Course on Analytical Chemistry
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Module 8
Lecture No 39
Thermal Methods of Analysis – II (Contd.)

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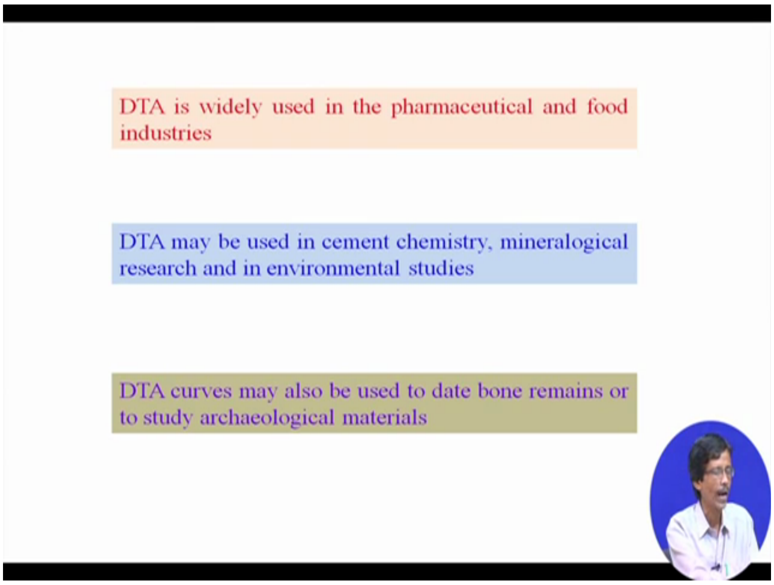

DTA is widely used in the pharmaceutical and food industries

DTA may be used in cement chemistry, mineralogical research and in environmental studies

DTA curves may also be used to date bone remains or to study archaeological materials

Okay welcome back to this class where we are discussing the application of your DTA technique and we know that there are several such applications and particularly the most important one is use of this DTA instruments in pharmaceutical industry, so in pharmaceutical industry this particular technique along with the next technique what are we talking about the DSC is widely use for the typical analysis of the drug, the medicine, the tablets, the capsules and all and similarly the DTA can also be very much useful in the food industries where the food industries can analyse the purity of the sample and its thermal stability of the sample and if we add something more to that particular food it can also be detected very nicely by using this particular technique.

So it can also be very much useful by the inorganic people the inorganic chemistry people are also interested to study this DTA because the DTA can be very much useful or cement industry. Similarly the geologist also used DTA for their mineralogical research and the last one is very important that the environmental studies because we have seen that the amount of gas what is coming out and how we can burn the gas in different atmosphere that is the most important topic terms of your air pollution and the environmental studies, so the to study environmental nicely in terms of the quality of the air and the other environments like your carbon dioxide environmental or the nitrogen environment if we talk in terms of whether it is contaminated with some of the gas molecules can be studied by your DTA and it can be very much useful for archaeological studies.

So it can be used to use the date that the dating we know that the radioactive dating we know and the bone remains because the bone the remaining one part of the living organism or (()) (2:28) in the simple dinosaurs and all, so the bone remains can be analysed initially by this particular technique study the archaeological materials what we basically on earth from the earth surface and down the earth surface also we find some unknown material, so if any unknown material in your hand you can always use to important technique one is your IR instrument use of IR instruments for IR spectroscopic study and then we can use the corresponding Tg and DTA plot for all these studies.

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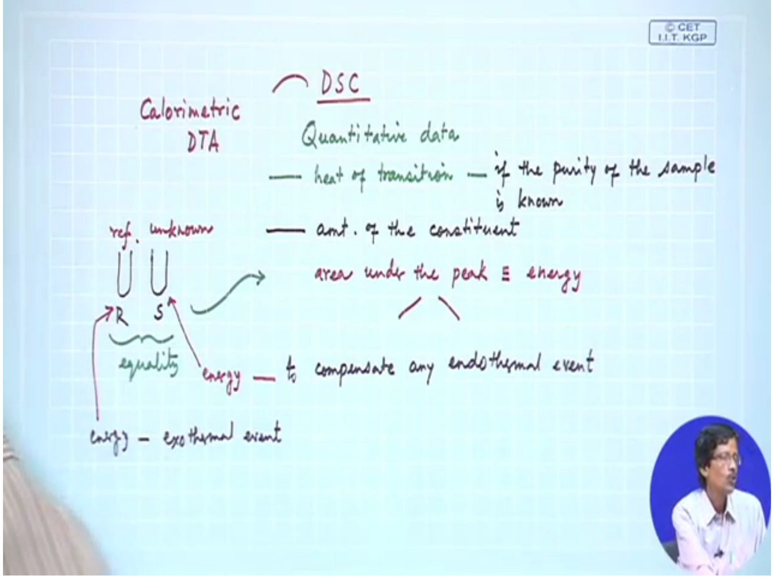

So next we will move to differential another differential need so which is differential scanning calorimetric technique which we consider it as a calorimetric DTA study so it is calorimetric DTA study because this DTA what we know that a conventional one we indicate the corresponding temperature where the corresponding heat effect is again see but the corresponding sign and amount of that particulars magnitudes of that particular change we cannot monitor so if we go for that a qualitative analysis is not very useful so it is impossible to obtain sometime the quantitative data.

So how we get the quantitative data out of this particular technique, it is sometimes very difficult it is from your DTA need, we should go for the corresponding DSC where we can locate the corresponding heat of transition. If the sample what we use the pure one, so if the purity of the sample, if the purity of the sample is known we can find very nicely the heat of transition. So then we can find is the sample purity is related in the amount of that particular constituent, amount of that particular constituent we can find.

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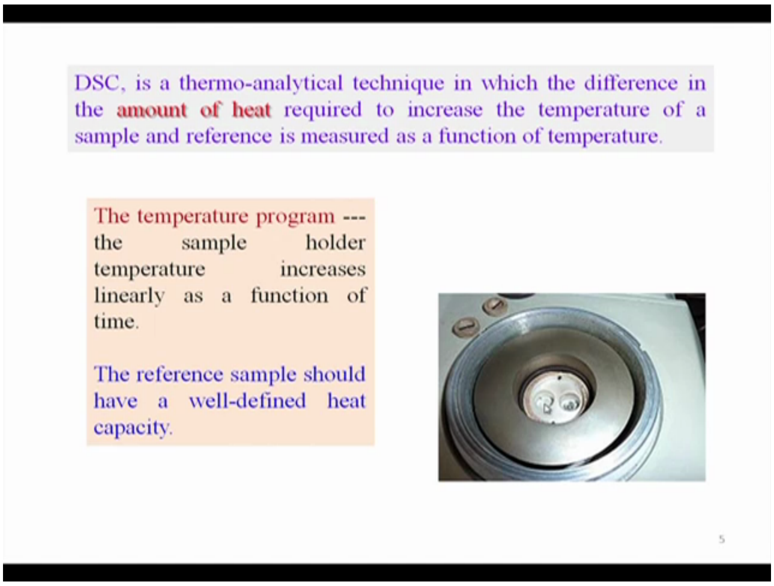

DSC, is a thermo-analytical technique in which the difference in the **amount of heat** required to increase the temperature of a sample and reference is measured as a function of temperature.

The temperature program --- the sample holder temperature increases linearly as a function of time.

The reference sample should have a well-defined heat capacity.

So all these things which is not very much control case of DTA we can monitor it or taking this particular one is to a calorimeter so you can have a good control regarding the responding furnace that we know that the amount heat we can put or the amount of heat we can it can come out, so is a Thermo analytical technique in which the difference in the amount of heat now we are talking not in terms of the corresponding temperature difference but we are now talking in terms of the corresponding amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature, so either the function of the temperature in terms of the temperature of the furnace temperature of the sample.

So we have a controlled temperature program and that control temperature program you can have a sample compartment what we can have earlier in case of your DTA apparatus and that sample compartment can now be converted to a differential calorimeter. So if you have a differential scanning calorimeter in hand within which you put both R and S the reference material and the sample material and if the differential scanning calorimeter is of a isothermal type and we have a corresponding resistive heater in your hand and the thermocouples are also connected which can register a voltage and you can have the automatic control loop and that control loop, it can goes through the Western Bridge and that gives rise to the corresponding recording of the system.

So the sample holder temperature increases nearly as function of time as we all know when we heat the thing and the reference sample should have a well-defined heat capacity so these are the 2 things that you can monitor within this particular thing so as we have seen just now that you have R within a cavity and S well so within a cavity so if everything is now enclosed so this is the corresponding furnace and that furnace can have the corresponding heating capacity or heating both the 2 things together. So this is the most important and useful one is the corresponding chamber for that.

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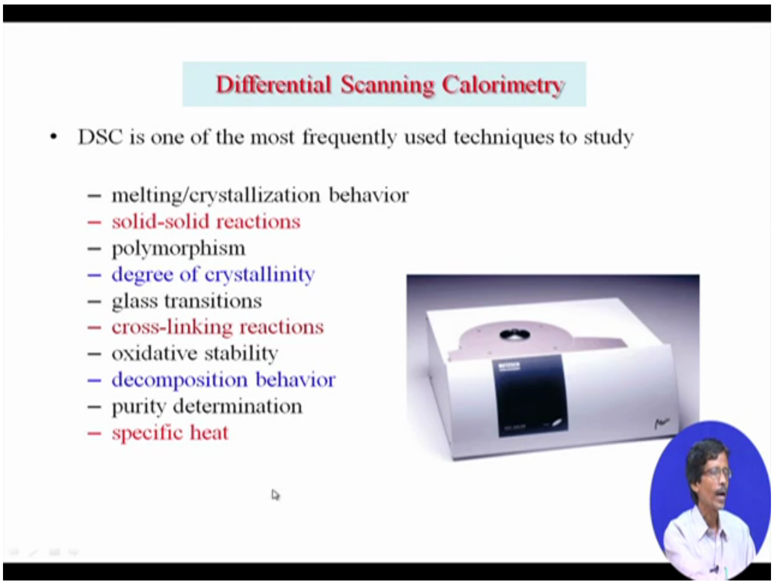

Differential Scanning Calorimetry

- DSC is one of the most frequently used techniques to study
  - melting/crystallization behavior
  - solid-solid reactions
  - polymorphism
  - degree of crystallinity
  - glass transitions
  - cross-linking reactions
  - oxidative stability
  - decomposition behavior
  - purity determination
  - specific heat

And this is the typical instrument how the instrument look like the DSC instrument, so this DSC instrument in our hand where we have the change the differential of the corresponding energy to heat the sample or the reference because these 2 samples and the reference we want to keep the 2 temperature within equality. So very close so if you have the reference as we seen just now and the sample, so we have R and S and we want to keep in to a very small temperature differences or the amount of power required because one can be cold and another can be heated up, so the 2 temperatures should be kept very close to its equality, then some connectivity we have that we have the recorder.

So the recorder will record the corresponding paying that means the corresponding one that how it can trace the corresponding plot and ultimately the plot we can have. So this thing that the instrument is and this scanning calorimetry what we can use, we can use it for so many things, so is a big list but if we see one by one so it has the same temperature effect or the thermal effect because you have the reference and the sample, so one is known the reference material and the reference sample is known, so if we have this thing at means the thermogram we get resembles that of your DTA but the area under the peak now, area under the peak for DSC measurements will be equivalent to the amount of energy supplied either to the sample to the reference, so the supplied amount of energy can be either absorbed or emitted.

So the position in the chart which indicate the temperature at which the transition is taking place but we can have the corresponding energy compensation in terms of the energy what we can put to the reference or to the sample. So we have the reference which is known and the sample which is unknown. This is our reference material, so if we put energy to the unknown only that means energy is being supply the unknown sample what we are monitoring.

So why because if it is only the corresponding endothermic process, to compensate that means we have to keep these 2 temperature very close by, so energy should be supplied to your sample to compensate any endothermal event, to compensate any endothermal endo thermal event. So similarly energy will be supplied to the reference material because the reference material if it is exothermic the temperature of the sample will be up, reference will lag behind so in that case energy will be supplied to the chamber where you have an exothermal event.

So these 2 events whether you have exothermal event or the endothermal event can be monitored very nicely for large number of reactions which are triggered by a change in the temperature of the medium which we keep in the furnace, so most interesting thing is the solid state analysis so solid state material any powder to polymer to rubber can be analysed very easily and we can study those things or their melting and crystallisation behaviour, so this melting and crystallisation behaviour is very important because we can see the corresponding melting is the transition process where solid is going to the liquid or the molten state.

So we record that thing (())(12:12) the corresponding transition temperature and be recorded and if it is high that means the it has the solid-state and the crystalline form has good stability, so the crystallisation behaviour can also be monitored if we hold down the system and we look at the recrystallization. Then some solid-state reactions we can see so the DSC trace for a particular type of solid-state reaction whether that particular solid-state reaction we all know that we can go for a simple metal complex preparation one good example is well known that, that preparation of reinecke salt, so the preparation of reinecke salt and be done by using simple solid-solid reactions, so on sand bath we do some solid component where the other solid component but the ultimate product is a well-known different of mental complex.

Then polymorphism as we have seen in case of DTA analyses that the polymorphism of the pharmaceutical industry will be very useful stopped then the degree of crystallinity, so the degree of crystallinity of the crystalline samples, the Tg we can measure that means the glass transition temperature is for the polymer material or the rubber material can measure, then any cross-linking reactions, so if we heat the polymer and if stirring you polymer by DSC technique, what we see that this cross-linking reactions can take place. Sometimes we had sulphur for vulcanisation also and sulphur can also be useful for the cross-linking processes.

So this particular reaction if we minutely see the corresponding heating rate and the energy change or that cross-linking reaction at can be monitored particularly the temperature where we can breakout the thing that string reaction is taking place at that particular temperature. Then oxidative stability which your environment is oxygen environment only, so the high temperature susceptibility or a particular solid-state reaction oxygen can also be monitored.

Then the decomposition behaviour as we have absurdly early is also that decomposition of your oxalate salt, metal oxalate salts, metal iron oxalate salts or the metal iron carbonate salts we can see even the sulphides. Then in terms of the corresponding medicine and importance or the pharmaceutical industry, it is the purity determination so purity determination starting from your sample which can be useful for pharmaceutical industry like that of your tablet, capsules and all these medicines to that of your any solid alloy sample or the iron sample or the steel sample. Then one specific entity you can measure is your specific heat, the specific heat measurement for the sample can also be useful if we look at this particular DSC measurements.

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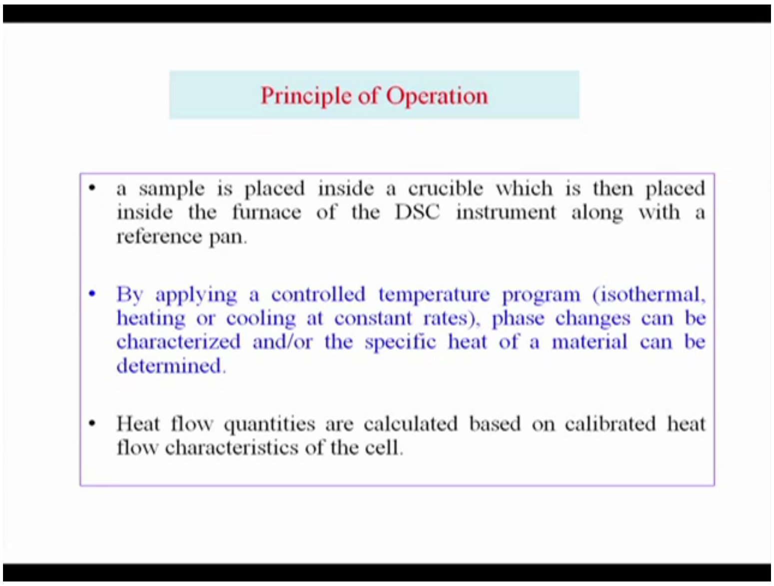

Principle of Operation

- a sample is placed inside a crucible which is then placed inside the furnace of the DSC instrument along with a reference pan.
- By applying a controlled temperature program (isothermal, heating or cooling at constant rates), phase changes can be characterized and/or the specific heat of a material can be determined.
- Heat flow quantities are calculated based on calibrated heat flow characteristics of the cell.

So what we see there that how you monitor this that the principle of operation is therefore very important and this principle of operation will tell us an initially what we can have a sample is in your hand and which is placed inside a crucible and then we placed the crucible inside the furnace of the instrument which is definitely now a (DC) DSC instrument which is different from your DTA instruments along with the reference pan but the mechanism of keeping the reference as the as well as the sample panel is same.

Then we apply the temperature, so it is programmed one because it has some rate of heating process, so rate of heating process is monotonous with time it is increasing at a rate of say 2 degree per minute or 5 degree per minute or 10 degree per minute. So heating can be done in an isothermal we, so isothermal heating or cooling at concentrate we can do in 2 different ways. So we can have phase changes, so the phase changes can be characterised or monitored and the specific heat of a material can be determined. So that is the last thing what we just tabulated is the measurement of the specific heat of the sample we can monitor.

Then when we give rise to the corresponding energy to the sample or the reference we are looking for some heat flow, so heat flow quantities are then we calculate out or calibrated heat flow characteristics of the cell. So when we get that the heat flow, we can calculate out based on the corresponding calibration what we have the corresponding cell or the furnace, cell is your furnace and how the temperature is going up we can monitor and how the sample temperature is going out with that particular on his temperature.

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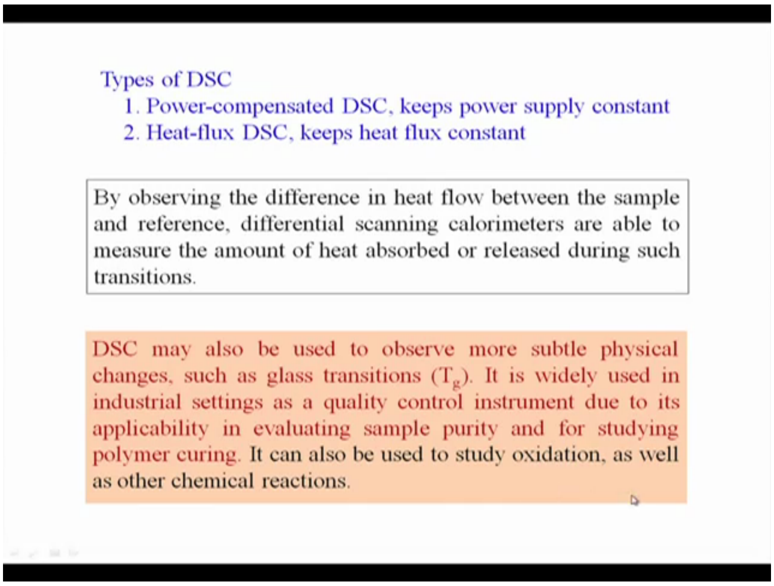

Types of DSC

1. Power-compensated DSC, keeps power supply constant
2. Heat-flux DSC, keeps heat flux constant

By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions.

DSC may also be used to observe more subtle physical changes, such as glass transitions (T_g). It is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing. It can also be used to study oxidation, as well as other chemical reactions.

So we can have different type of DSC and one such is your power compensated (DH) DSC, so one particular technique will be calling as your power compensated DSC, where we compensate the power which is applied to either sample or the reference where we keep the power supply thing constant like we when we study in our next classes onwards that the electrochemical studies that we can have some measurements where the temperature like this temperature we can fix the corresponding current or we can fix the corresponding voltage.

So similarly here if you keep the power supply constant so it can be known as the corresponding power and said it DSC or the heat-fluk DSC, keeps the heat flux constant. So these 2 parameter, either the supply of power or heat-flux what is being received by the sample and the reference, we can keep constant for these 2 types of measurements. Then what we find that by observing then the difference in the heat flow, so when we talk in terms of the corresponding heat flux which is being received but it is not kept constant when the power we kept constant, so eat flow will be different, so the heat flow between the sample and the reference, so what the calorimeters what we have, the calorimeter can measure corresponding amount of heat absorbed or released during such transitions.

So we can have solid state transformations and those solid-state transformations we can monitor using a calorimeter now by looking at the corresponding amount of heat absorbed or emitted. So again we are coming back to the same question that whether we have a exothermic process or by a endothermic process and in that particular situation, so the corresponding position of the chart paper will basically indicate the temperature of a particular type of transition.

Transition can take place whether you have a endothermic transition or an exothermic transition but we should be able to locate the temperature where the process is taking place and if the process is taking place at a constant supply mode, we will find the amount of heat being supplied to these 2 things. So what we find at a very important parameter will be able to find which is your Tg.

So T small g is a subscrib g is not your T capital g is a subscrib g so we can observe a subtle physical change such as the glass transition temperature what we use in industrial processes, the quality control instruments because it is at a fix like that of your melting temperature the melting point we all know the purity of a particular sample is known by looking at the constant melting point. Either if you have a impurity in the sample solid sample, we know that there is be some change the corresponding melting point.

So that is the depression of the corresponding freezing point and the elevation of the corresponding boiling point as we know our school days, so that particular criteria we can use to fix or we can monitor corresponding glass transition temperature. So if we have a fix glass transition literature for a particular pure sample what we can see that is fixed for or can be tagged with that particular sample.

So industrial settings that means if we go for a typical quality control, the instrument can be used the quality control, so a DSC instrument must have to a quality control chemist or a quality control engineer was looking at the corresponding purity of the sample or any other solid material such that it can be used for recording its purity and for studying if it is a polymer sample the polymer curing process.

So polymer curing process a very important process which can be directly related to the corresponding Tg and other parameters, so Tg is very much useful because we are curing is particular polymer sample at this temperature like what we use to have that means we want to eliminate trapped water molecule any solid sample, we use this particular temperature is as a drying temperature and that drying temperature we use in some air oven. So it can also be used to study oxidation because in air some sample can go for oxidation and as well as for other types of different chemical reactions. So these 2 techniques are therefore very much useful

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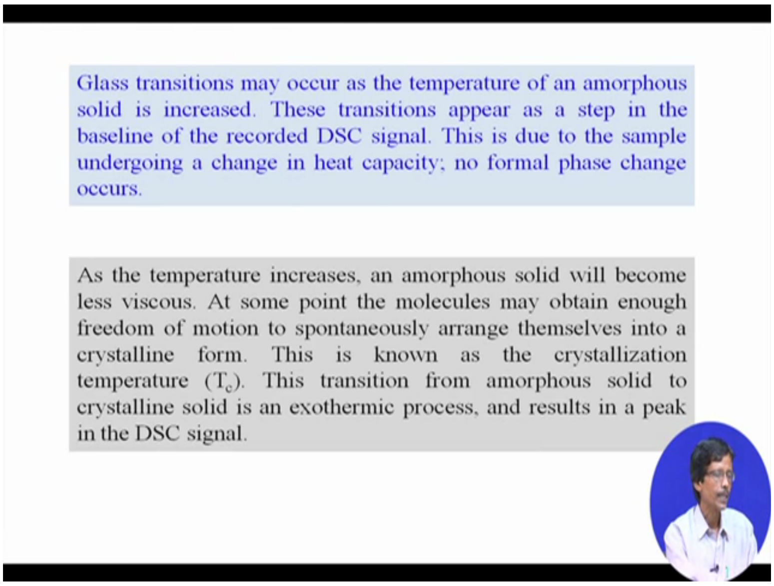

Glass transitions may occur as the temperature of an amorphous solid is increased. These transitions appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity; no formal phase change occurs.

As the temperature increases, an amorphous solid will become less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (T_c). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a peak in the DSC signal.

So these 2 techniques are therefore very much useful and the Tg course when the temperature of an amorphous solid is increased, so why we see that the glass transition may occur as the temperature of an amorphous solid is increased. So as a we may have a amorphous solid and its particular point we see the corresponding inflection that means a corresponding change in the delta T value as we have noticed case of DTA. Similarly (DT) DSC will also record the corresponding temperature Tg in this fashion.

So as a step basically in the baseline of the recorded DSC signals, so when we have the recorded DSC signal, you get a corresponding step like that of your Tg plot for your this recording of your Tg temperature. This is due to the sample undergoing a change in heat capacity, no formal face change occurs. So here we do not have any formal phase change but the heat capacity is changing at the point of your class transition. So as we increase the temperature we keep on increasing the temperature, what we have started with the thing is not a glasses substance is a amorphous solid will be less viscous is less viscous.

So is basically trying to solid defying it at that particular point at some point then the molecule may obtain enough freedom to for motion to spontaneously arrange themselves into crystalline form. So it is less viscous that means viscosity is decreasing at Tg temperature glass transition temperature. So you have more freedom of movement of the molecules and this temperature basically is responsible for the crystallisation of the molten species as we grow crystals from the solutions. So this TC now is useful to monitor the corresponding crystallisation process so not only the glass transition, we can also monitor the corresponding crystallisation temperature.

So what we get, we get a change from the amorphous solid who the crystalline solid because most of the time when we synthesise some new compound we know that if it is in the room temperature (())(24:35) condition or it is in some high temperature reflux in condition at the boiling point of the solvent, we get when it cool down the thing at room temperature or (()) (24:46), we get some time a crystalline matter or a crystalline solid compound but in all other cases we get some amorphous solid, but for material of very (imp) materials of highly important thing what we get for this rubber like material or the polymer like samples, we get that the crystallinity is important.

So the transition from amorphous to crystalline solid and there we find a corresponding courses, the exothermic process so the nature is known and the amount of heat is being there evolved or this exothermic process, resulting the corresponding peak in the DSC signal and that DSC signal we can monitor and that particular DSC signal will be also useful for our measurement not only knowing the temperature TC the crystalline temperature is that the temperature which is require for our crystallisation but also the amount of heat is required for that particular transition.

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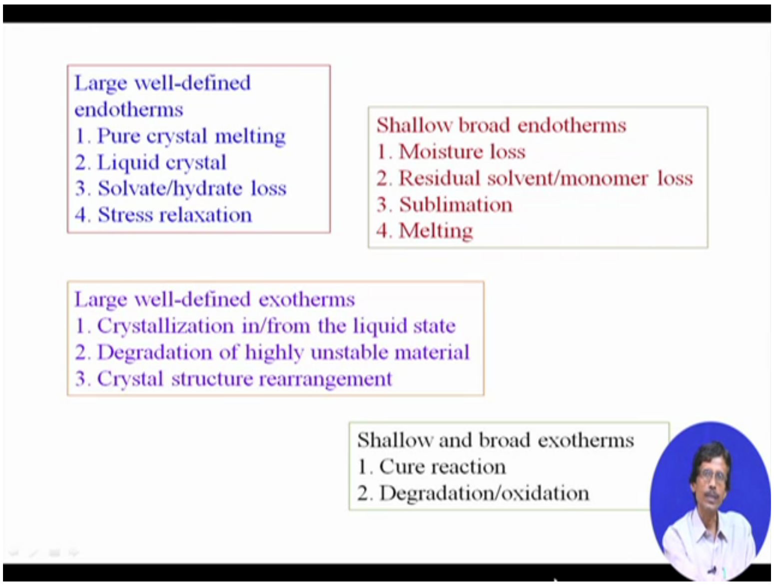

Large well-defined endotherms
1. Pure crystal melting
2. Liquid crystal
3. Solvate/hydrate loss
4. Stress relaxation

Shallow broad endotherms
1. Moisture loss
2. Residual solvent/monomer loss
3. Sublimation
4. Melting

Large well-defined exotherms
1. Crystallization in/from the liquid state
2. Degradation of highly unstable material
3. Crystal structure rearrangement

Shallow and broad exotherms
1. Cure reaction
2. Degradation/oxidation

So we can have these 2 different types of these transitions one is your endotherms and another the exotherms, now we can separate out we can differentiate out these 2 things as one is large another is small one. So large well-defined endotherms are there so for different processes like these, so where we get the large well-defined endotherms, so when we have a pure crystal and a pure crystal is getting undergoing the corresponding melting process, so pure crystal melting will show a large well-defined endotherms.

Then liquid crystalline material also the changing one phase to the other phase also will show you the endotherm. Then solvate or the hydrate loss, the solvate the sample can be solvated or your hydration is can be hydrated, so these hydrations that means the water molecules will go out, so that will also give you this sort of endotherm and then stress relaxation of the material that means material is in one form the other. The opposite one is the shallow and broad, it was large and well-defined but if you have a shallow and broad and endotherm is due to the moisture loss is variable also because it is not fixed amount of moisture we are looking for, for the loss.

Then residual solvent or sometimes some monomer is also losing from the polymeric material. Then sublimation process and the melting process is accompanied by showing you the corresponding shallow broad endotherms in the DSC plot. Then we can have the opposite one in terms of the same large and well-defined but endotherm is now exotherms, so what we find what we see for these exotherms is now the crystallisation because so far what we have tabulated for the 4 processors over here, another for processes are here.

Nowhere we are seeing the TC the crystallisation in temperature so you are also we will see large well-defined exotherms, so the crystallisation processes this exothermic process and it very large peak area will get, so the temperature change or the energy change of this process is also very high and the crystallisation in and from the liquid state, from the liquid state we get some crystals and that particular crystallisation from the liquid state so can be monitored what (())(28:32).

Then we can have the degradation and that degradation of highly unstable material is also accompanied by this side of exothermic process so then the rearrangement of the crystal structure that means rhombic to monoclinic, monoclinic to some another form. So crystal structure rearrangement can also be accompanied by large well-defined exothermic processes. So the last one will therefore be in our hand as the fourth one which will be shallow one but exothermic.

So shallow and broad exothermic processes will be there which is for a curing reaction, so the curing reaction what we can take for a curing of the polymeric sample or sometime is sample is getting degraded, we want to have some degraded or we want to have some oxidised form because sometimes we want to monitor and some oxidised form can also be useful on also have some application for that particular sample so we allow it for degradation. We allow the sample also for its oxidation, so that can be monitored by a very small and which exotherms is a broad one.

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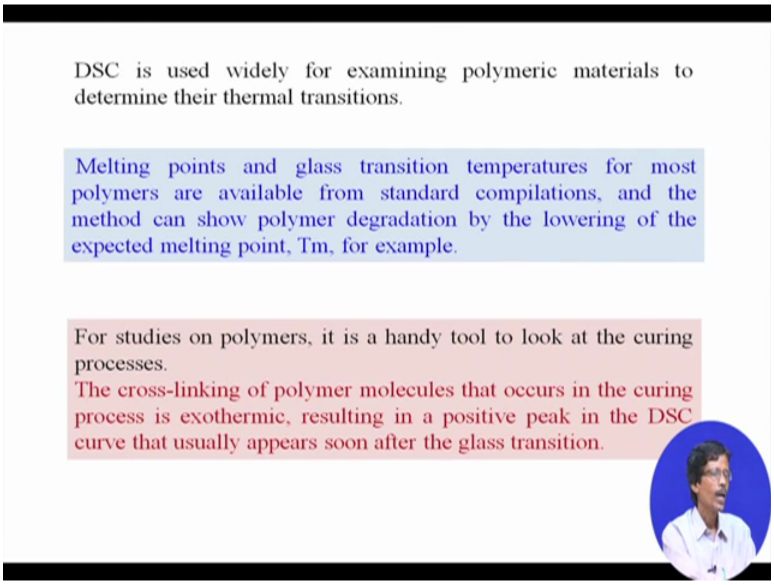

DSC is used widely for examining polymeric materials to determine their thermal transitions.

Melting points and glass transition temperatures for most polymers are available from standard compilations, and the method can show polymer degradation by the lowering of the expected melting point, Tm, for example.

For studies on polymers, it is a handy tool to look at the curing processes.
The cross-linking of polymer molecules that occurs in the curing process is exothermic, resulting in a positive peak in the DSC curve that usually appears soon after the glass transition.

So DSC is used widely for examining polymeric materials to determining their thermal transitions so is useful mostly and in most different ages the DSC used for the polymeric samples. This melting point and glass transition temperatures for most polymers are available from standard compilations because the tabulated form or the literature known values we can have in our hand, so once we make a new polymer or new sample we have to compared that with the well-known values what is there in the standard of this differences and the method can show the polymer degradation while lowering of the expected melting point Tm for example.

So we can have a new process of making the polymer such that we can have a new parameter that means the Tm value can be less such that at this particular thing that means the rosters what we have developed that the processed develop men can also be benefited or your DSC measurements. Then for studies on polymer, it is a handy tool to look at the curing processes and we see that the cross-linking of polymer molecules that occurs in the curing process is exothermic, resulting in a positive peak that means the upward peak of the DSC curve and usually appears soon after the glass transition. So what we get after the glass transition so the cross-linking thing, the temperature we should know, then the glass transition temperature and where the cross-linking will appear related to that of your glass transition that will also be able to know from a good DSC plot.

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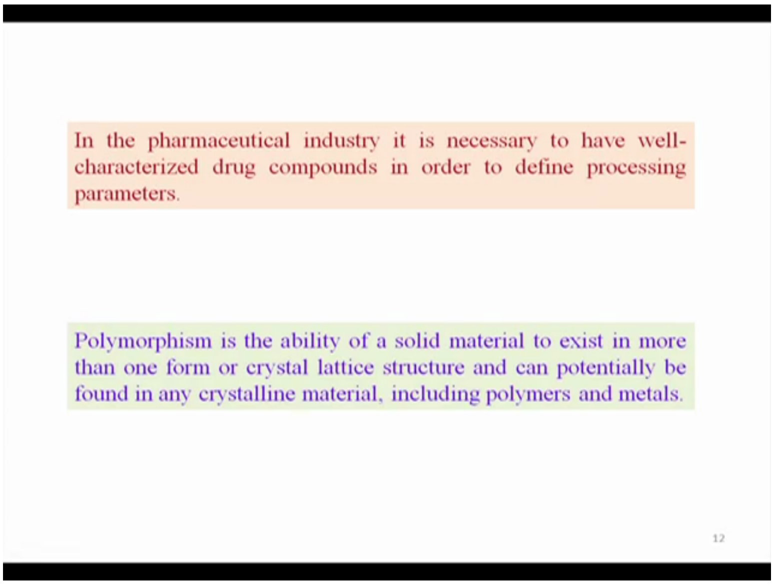

In the pharmaceutical industry it is necessary to have well-characterized drug compounds in order to define processing parameters.

Polymorphism is the ability of a solid material to exist in more than one form or crystal lattice structure and can potentially be found in any crystalline material, including polymers and metals.

Then we how the pharmaceutical industry, they basically look for their studies the pharmaceutical industry, it is necessary to have a well-characterised drop compounds because the purity is very high and only via using some amount of milligram level samples, so this milligram level samples should not have impurities in the microgram level or the nanogram level, so the purity should have a very high purity and either in order to define the processing parameter that means how you make the sample, so we always we have any pharmaceutical material or any pharmaceutical compound, we should go through a DSC analysis.

So starting from your quality control to processed development in industry, we use this particular and useful technique of your measurement. Then the last one which is also very important is the polymorphism which we can also study by using this particular technique where a solid can be able to exist in one or more form in the crystal lattice structure but it can have potentially found different crystalline material including polymers and metals.

So if they stay in 2 different crystal lattice form one is one polyformic form and another is the other polymorphic form and for this drug material which know that one particular drug material in one polyformic form is active but the other may not. So the characterisation in terms of their polymorphic nature we can use this particular technique very nicely or their complete analysis, okay. Thank you very much.