almost becomes 0% or losses everything at extremely high temperature. This temperature where the loss starts is called onset temperature, T_d onset, and this temperature where 50% weight loss happen we call T_d half or T_d 50%.

These actually are used to compare the thermal stabilities of different polymers. In this case PI is a much more stable than a PVC or PMMA. This stability also depends on the heating rate. If we heat the polymers faster then, as I discussed earlier, then polymer sample cannot follow the furnace temperature. So effective temperature the polymer sees is much lower compared to actual temperature, which is shown by the thermometer.

If we heat faster, then the stability or the T_d half or T_d onset is actually little higher. Generally, we heat the samples around 10 °C per min to have a balance. If we heat too slowly then the experiment takes much longer time which we cannot afford all the time. So generally, we heat about 10 °C / minute, standard heating ratio find out the thermal stability.

(Refer Slide Time: 41:19)



Thermal Transitions: Summary

- Heat Distortion Temperature (HDT)
- Glass transition temperature (T_g)
- Melting point (T_m)
- Decomposition temperature (T_d)

This is a chart which gives the comparison of different thermal transitions like glass transition temperature, melting point, heat distortion temperature HDT and decomposition temperature. A semi-crystalline polymer, at the beginning at low temperatures, is hard and glass. First, we get HDT, then we get T_g followed by Tm and then we finally get the degradation temperature.For thermoset we get HDT and then T_g and we do not actually get T_m, and then we get degradation degradation temperature T_d. With this we conclude this lecture and in the next lecture we will talk about thermo-mechanical properties of polymer.