Lecture 44- Polymer Testing 09

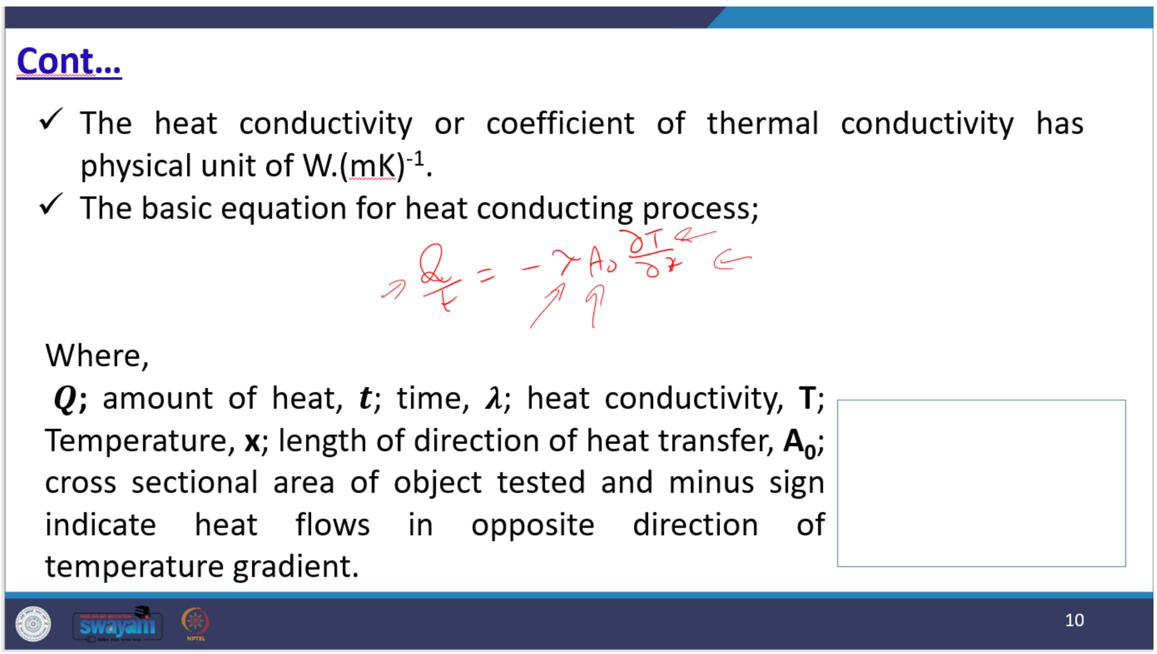
Hello friends, welcome to the thermal and optical properties of polymers, types, and testing under the edges of polymer process engineering. In the previous lecture, we covered the tear, the test piece geometries, and standard methods and discussed fracture toughness. In this aspect, we discussed the fundamental concepts of fracture toughness. Then, we discussed the various testing methods like ASTM, BS, and ISO. In this particular segment, we will discuss the physical and thermal properties like heat conductivity and diffusivity. We will discuss differential scanning, calorimetric, DSC, thermo gravimetric analysis like TGA, thermo mechanical analysis, and TMA.

We will also discuss the optical properties like refractive index, refractometer, polarization, and polarization optical testing. So, we are going to cover all this in this particular segment. So, let us start with the thermal properties. See the macromolecular structure of polymers and the resulting bonding relationship; they significantly determine their thermal characteristics.

The chemical and physical makeup of the polymer affects the movement of atoms, segments of molecules, and molecules that are subjected to thermal energy. Due to the increased motion of atom side chains and a molecule segment after being subjected to heat, the proportion of secondary valence bonds reduces the thermoplastic material. So, in contrast, in the thermoset, the molecule's ability is governed by its 3D network. The head application causes the softening but not melting, and the primary valence bond in the network is broken away during the decomposition process. Additionally, the movement of the molecules and their components were related to their mechanical properties; therefore, it is particularly important to determine the polymer's thermal characteristics.

The thermal analysis technique measures the physical and chemical properties as a function of temperature and time. The specimens are subjected to the defined temperature programs in dedicated ovens, where they specify gas temperatures like inert gas or air. To determine the material's glass transition temperature, melting temperature, melting enthalpies, temperature ranges of the secondary relaxation regions, thermal degradation, and degree of crystallinity corresponding to heating or cooling curves that exhibit the material's specific dependencies are recorded. The thermal analysis technique can conduct different analyses like structural change, phase transition, glass transition, melting, crystallization, cross-linking, volatilization, sublimation, etc. The mechanical properties are like damping and elastic behavior, and the thermal properties are like specific heat capacity, melting, crystallization, temperature, coefficient of expansion, expansion shrinkage, etc.

The chemical reactions, the chemical reaction solution or liquid phase, thermal stability, and decomposition in various gas source conditions. The thermal analysis method now includes differential scanning calorimetry, thermogravimetric analysis, thermal mechanical analysis, dynamic automated thermal analysis, and thermo optical analysis. So, before we go into the details, let us talk about the heat conductivity. The typically elastic waves in a solid body can transmit heat in polymers, and energy exchange occurs when molecular segments collide. The heat conductivity, which can be thought of as a quaternized transfer process occurring at a sound velocity, this is measurement of the energy transmission in the material.



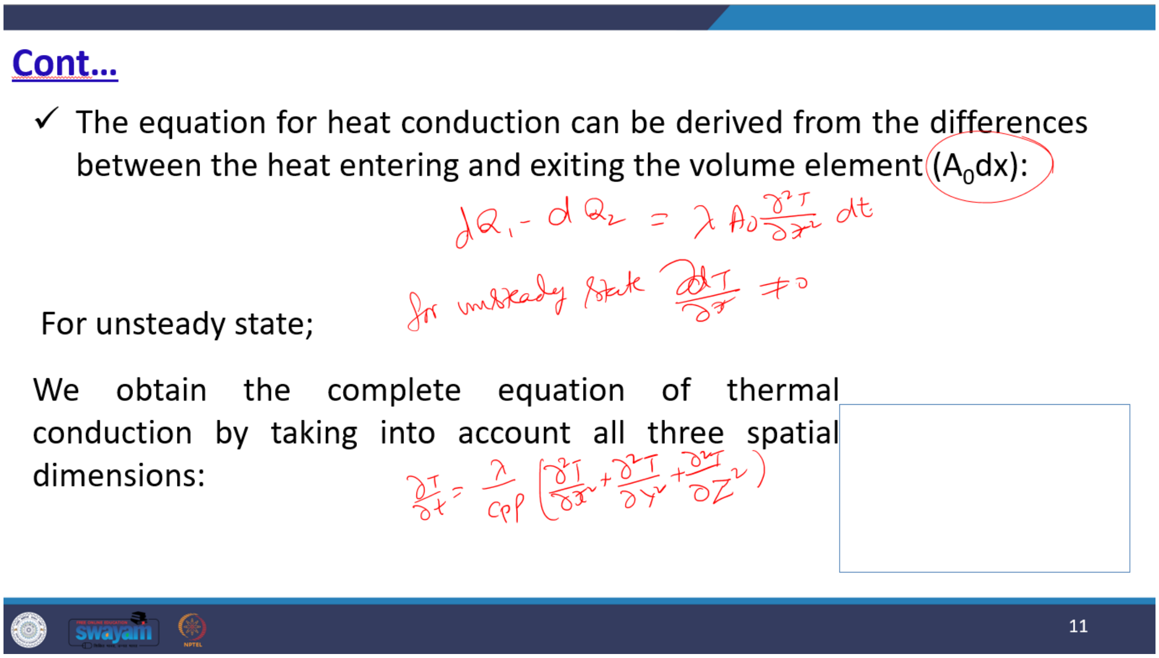
The relationship expressed by Debye and which is given like this.

$$\boldsymbol{\lambda \approx c_P . \rho . c . l}$$

Here, the Cp is the specific heat capacity, ρ is the density, C is the sound velocity, l is the distance between the molecules, and lambda is the coefficient of thermal conductivity. The heat conductivity or the coefficient of thermal conductivity has a physical unit of watt per meter Kelvin. The basic equation for the heat conducting process is

$$\frac{Q}{t} = -\lambda A_0 \left(\frac{\delta T}{\delta x}\right)$$

Q is the amount of heat, T is the time, lambda is the heat conductivity, T is the temperature, X is the length of the direction of heat transfer, A zero is the area of the cross-section object, the minus sign indicates that heat flows in opposite direction of the temperature gradient. The heat conduction equation can be derived from the differences between the heat entering and exiting the volume element that is A_0 dX.



So, it can be represented as

$$dQ_1 - dQ_2 = \lambda A_0 \left(\frac{\delta^2 T}{\delta x^2}\right) dt$$

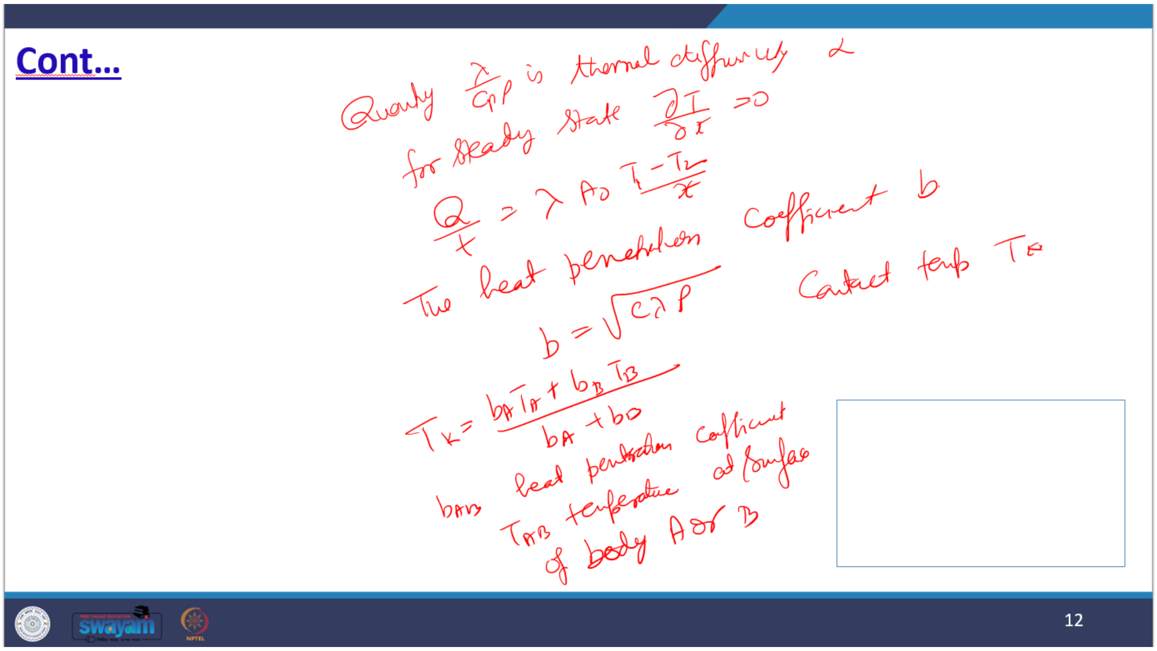
For unsteady state;

$$\frac{\delta T}{\delta x} \neq 0$$

So, we obtain a complete thermal conduction equation by considering all three spatial dimensions. It can be represented as

$$\frac{\delta T}{\delta t} = \frac{\lambda}{C_P \rho}\left(\frac{\delta^2 T}{\delta x^2} + \frac{\delta^2 T}{\delta y^2} + \frac{\delta^2 T}{\delta z^2}\right)$$

Now, quantity, the quantity $\frac{\lambda}{C_P\rho}$ is thermal diffusivity α.



So, for steady state,

$$\frac{\delta T}{\delta x} = 0$$

Then, on solving this equation, we have

$$\frac{Q}{t} = \lambda A_0 \left(\frac{T_1 - T_2}{x}\right)$$

The heat penetration coefficient "b" can be defined as

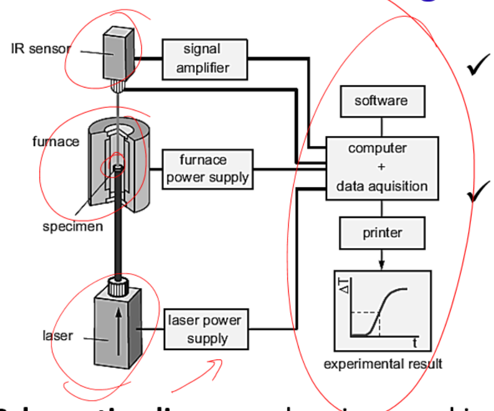
$$b = \sqrt{c\lambda\rho}$$

Now, for determining the contact temperature (T_k),

$$T_k = \frac{b_A T_A + b_B T_B}{b_A + b_B}$$

where B_A, B_B is the heat penetration coefficient and T_A,T_B are the temperature at the surface of body A or B. This is the basic protocol for our schematic diagram showing the working principle of measuring thermal diffusivity using the laser flash method.

Measuring of thermal diffusivity



Schematic diagram showing working principle for measuring of thermal diffusivity by laser flash method (**system type; Netzsch LFA 427**)

- ✓ The specimen is heated on one side, while the other side is used to measure the result.
- ✓ Thermal diffusivity can be measured with this technique throughout a temperature range of -40 °C to 2000 °C.

Here, the specimen is heated on one side while the other is used to measure the result. This technique can measure thermal diffusivity from -40 °C to 2000 °C. Here, you can see that this is an IR sensor, a furnace for heating, and you can subject the specimen over here. This is a laser gun or laser power supply. Apart from this, these are the units where you can record things or data.

Cont...

- ✓ On the specimen's bottom side, a heat impulse is produced, and on its top, an IR sensor detects the rise in temperature.
- ✓ The time-dependent temperature change can be used to calculate thermal diffusivity.
- ✓ The relationship produces heat conductivity;

$\lambda = a \rho C_p$

$a \rightarrow$ thermal diffusivity

$\rho \rightarrow$ density

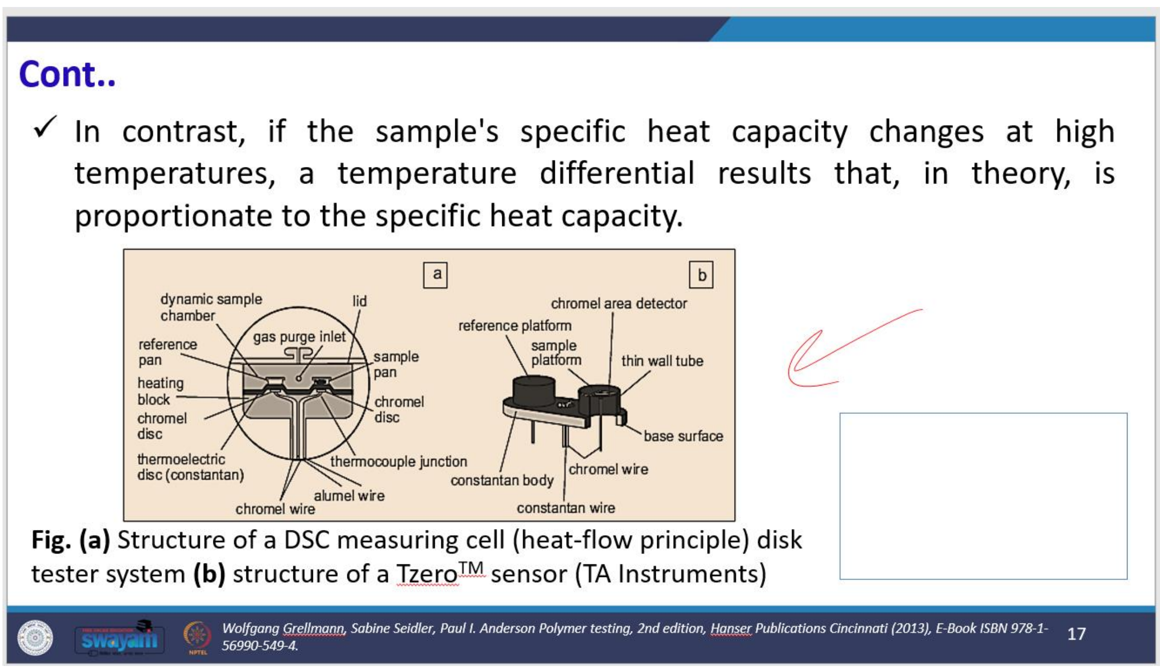
$C_p \rightarrow$ specific heat

Now, the heat impulse is produced on a specimen's bottom side. On its top, the IR sensor detects the rise in the temperature and the time dependent temperature change can be used to calculate the thermal diffusivity. So, the relationship that produces the heat conductivity can be given as

$$\lambda = \alpha \rho C_P$$

α is thermal diffusivity, ρ is the density, and C_P is the specific heat. When measuring the thermal diffusivity or using a DSC, a specific heat C_P is determined by comparing the temperature curve of the specimen to that of a known specific heat reference material.

Let us talk about the differential scanning calorimetry DSC, the heat flux calorimetry, and the power compensation calorimetry, which are the two fundamental measuring principles that guide the design of DSC devices. According to a chosen linear temperature program, two beam-sized pan tray dishes containing a sample and an inert reference are heated concurrently, and the reference is frequently used to be air.



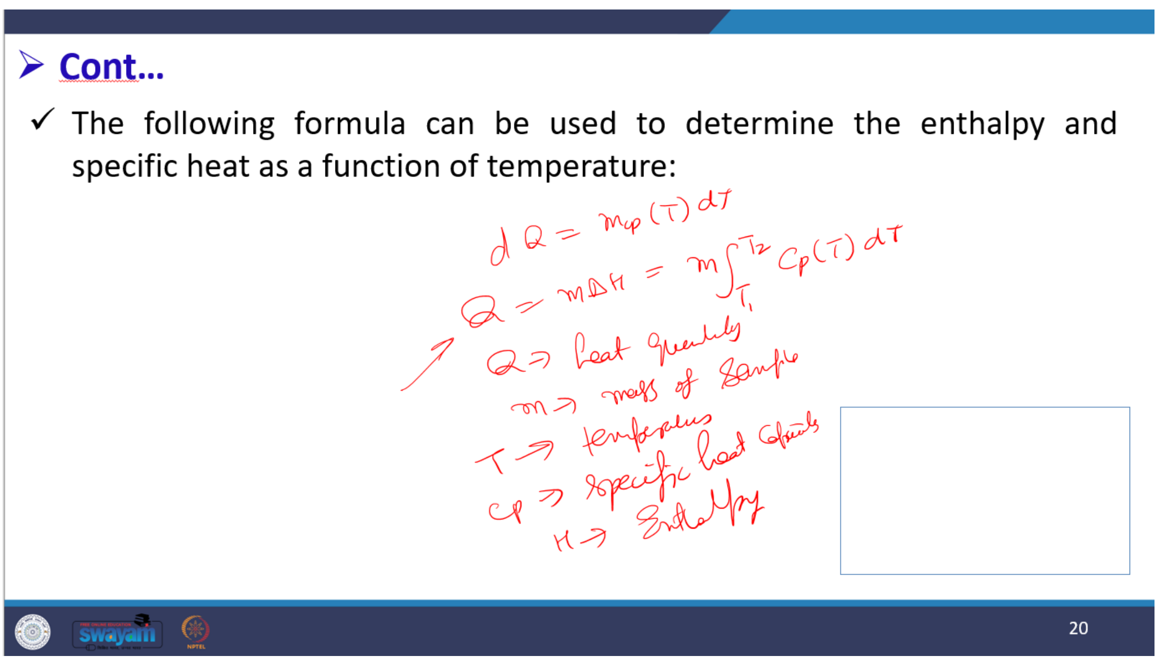
This is the typical figure. The sample and reference are placed within a cylindrical oven for heat-flux calorimetry. Since the configuration is thermally symmetrical, there is no temperature differential between the pans while the oven heats up. In contrast, if the sample's specific heat capacity changes at high temperatures, a temperature differential results that, in theory, is proportionate to the specific heat capacity. It is possible to calibrate and utilize this setup to measure specific heat capacity. The so-called TzeroTM technology has improved the heat-flux calorimetry's ability to resolve small differences. In contrast to traditional heat-flux calorimetry by disc measuring devices, which measure sample and reference temperatures, a sensor that includes, among other things, an extra thermocouple is used.

Now, with the help of the additional temperature sensor which gauges the ovens baseline temperature, thermal symmetric can be corrected in the oven more effectively. The following formula which we are going to write this can be used to determine the enthalpy and the specific heat as a function of a temperature

$$dQ = mC_P(T)dT$$

$$Q = m\Delta H = m\int_{T_1}^{T_2} C_P(T)dT$$

Now, here, Q is the heat quantity, m is the mass of the sample, T is the temperature, C_P is the specific heat capacity, and H is the enthalpy. Now, let's talk about the phase transition. The specific heat capacity and enthalpy curves shift characteristically with the temperature, and the dependence of specific heat capacity and temperature rises sharply in a glass transition zone that is on the left while the melting range peaks there that is on the right.



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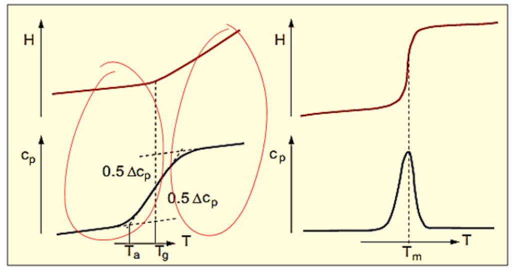
At phase transitions;

- ✓ Specific heat capacity and enthalpy curves shift characteristically with temperature.
- ✓ The dependence of specific heat capacity on temperature rises sharply in the glass transition region (**left**), while the melting range peaks there (**right**).



Figure; Showing glass transition with Tg determination and melting range

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The glass transition (T_g) measurement of specific heat capacity and temperature is based on ISO 11357, and semicrystalline polymers have a comparatively large melting range compared to metallic material. The temperature and mechanical history of the polymer material have a significant bearing on the material and, consequently, the melting curve. So, the temperature T_m of the endothermic peak in the dependency

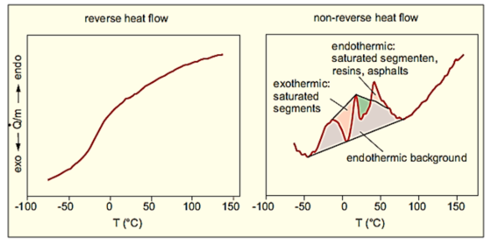
$$Cp = f\,(T)\;or\;(dQ/dt)/m = f\,(T)$$

is a function of temperature. It is referred to as the melting point for polymer and is the temperature at which most crystallites melt. Identifying the polymer for quality control is one of the key implications of DSC. In most cases, this is accomplished using the transition temperature, a glass transition for the amorphous template polymer, and the glass melting temperature for the semicrystalline polymers.

Let us talk about the temperature-modulated DSC (TMDSC). This technique can separate nonreverse processes like cross-linking, breakdown, and evaporation from reverse processes like glass transition and melting. According to the standard DSC measurement, reverse and nonreverse heat flow are separated from overall heat flow signal. Repeated heating can produce the reverse component, which depends on heating rate, heat capacity, and other factors. Now, it is impossible to duplicate the finished nonreverse component.

➢ Cont…

- ✓ It is impossible to duplicate the finished non-reverse component.
- ✓ The sample is periodically heated using either sinusoidal, triangular, or sawtooth modulation, which is the key distinction from the conventional measuring approach using a linear heating rate.
- ✓ In circumstances when there are superimposed effects, TMDSC is a crucial aid.



Use of temperature modulated DSC (TMDSC) for characterizing bitumen

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The sample is periodically heated using sinusoidal triangular or saw tooth modulation, which is the key distinction from the conventional measuring approach using a linear heating rate. When there are superimposed effects, the TMDSC is a crucial aid. In this particular figure, we can see the use of temperature-modulated DSC for characterizing bitumen. The nonreverse heat flow has a rather complicated curve in the temperature range of - 50 to 90 °C. The energy needed to release the degree of alignment created during the cooling in the individual bitumen segments is referred to as an endothermic background and expands the specified temperature range.

Then, the cold crystallization of a low molecular saturated hydrocarbon at around 5 °C and that of a high molecular saturated segment at roughly 25 °C superimposes this process. The release of asphalts and resin into the alignment and the melting of previously cold crystallized high molecular weight and saturation segments cause the endothermic peak at about 40 °C.

Oxidation induction time/temperature (OIT): By calculating the oxidation induction time DSC can also be used to compare and assist the resistance of polymer to thermo oxidative degradation. The so-called static approach is dynamic with a relatively low sensitivity where DSC measurements are made in an oxygen or airfield environment at a temperature where exothermic oxidation is detected. When the sample is heated in the presence of an inert gas to a specific temperature higher than T_m.

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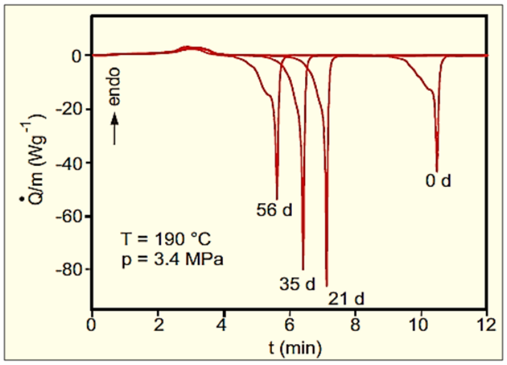

Figure; Showing Influence of oven ageing time on oxidative induction time in POM homopolymer pellets

✓ Figure shows the impact of oven ageing on the oxidative induction time, which was determined using POM homopolymer pellets at 190 °C and 3.4 MPa of pressure.

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This temperature is maintained when equilibrium has been reached, and the environment is changed to an oxidative one. This method involves timing the oxidation reaction to happen, and the ASTM D3895 standardized the statistical OIT approach. Now, this figure shows the impact of oven aging on the oxidative induction time, which was determined using the POM homopolymer pallets at 190 °C and 3.4 MPa of pressure. Let us talk about the thermogravimetric metric analysis, a tool for measuring mass changes in a sample as a function of time and temperature provided by the thermogravimetric analysis, evaporation, decomposition, chemical reaction, magnetic or electrical transition, and other processes all results in all result in mass changes. When gases such as oxygen, humidity, etcetera are absorbed, there is also quantifiable mass change. ISO 11358 standardizes this particular process.

Cont…

- ✓ Combining it with mass spectroscopy (MS) or FTIR (see Figure) gives you a tool to identify the substances that are responsible for a specific mass loss, which can be useful for solving polymer analytical issues.

Thermogravimetric analysis coupled with a quadrupole mass spectrometer

Combining it with mass spectroscopy or FTIR, as per this figure, gives a tool to identify the substance responsible for a specific mass loss, which can be useful for solving polymer analytical issues. Various purge gases are employed depending on the measurement requirement to record mass change as a function of temperature or time as per this figure. For the interpretation and separation effect, the differential measurement signal, also known as the DTG curve, is frequently introduced, and additional details on the kinetics of deterioration of the DTG signals are provided. So, at about 300 °C, the first decomposition, now here you see that around 300 °C the first decomposition the maximum happens. Now, plasticizer and low molecular segments volatilize at temperatures up to 400 °C, and EPDM polymer parts decompose at temperatures between 400 and 500 °C.

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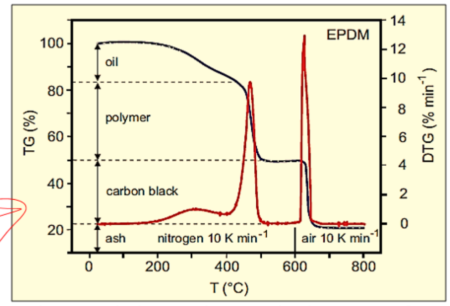
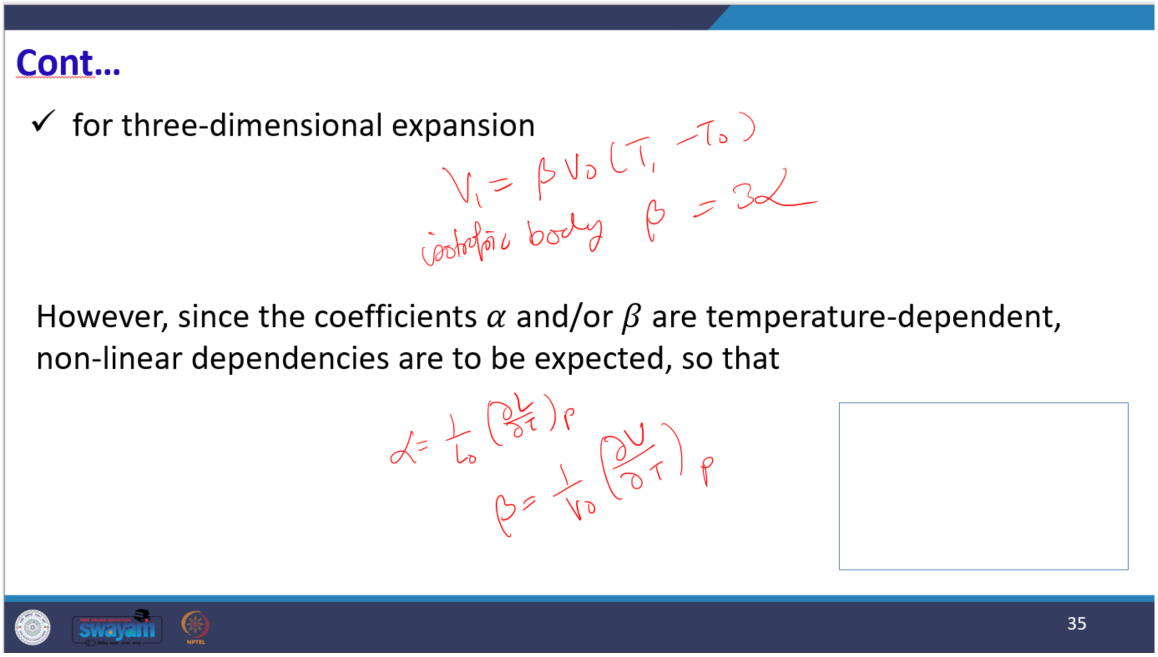
- ✓ Various purge gases are employed, depending on the measurement requirement, to record mass change as a function of temperature and/or time as illustrated in the figure.
- ✓ For the interpretation and separation of effects, the differential measurement signal TG/dt, also known as the DTG curve, is frequently introduced.
- ✓ Additional details on the kinetics of deterioration are provided by the DTG signal..



Thermal degradation behavior of EPDM

The atmosphere is changed from nitrogen to oxygen at 600 °C, which causes the carbon black to burn off, and ash is the residue left behind.

Thermo mechanical analysis: As the temperature rises, polymers expand because of the unentanglement of the chain. The average linear α, also known as a thermal expansion number or the cubic β coefficient of thermal expansion of the specific material, is revealed by measuring thermal expansions together with significant transitional effects during heating. When a body's length, say L_1 or a volume V_1 changes with the temperature increase of, say 1 Kelvin, the term thermal expansion coefficient K^{-1} is used.



When only a small temperature range is considered, the resulting length change can be given by this formula, which is

$\boldsymbol{L1 = \alpha L_0(T_1\text{-}T_2)}$

For three-dimensional expansion;

$$V_1 \beta V_0 (T_1 - T_0)$$

and the isotropic body β

$$\beta = 3\alpha$$

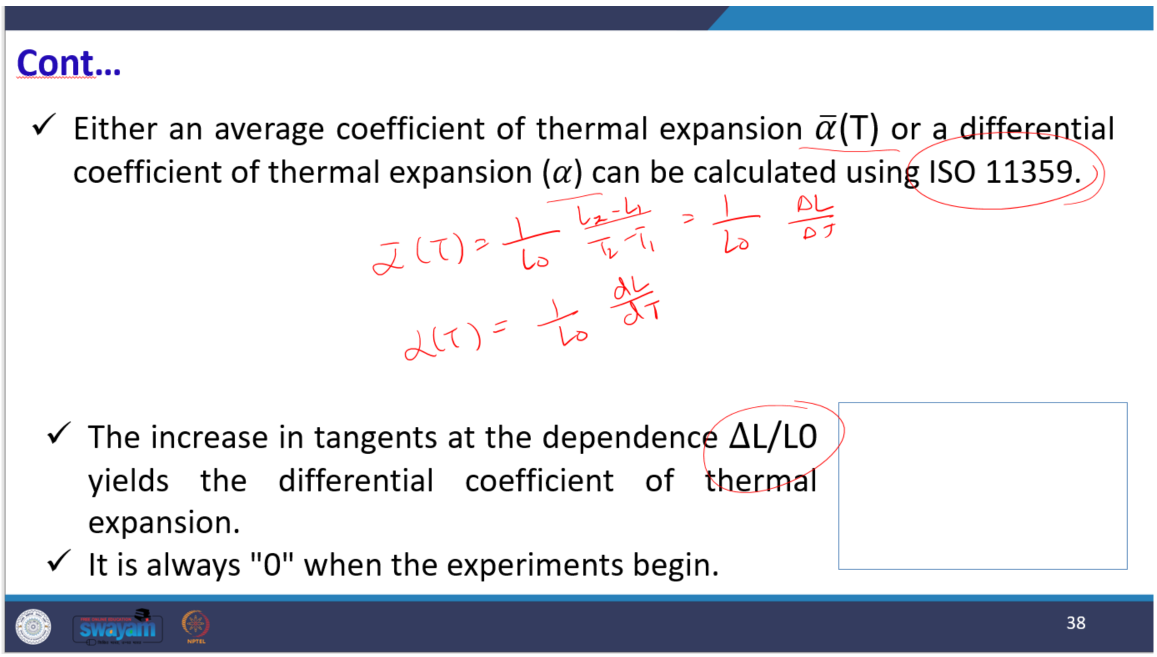
However, since the coefficient alpha and beta are temperature dependent, nonlinear dependency is to be expected. So,

$$\alpha = \left(\frac{1}{L_0}\right)\left(\frac{\delta L}{\delta T}\right)_P$$

$$\beta = \left(\frac{1}{V_0}\right)\left(\frac{\delta V}{\delta T}\right)_P$$

Now, the secondary relaxation, which occurs as temperature rises, causes the local motion of a tiny group of molecules. The primary relaxation that follows causes the cooperative motion of the entire molecule segment.

Now, in the transition ranges, the thermal expansion coefficient fluctuates irregularly. A reliable method for figuring out the linear thermal expansion coefficient of the polymer is thermo mechanical analysis or TMA. Unlike noncontaining dilatometry, TMA measurement uses a steady light-applied load. Utilizing a cylindrical or rectangular specimen with plain parallel measurement surfaces is common. A quartz punch is used to apply a small load of, say, 0. 1 to 5 grams.



An inductive measuring device is used to detect the thermal expansion at the same time. The test is set up in an oven that is being heated slowly. So, an average coefficient of thermal expansion that is $\bar{\alpha}(T)$ or a differential coefficient of thermal expansion α can be calculated using ISO 11359. So, this can be written as

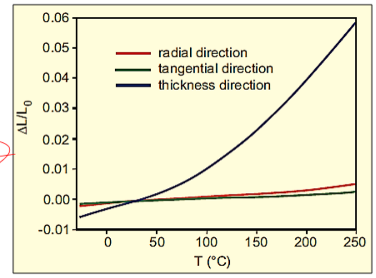
$$\bar{\alpha}(T) = \frac{\left(\frac{1}{L_0}\right)\left(\overline{L_x} - L_1\right)}{T_2 - T_1} = \frac{1}{L_0}\frac{\Delta L}{\Delta T}$$

$$\alpha(T) = \frac{1}{L_0}\frac{dL}{dT}$$

So, the increase in the tangent at the dependence $\Delta L/L_0$ yields the differential coefficient of thermal expansion, and it is always not when the experiments begin.

Cont…

- ✓ Figure demonstrates how fiber reinforcing affects a circular plate's thermal expansion behavior.
- ✓ A significantly higher thermal expansion occurs in the direction of thickness, which is mostly controlled by the thermal expansion behavior of the unreinforced matrix, as opposed to the slight changes in thermal expansion behavior that are observed in the radial and tangential directions.
- ✓ The anisotropy of thermal expansion behavior allows for inferences about fiber orientation.



Figure; Showing thermal expansion of a fiber-reinforced PPS plate

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The first heating cycle in the TMA always delivers data on the thermal and mechanical history, much like the DSC. Now, heating can induce the post-crystallization, release orientation, residual tension, and evaporation. These all result in shrinking and prevent thermal expansion. In thermosets, post-curing has the same effect, and injection molded and extruded parts must also consider the anisotropy effect. This is true for the filled and reinforced materials. A more or less dramatic contraction occurs in heated semicrystalline polymers, and the linear expansion coefficient is in the molecular direction. This can take on negative values due to the tie molecules' undisturbed return on their amorphous ranges in the upper elastic state.

Since the volume measurement yields a positive value, the expansion coefficient perpendicular to the direction of orientation must also strongly rise since the volumetric measurement yields positive values. The thermal expansion coefficient depends on the components' contribution and phase compatibility in amorphous multi-phase systems comparable to semicrystalline polymers. The expansion coefficient often adheres to the straightforward additive rule when both components are above the glass transition temperature. This is only partially true in the region between the transition temperature of the relevant polymer. Since matrix material expands to a greater extent than the filler, the polymer composites with inorganic filler often display lower thermal expansion induced by filler quantity, particle shape, and the process-dependent degree of alignment.

As a result, the anticipated internal stresses are stronger, particularly at the polymer filler interface. The expansion coefficient of a composite can only be analyzed to a limited extent using the laws of the mixture. This particular figure demonstrates how fiber reinforcement affects circular plate thermal expansion. A significantly higher thermal expansion occurs in the direction of a thickness, which is mainly controlled by the thermal expansion behavior of the unreinforced matrix as opposed to the slight changes in the thermal expansion behavior that are observed in the radial and tangential directions. The anisotropic thermal expansion behavior allows for an interface between fibers.

Now, let us talk about the optical properties. The plastic optical properties tests are necessary for product aesthetics and characterizing the polymers and molded parts made from them. The product's market value is significantly influenced by its surface features. The critical optical characteristic values of opaque or transparent molded parts are color, glass, and surface texture. So, basic optical principles, including reflection, reflection, dispersion, deflection, interference, and polarisation, provide the basis for some tests involving the optical properties of the plastic.

In this, the refractive index determination plays a very vital role. So, when light travels non-perpendicularly from one medium into another with the variable refractive index, it also changes direction. The constant n in the ratio of the sine of the angle of incidence (ϵ) to the sine of the deflection angle (ϵ'), also known as the refractive index and deflection index or deflection quotient, describes the substance that passes through.

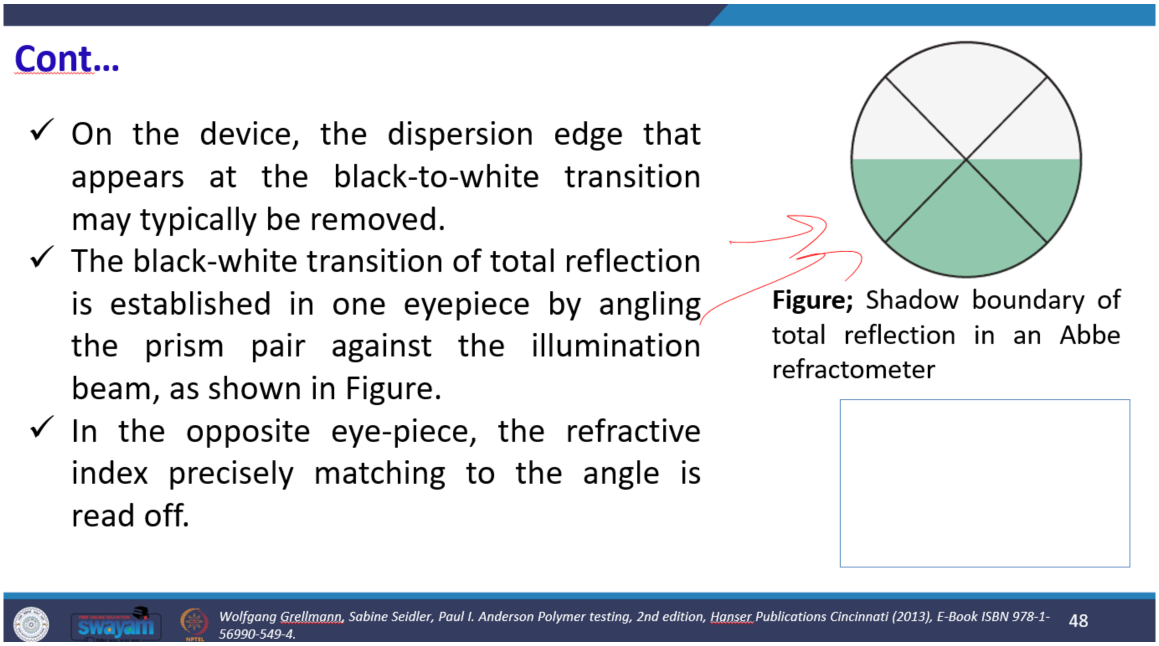
$$\frac{\mathbf{sin}\ (\boldsymbol{\varepsilon})}{\boldsymbol{sin}(\boldsymbol{\varepsilon}')} = \boldsymbol{n}$$

Snellius laws of diffraction are applicable in the light ray passing an interface of two media with the deflection indices n and n'.

$$\mathbf{n.\,si\,n}(\boldsymbol{\varepsilon}) = \boldsymbol{n}'.\,\boldsymbol{sin}(\boldsymbol{\varepsilon}')$$

On diffracting the product of $\mathbf{n.\,si\,n}(\boldsymbol{\varepsilon})$, this remains constant, known as Abbe's invariant.

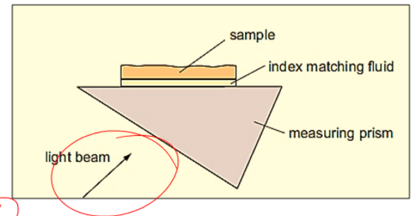
Refractive index determination, the temperature control to prism a bay reflectometer, is an excellent choice for evaluating polymers. A thin lamella is positioned between the prism with one serving at the lighting as prism and other as the measurement prism to calculate the refractive index of liquid. So, at a measurement temperature of 20 °C, illumination is given by monochromatic light from a sodium vapor lamp. Now, on the device, the dispersion edge that appears at the black-to-white transition may typically be removed. The black-white transition of the total reflection is established in a one-speed eyepiece by angling the prism pair against the illumination beam as per this figure. Only one flat surface of solid material, roughly the size of the measuring prism, must be polished.



On the measuring prism, this particular plane is placed within an immersed liquid, and the liquid must not damage the interacting material. Have a refractive index greater than the space but less than that of the prism, and an arrow indicates the light incidence direction. Let us talk about polarization, and the transfer waves can polarize when they are in perfect oscillation conditions. In this case, the propagation direction is perpendicular to the oscillating value of the light or a field distance curve vector. In non-polarized light, this light vector is perpendicular to the propagation direction in all conceivable directions. However, when the light is polarized, the vector at every point in space adopts a parallel position to a clearly defined direction, and polarization direction refers to this particular optimum oscillation direction.

Cont...

- ✓ Only one flat surface of a solid material, roughly the size of the measuring prism, needs to be polished.
- ✓ On the measuring prism, this plane is placed with an immersion liquid.
- ✓ The liquid must not damage the interacting materials and have a refractive index that is greater than that of the specimen but less than that of the prism.
- ✓ The direction of light incidence is indicated by an arrow.



Arrangement of refractive index determination on solid materials using a refractometer.

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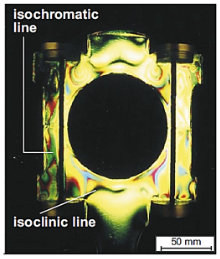
So, when the oscillation directions of two polarized light waves are perpendicular to one another, the overlapping does not result in density interference but rather a change in the oscillation state of the polarized wave. The phase difference between the two polarized waves' amplitude determined how the resulting field vector moves. So, the linear polarized light is produced by overlapping when the phase difference is 0° or 180° and elliptically polarized light in all other situations. Circularly polarized light is produced whether the phase difference is 45° or 270°. When we talk about polarization optical testing methods, measuring mechanical stress in a polarimeter comes into existence. These isotropically are the transparent model bodies made material like epoxy resin or PMMA and in an upper-loaded state, they mostly appear black between crossed polarizers.

In a polarimeter, the specimens are loaded adequately for practical use and resulting optical stress; the frequency is measured and recorded digitally. Then the assessment of stress and deformation under both static and dynamic loading can be carried out. This figure displays the stress optical recording of the model body to distinguish between the colored and black isochromatic lines. The network of isoclinic lines can be geometrically translated into an isotactic line network, depicting the progression of the main stresses in the model body. The polarizer and analyzer are quickly rotated about the model body to separate the isochromatic and isoclinics; thereby, the isoclinic network travels and can no longer be seen by the naked eye at high velocities. So, in the illustration, only the stationary isochromatic image remains visible.

Cont…

- ✓ Figure displays the stress optical recording of a model body to distinguish between colored and black isochromatic lines.
- ✓ The network of isoclinic lines can be geometrically translated into an isostatic line network, which depicts the progression of the main stresses in the model body.



Figure; showing Stress optical image of model body under loading in linear polarized transillumination

Now, to eliminate the isochromatics of polymers such as PMMA, it is used that has an optical stress constant that is as low as possible. Now, despite high loading, only isoclinic appears, and to perform such a stress optical test, the literature should be consulted without determining the absolute numerical stress value; the stress optical image permits the recognition of the direction of the principal stress and low-stress region as well as the area of local stress concentration. So, dear friends, we discussed the various test protocols with the thermal and the optical ones. We have enlisted several references for your convenience, which you can utilize. Thank you very much.