Exclusive Solutions for Innovative Minds

THERMAL ANALYSIS

PRINCIPLES AND APPLICATIONS IN THE FIELD OF POLYMER AND COMPOSITES
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Thermal analysis is a branch of materials science where the properties of materials are studied as they change with temperature. Wikipedia

“a group of techniques in which a property of a sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.” **ICTAC**

A composite material is a material which is produced from two or more constituent materials. These constituent materials have notably dissimilar chemical or physical properties and blended to create a material with properties unlike the individual elements. Wikipedia

- Cost effective
- Lighter
- Chemically resistant
- Mechanically Stronger
- Defined performance

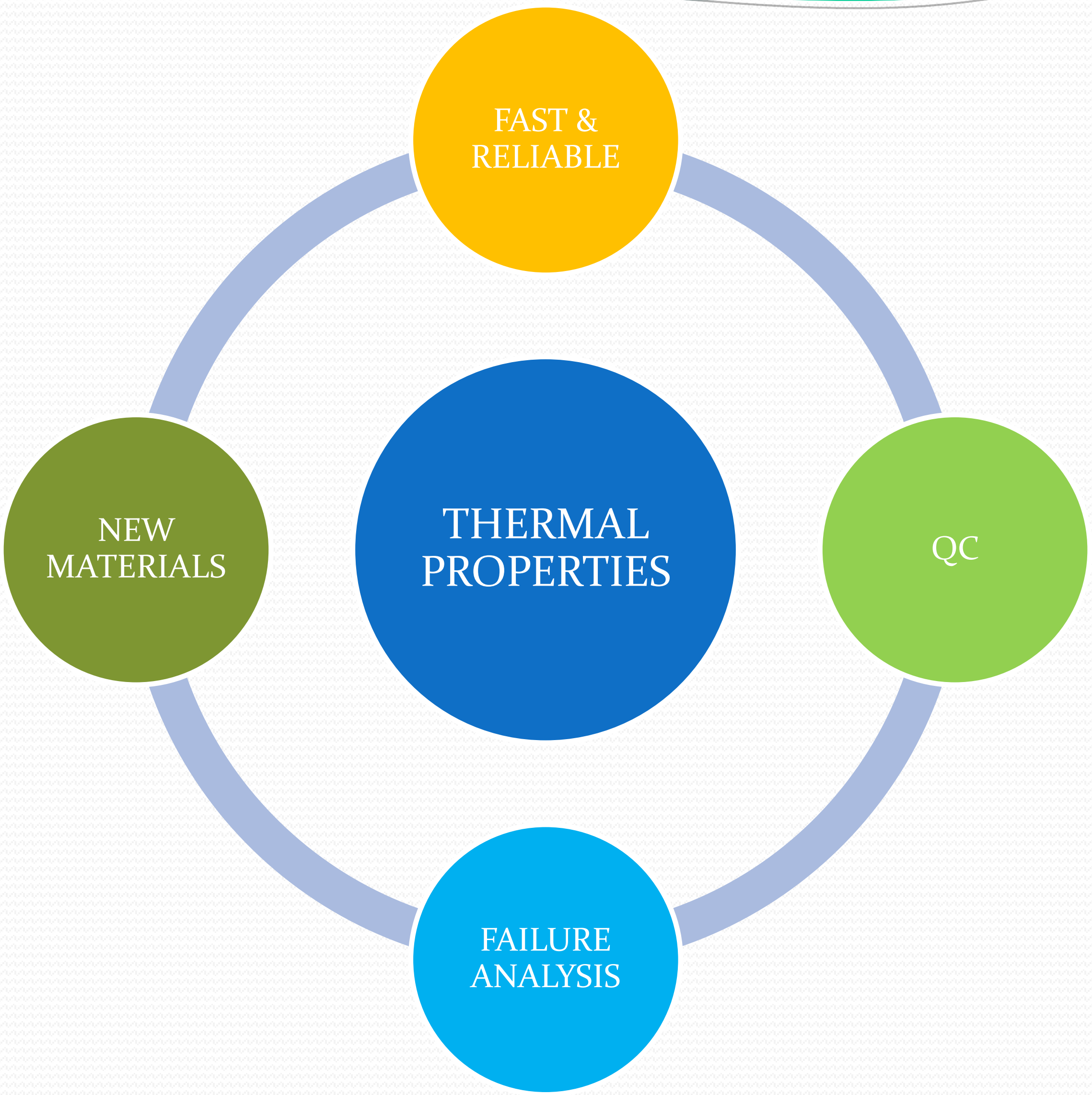
CLASSIFICATION OF COMPOSITES

MATRICES

REINFORCED

POLYMER
CERAMIC
METAL
GRAPHITE

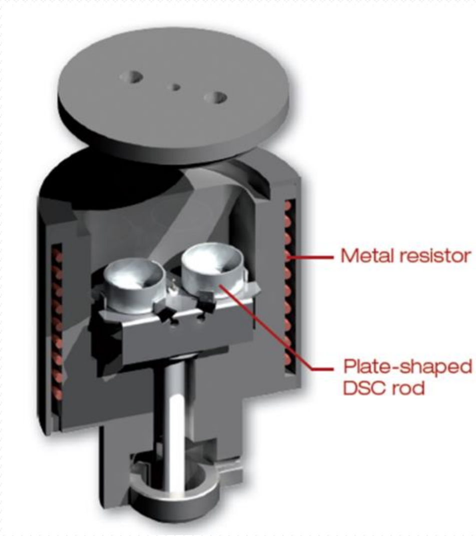
FILLED
FIBERS
MICROSPHERES


FAST & RELIABLE
NEW MATERIALS
THERMAL PROPERTIES
QC
FAILURE ANALYSIS

TECHNIQUE	WHAT IT MEASURES	APPLICATIONS
DSC	Heat Flow/Flux	Curing, quality control etc
TGA	Mass change	Decomposition, quantification
DMA	Viscoelastic	Glass transition, Modulus
TMA	Dimensional change	CTE (thermal expansion)
COUPLING	Evolved gases	Corrosive and environmental
TRIDENT*	Conductivity-thermal	Heat transfer

DSC (Differential Scanning Calorimetry)

A technique in which the **heat flow rate** (power) to the sample is monitored against time or temperature, while the temperature of the sample, in a specified atmosphere is programmed.



DSC

A simple and powerful solution for Differential Scanning Calorimetry

- -170 to 700.C
- Regular crucibles (Al, Al_2O_3)
- High pressure (500 bar, 400.C)
- Majority of needs covered
- Heating and cooling controlled
- Specific heat as per ASTM

Typical applications

Applications overview

- **Temperatures and enthalpies of melting and crystallization of most materials**
- **Glass transition temperatures of polymers**
- **Heat of curing / degree of curing of polymers**
- **Oxygen Induction Time of polymers**
- **Purity of chemicals using the Van’t Hoff method**
- **Materials decomposition and thermal stability**
- **Materials phase Diagram**
- **Heat capacities of solids or liquids**

Typical DSC Plot and inferences

Conditions

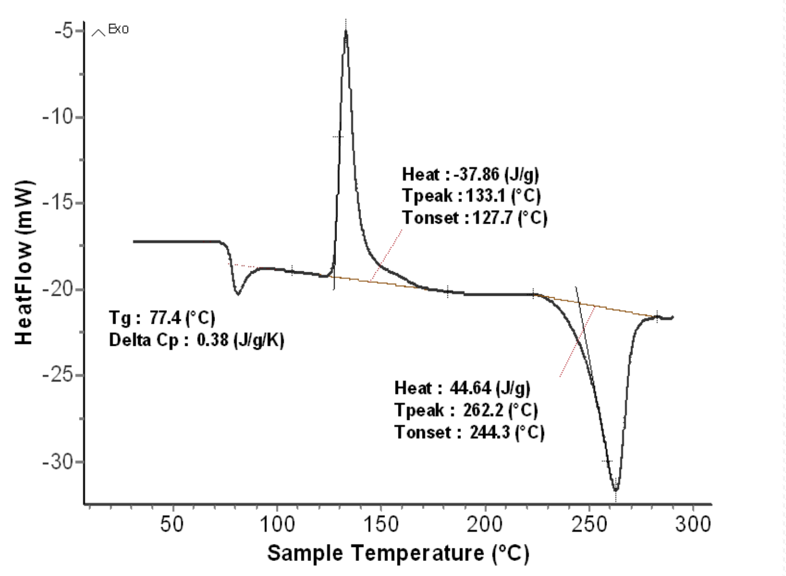
DSC trace of a 25 mg sample of PET (Poly Ethylene Terephthalate) sample heated at 10 °C/min.

Results

From left to right: **glass transition**, exothermic **crystallization** of the amorphous phase, and endothermic **melting**.

The related temperatures and heat are simply and accurately determined using Calisto software.

These are key data for the understanding of the thermal behavior of this polymer.



Typical applications

Oxidation Induction Time (OIT)

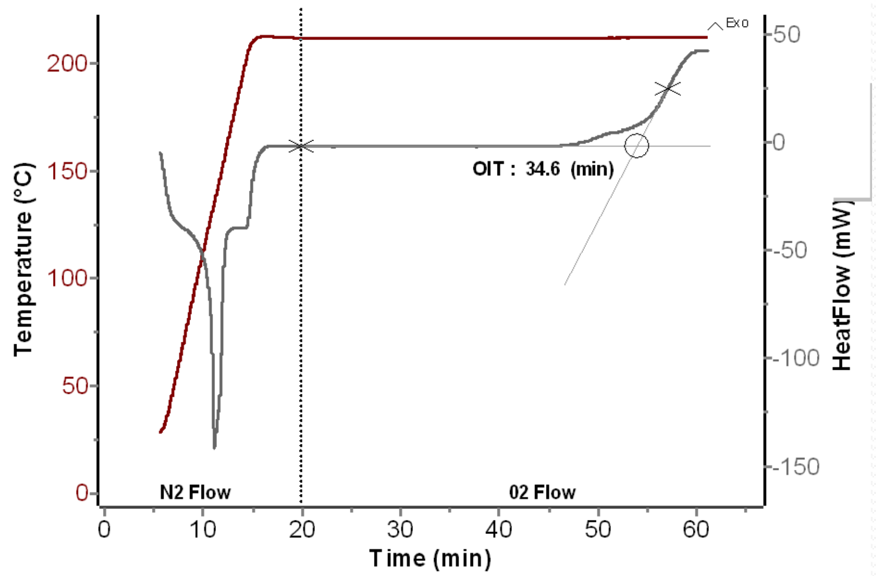
Conditions

The sample is firstly heated up to 210°C under inert gas flow (nitrogen). After signal equilibration (20 minutes), the gas flow is changed to oxygen.

Results

An exothermic effect of oxidation of the polymer is observed at roughly 45 minutes. The OIT, defined as the time between the switch to oxygen and the onset time of the effect, is found equal to 34.6 min.

The OIT could be increased by the addition of antioxidants.

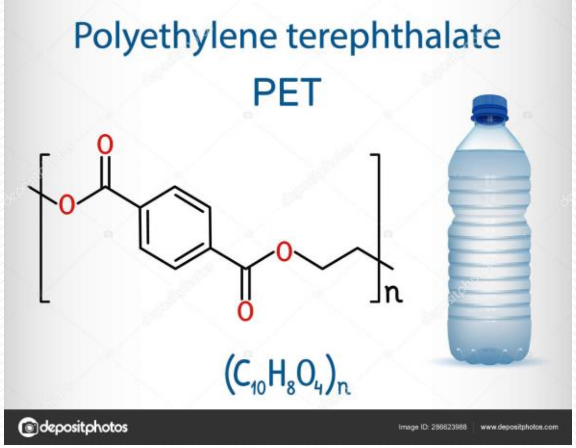


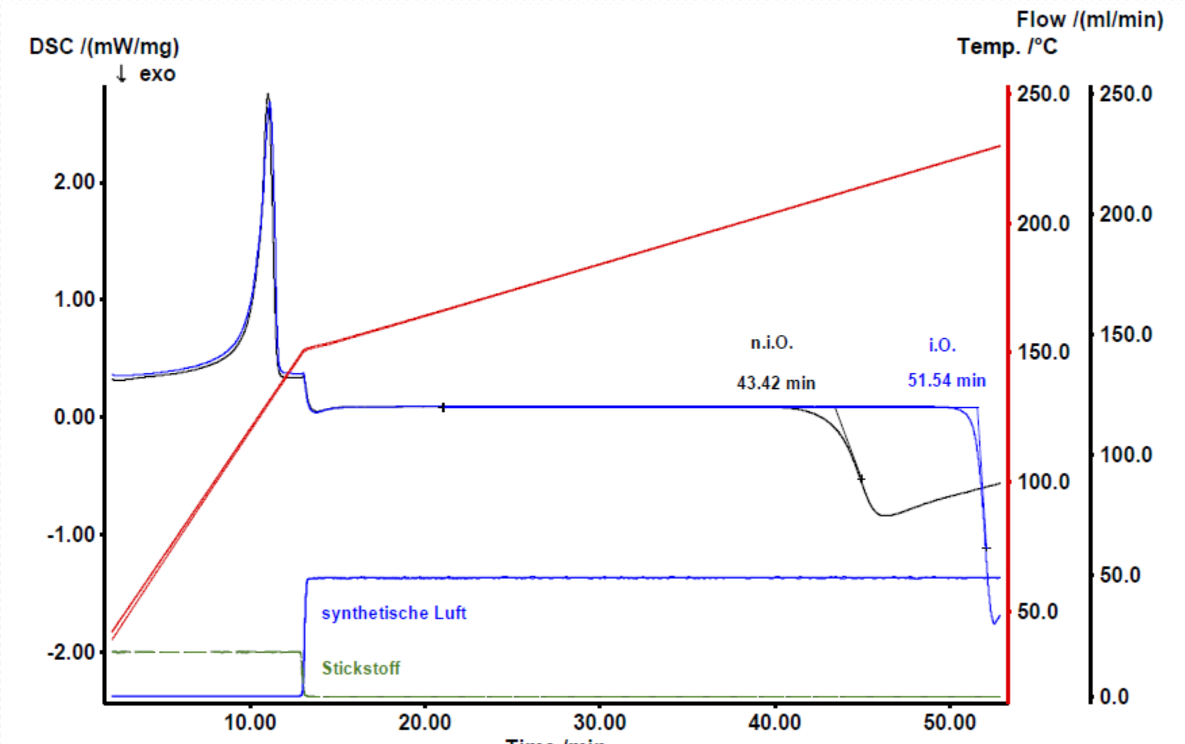
PET (Polyethylene) , a commercially so useful Thermoplastic

Radical/Anionic/Ion Polymerization

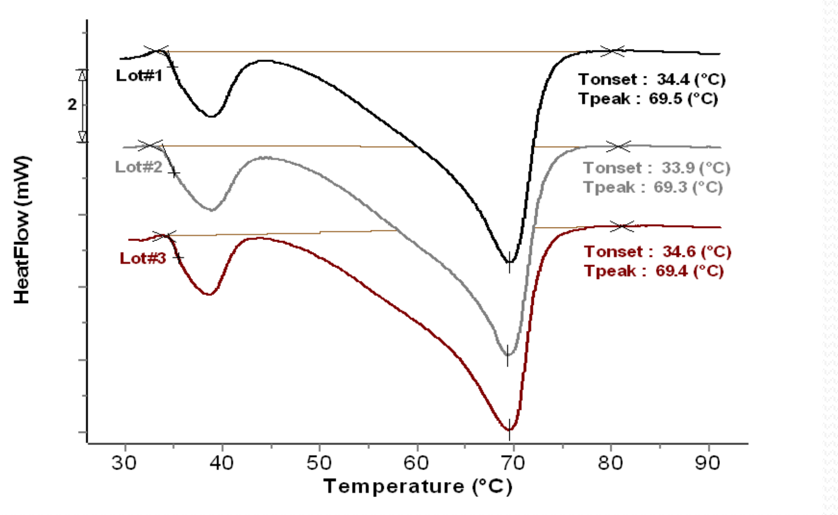
Regardless of the process, they age during usage & storage.

Oxidation plays a key role in aging





Melting profiles



Experimental Conditions

3 different lots of the same cosmetic ingredient (lipstick), heated from 25°C to 100°C at 5°C/min under nitrogen flow (40 ml/min)

Results

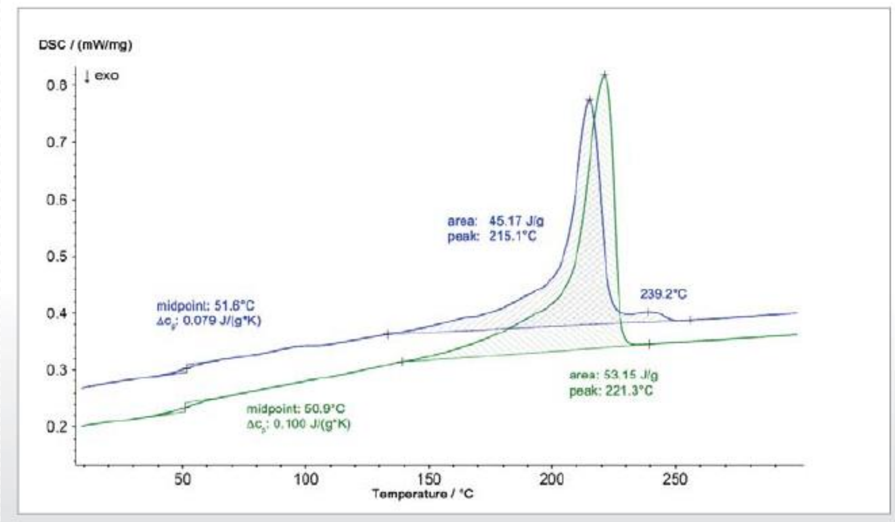
The profiles of the endothermic melting of each lot are treated by Calisto using a macro to determine each start (onset) and end (peak) temperatures of melting.

Macro programming is a fast tool to ensure QA batch after batch.

FAILURE ANALYSIS a case study

Manufacturing process → Mechanical Properties → Performance and durability

GF reinforced PA6 , embrittlement and breakage reported
Investigation started at the manufacturing process



Tg at 50ºC, Tm at 221ºC & 54J/g PA6

Damaged part peak 215.C and different Enthalpy, additional endo peak at 239.C PA6 and PA66 merged to form eutectic And so failure.

Fast Check for Quality Assurance

Degree of curing / Cross-Linking

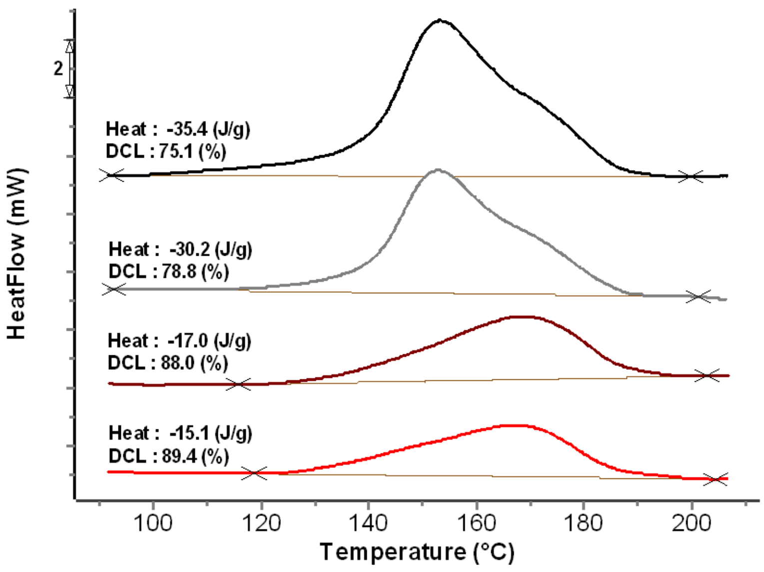
Conditions

Ethylene-vinyl acetate (EVA) copolymers films after lamination, meant to be used as encapsulants for photovoltaic applications.

Heated up to 210°C at 10°C/min under nitrogen flow (40ml/min).

Results

The heat of the residual curing reaction is measured and divided by the heat of reaction of an uncured sample to calculate DCL.



First heating exhibits both Tg and curing reaction, while the second heating Reports only Tg, as the curing is complete in the first heating, another easy to ensure way for cured or uncured samples

TGA

Technique in which the mass of the sample is monitored as a function of temperature or time, while the sample is subjected to a controlled temperature program. The program may involve heating, cooling or isothermal steps.(ICTAC)

ISO 11358, ASTM E 1131 & DIN 51006

Typical applications

- **Thermal stability, ageing, and decomposition pathway of most materials**
  - Polymers, elastomers, pharmaceuticals, biomaterials,
  - organic substances like coal, oils, lubricants…
- **Compositional analysis:**
  - Ashes, carbon, fillers, additives contents
  - Moisture, solvent contents
- **Study of thermal effects like:**
  - Pyrolysis, combustion
  - Desorption
  - Dehydration, dehydroxylation

Typical applications

Decomposition pathway of a mineral A fingerprint

Conditions

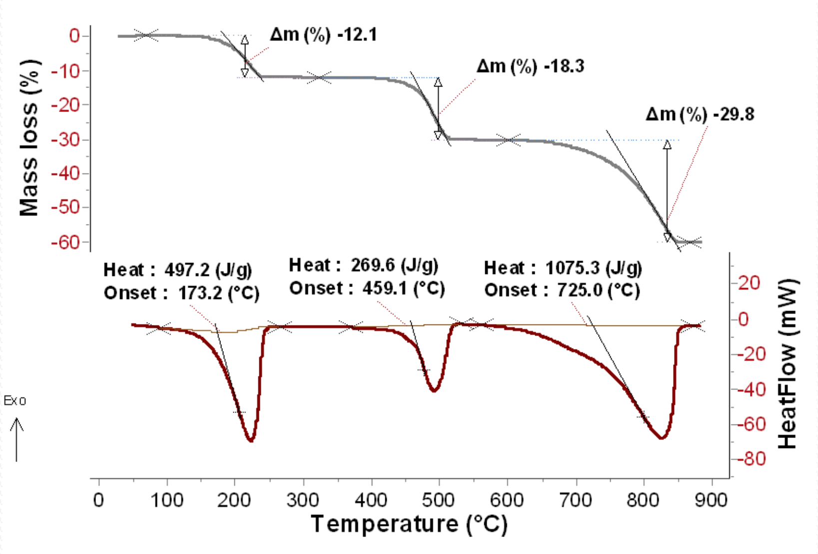
A 40 mg calcium oxalate monohydrate (CaC_2O_4, H_2O) sample heated up to 900°C at 10 °C/min.

Results

Mass loss (TG) and Heatflow (DSC) traces.

From lower to higher temperatures: endothermic dehydration, formation of calcium carbonate, and formation of calcium oxide.

This rather simple example highlights the quantitative aspect of thermogravimetry measurements.



GFRP/CFRP:

Main attractions:
Light weight,
Customizable to suit different applications
Cost effective and environment friendly
Newer markets (sport cycles, laptops, etc) in addition to high margin aerospace and Leisure sports

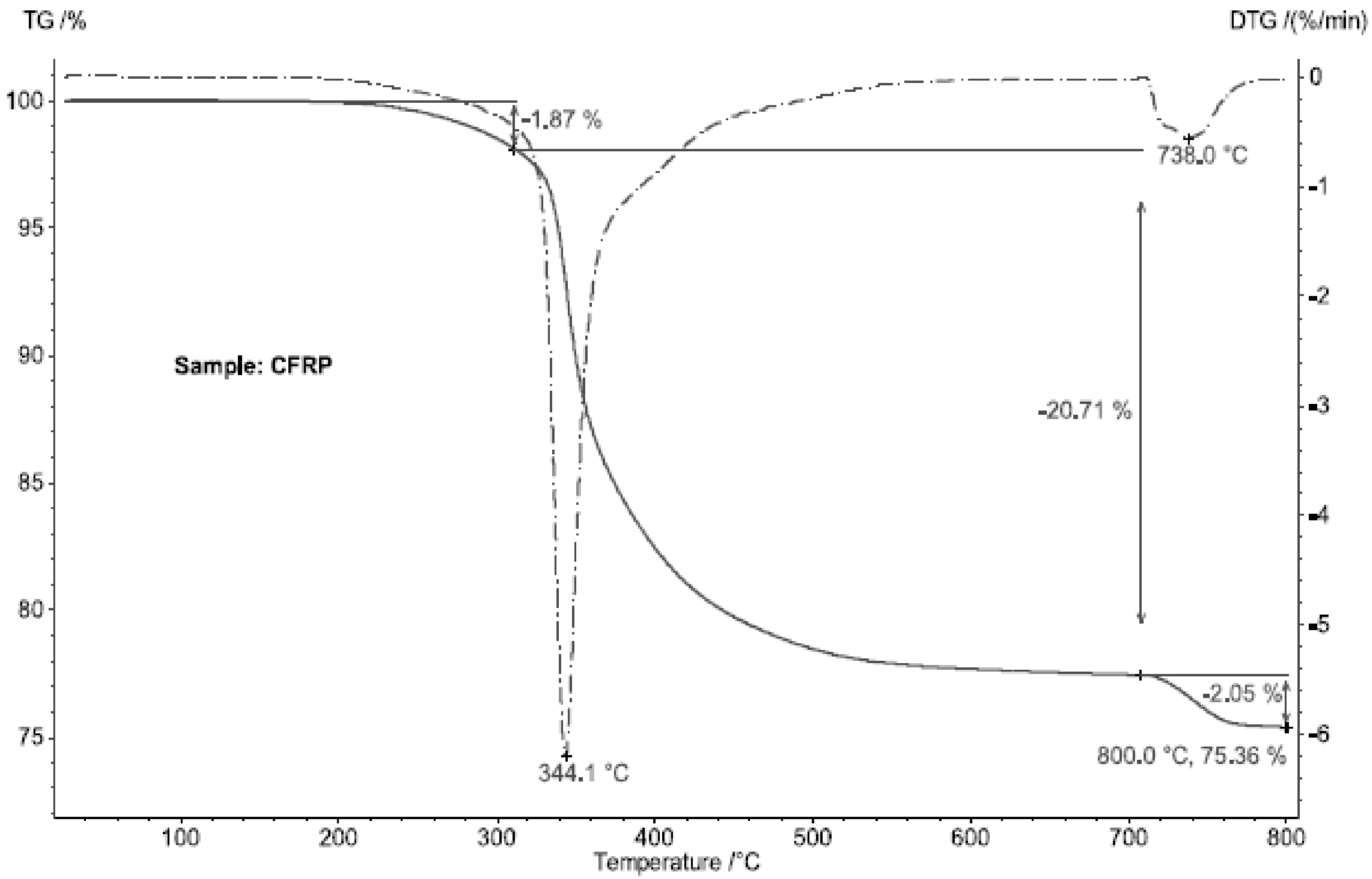
GF reinforced composites, QC Demands:

Unique properties such as high corrosion resistance, high mechanical strength despite light weight,

However thermal stability Vs higher temperatures in service conditions a Challenge

Resin	Temp Limit
Polyester	60….150.C
Epoxy	80….200.C
Phenol-Formaldehyde	150 to 250.C
Polyimide	200… to 400.C

Mass loss with increase in temperature, a conclusive indicator for thermal Stability of materials to make the right choice. TGA is the Go to.


TG /%
DTG /(%/min)
100
95
90
85
80
75
0
-1
-2
-3
-4
-5
-6
-1.87 %
738.0 °C
Sample: CFRP
-20.71 %
-2.05 %
344.1 °C
800.0 °C, 75.36 %
100
200
300
400
500
600
700
800
Temperature /°C

Summary of this Measurement:

Nearly 700mg of sample taken
RT…1000.C, 10K/min , inert upto 700 and then to Oxygen switch

1.87% and 20.71% due to pyrolytic decomposition of Epoxy

75% GF content and flame retardants

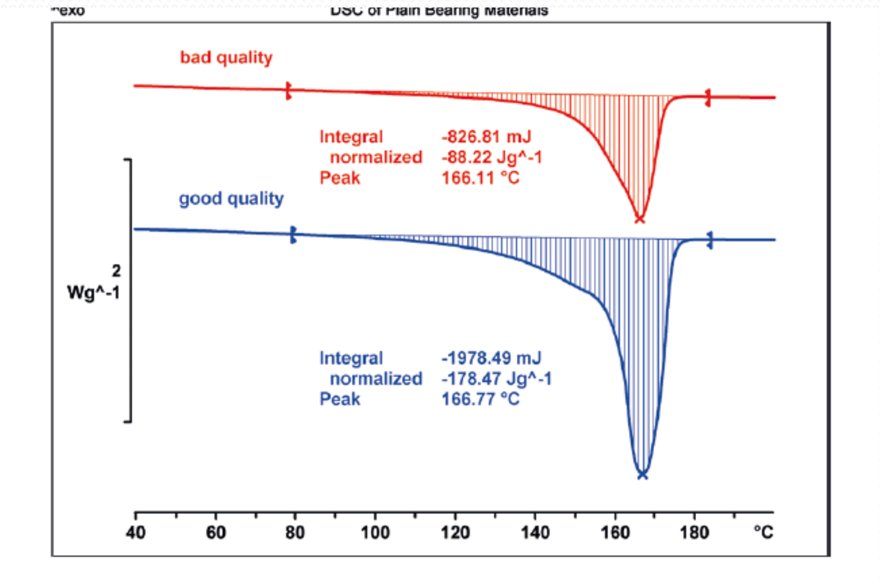
Decomposition of plastic and glass fibre at 344.C and 740.C approx.

TGA allows higher sample loading upto 1g, depending on the Version and possibilities with the device

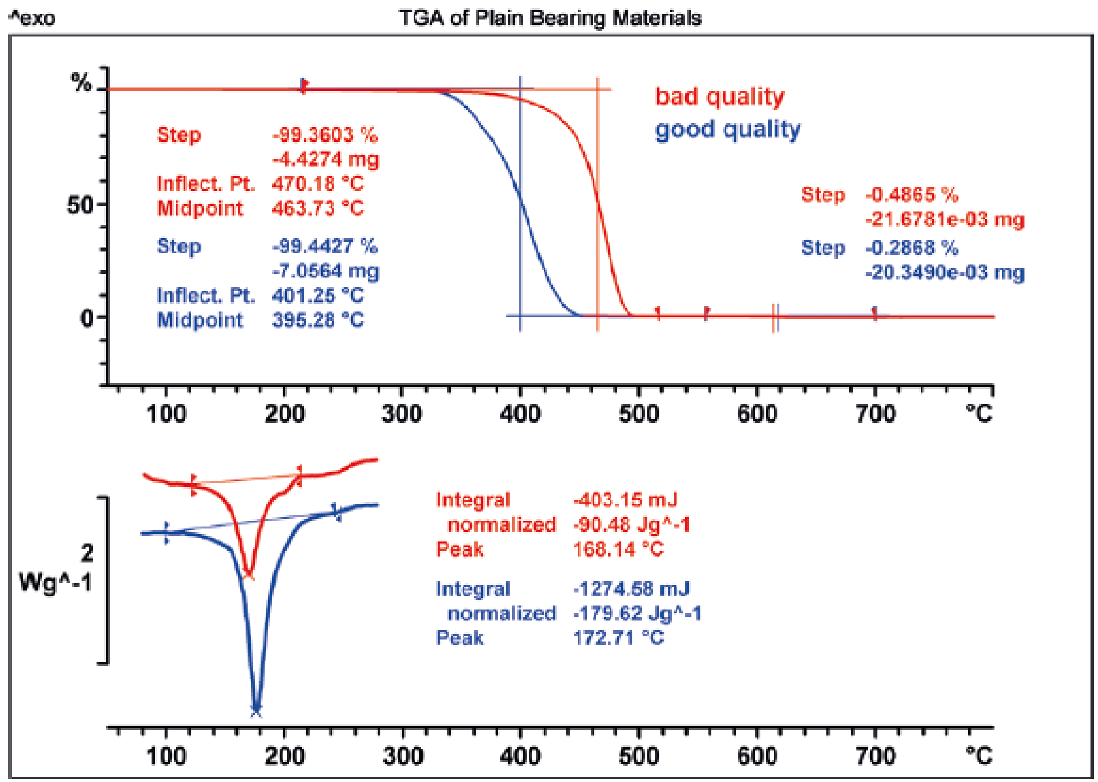
Glass fibre content, residual mass, gas switch over- highlight

Failure analysis TGA case study:

Plain bearing from an unknown source ,
Injection moulded from plastic.



DSC graph wasn't much helpful, similar melting
But different enthalpies,
Different polymers in both cases (may be)
Or different or inferior fillers in the failed part



The polymer for good quality decomposed earlier, while the bad later (395º C & 464º C respectively)

Together with DSC data of enthalpy of fusion one could conclude that

The good polymer was POM (polyoxymethylene) while the bad one corresponds to PP.

TGA complements well DSC in such cases.

THERMAL CONDUCTIVITY

A MEAUSRE OF HEAT TRASFER PROPERTY

Thermal Conductivity:

- What
- Why
- How
- Application Areas
- Summary

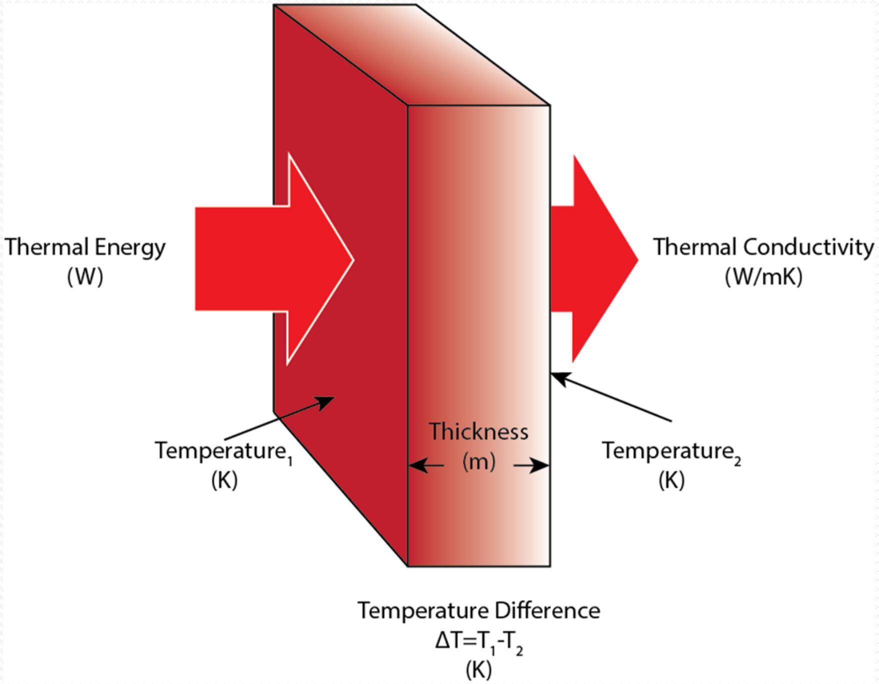
Thermal conductivity is the rate at which heat flows through a material under a temperature gradient.

It is a physical property of a material

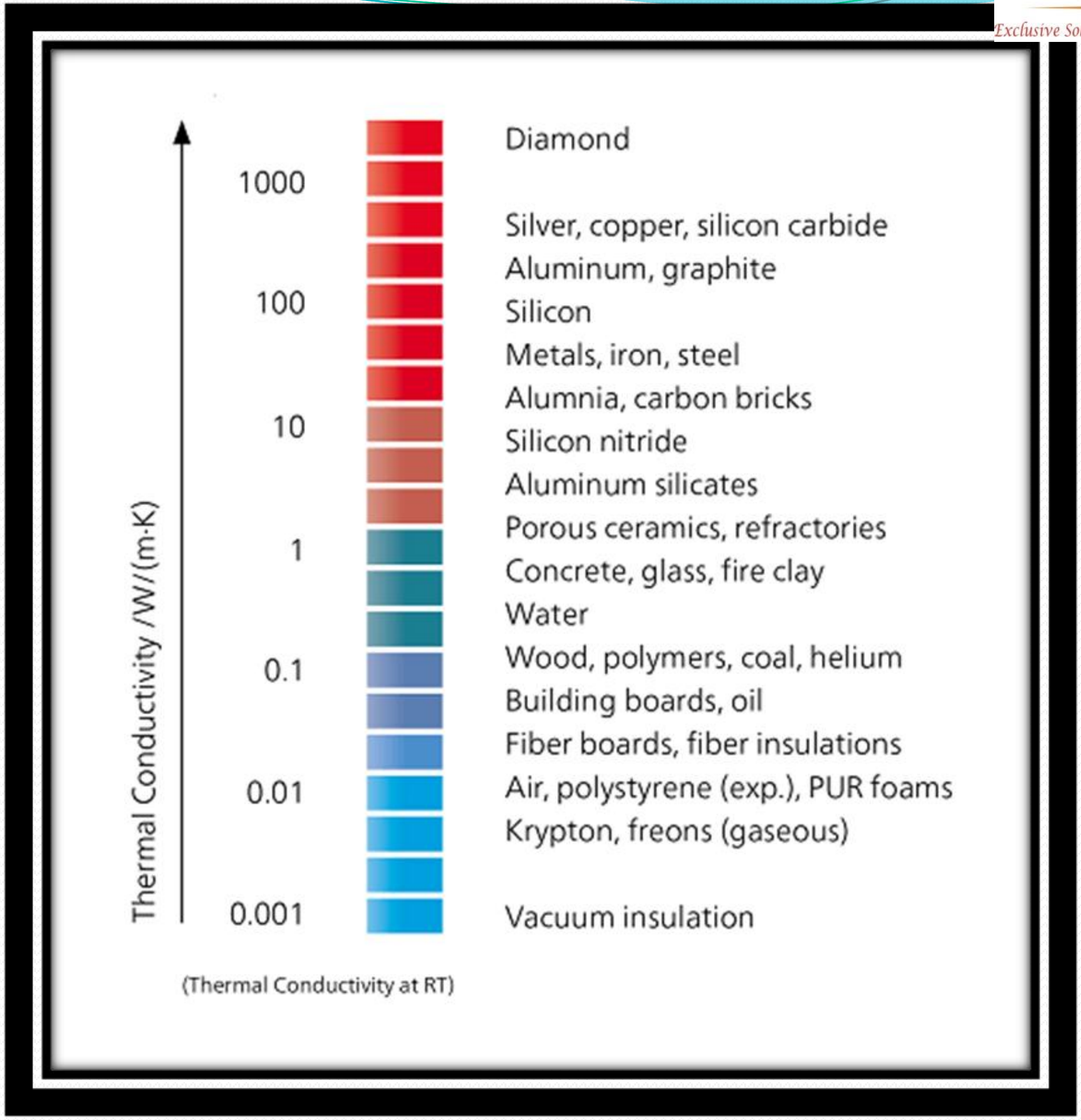
The value of thermal conductivity determines the quantity of heat passing per unit of time per unit area at a temperature drop of 1ºC per unit length.

Expressed as W/m.K

Structure, Density, Humidity, Porosity Pressure, Temperature are **key factors** contributing to **differences** in Materials behaviour in this context.


Thermal Energy
(W)
Thermal Conductivity
(W/mK)
Thickness
(m)
Temperature$_1$
(K)
Temperature$_2$
(K)
Temperature Difference
$\Delta T = T_1 - T_2$
(K)

W/m.K



Diamond
1000
Silver, copper, silicon carbide
Aluminum, graphite
100
Silicon
Metals, iron, steel
Alumnia, carbon bricks
10
Silicon nitride
Aluminum silicates
Porous ceramics, refractories
1
Concrete, glass, fire clay
Water
0.1
Wood, polymers, coal, helium
Building boards, oil
Fiber boards, fiber insulations
0.01
Air, polystyrene (exp.), PUR foams
Krypton, freons (gaseous)
0.001
Vacuum insulation
Thermal Conductivity /W/(m·K)
(Thermal Conductivity at RT)

TYPES OF HEAT TRANSFER

Heat ***Conduction,*** also called diffusion, is the direct microscopic exchange of kinetic energy of particles through the boundary between two systems. When an object is at a different temperature from another body or its surroundings, heat flows so that the body and the surroundings reach the same temperature, at which point they are in thermal equilibrium. Such spontaneous heat transfer always occurs from a region of high temperature to another region of lower temperature, as described in the second law of thermodynamics.

Heat **Convection** occurs when bulk flow of a fluid (gas or liquid) carries heat along with the flow of matter in the fluid. The flow of fluid may be forced by external processes, or sometimes (in gravitational fields) by buoyancy forces caused when thermal energy expands the fluid (for example in a fire plume), thus influencing its own transfer. The latter process is often called "natural convection". All convective processes also move heat partly by diffusion, as well. Another form of convection is forced convection. In this case the fluid is forced to flow by use of a pump, fan or other mechanical means.

Thermal ***Radiation*** occurs through a vacuum or any transparent medium (solid or fluid or gas). It is the transfer of energy by means of photons in electromagnetic waves

It can so happen that all the three forms of heat transfer are present in a given situation

Convection is the transfer of heat by the actual movement of the warmed matter.

Heat leaves the coffee cup as the currents of steam and air rise. Convection is the transfer of heat energy in a gas or liquid by **movement of currents.**
The heat moves with the fluid.

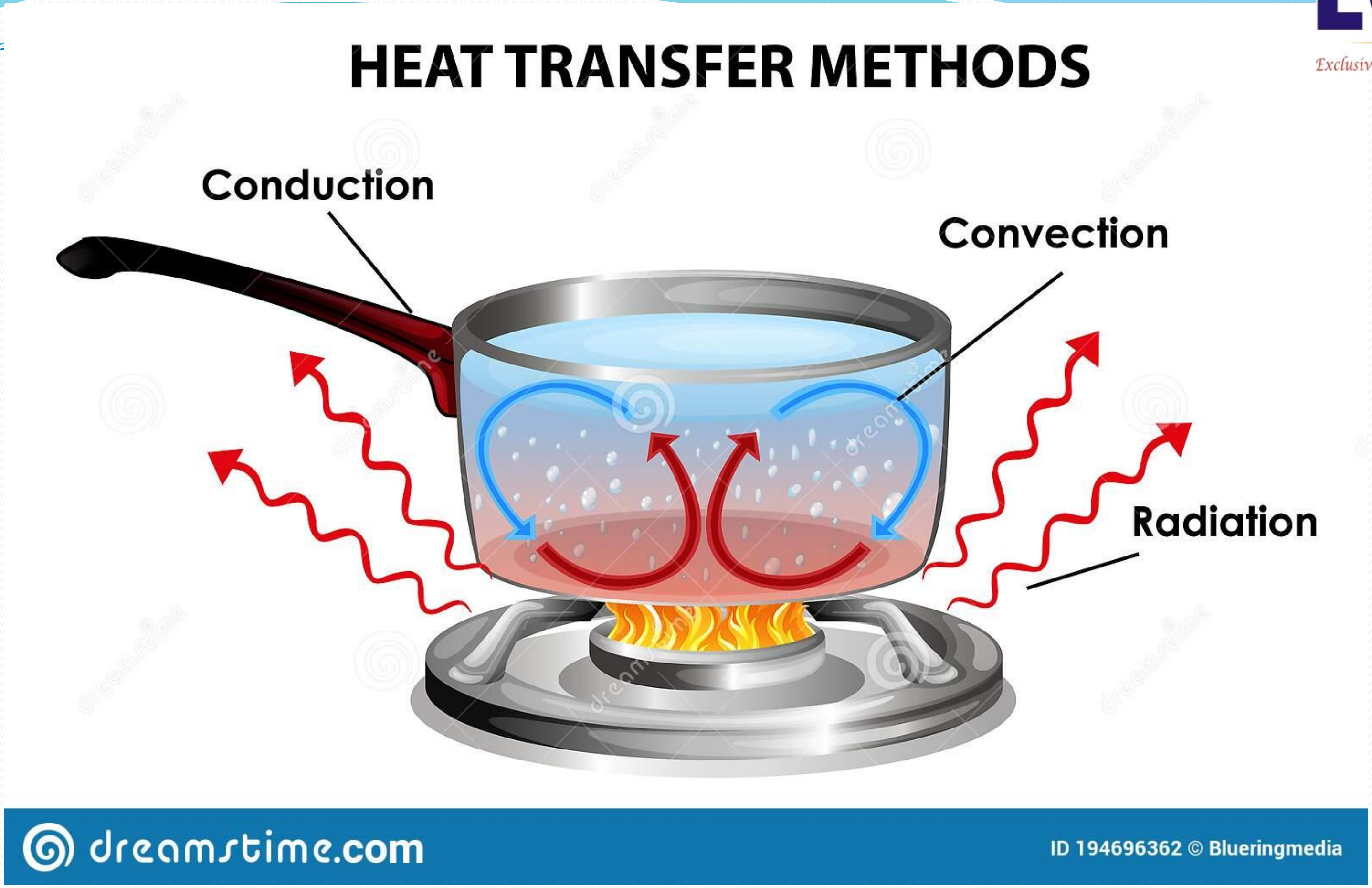
Viscosity and Convection are inversely proportional

Conduction is the transfer of energy through matter from **particle to particle**.

It is the transfer and distribution of heat energy from atom to atom within a substance.

For example, you need to be careful in picking up a frying pan by its metal handle due to Conduction

The heat is transferred through the metal through conduction.



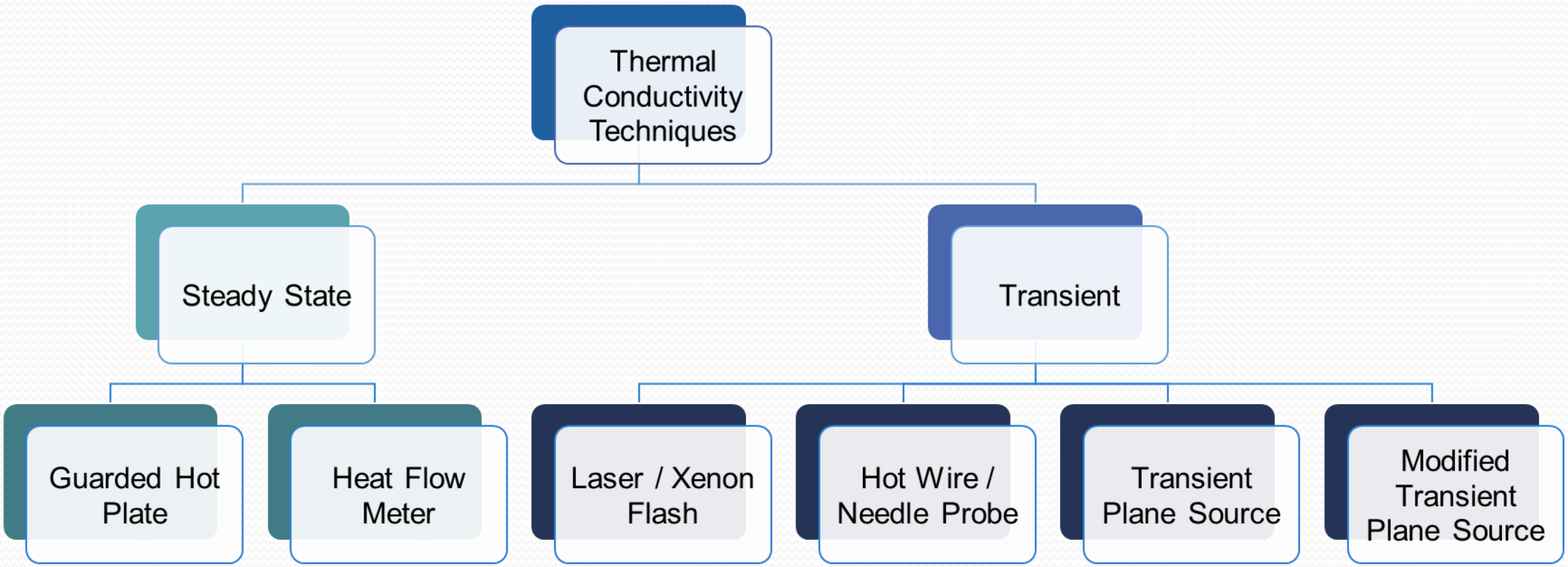
- Conduction when direct contact is possible
- Convection within a medium
- Radiation through electromagnetic means

Higher or Lower thermal conductivity values indicate an important property of a material which would decide its end-use. For example, **fire retardants** Need to exhibit a low conductivity value where as **Cooking vessels** otherwise.

Stainless Steel	16
Lead	35
Carbon Steel	51
Wrought Iron	59
Iron	73
Aluminium Bronze	76
Copper Brass	111
Aluminium	237
Copper	401
Silver	429

This Awareness helps in selection, measurement of K helps this

Classification of Techniques



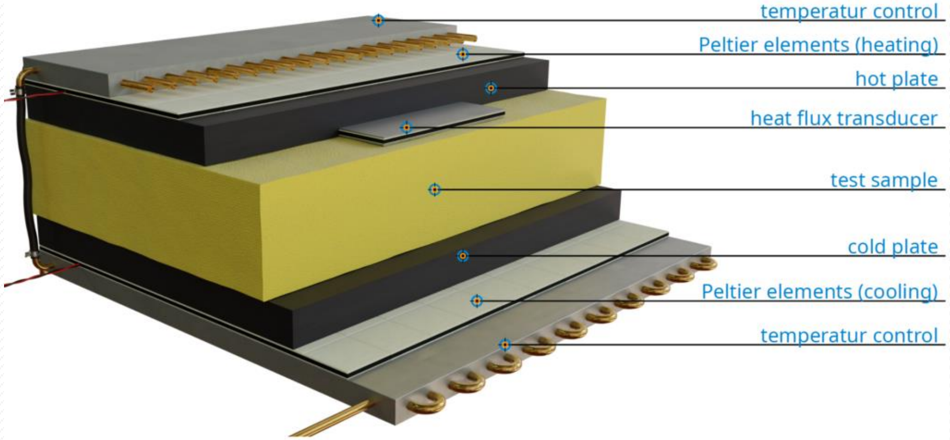
HEAT FLOW METER :

ASTM C518
ASTM C1784
ISO 8301
DIN EN 12664
DIN EN 12667
JIS A1412

A temperature gradient is set between two plates through the material to be measured. By means of two highly accurate heat-flow sensors in the plates, the heat flow into the material and out of the material, respectively, is measured. If the state of equilibrium of the system is reached and the heat flow is constant, the thermal conductivity can be calculated with the help of the Fourier equation as long as the measurement area and thickness of the sample are known.

Heat Flow Meter , typically 0.007 W/m.K , but limited to max 2 W/m.K typically for insulations:
Samples need to be of a particular minimum dimensions like 30 x 30 cm
Steady state , concerned with Mean temperature upto 90.C

Applicable to solids PU Foams a strong candidate



Typical schematics of a Heat Flow Meter , steady state method

Guarded Hot Plate, when one wants to reach extreme low temperatures:

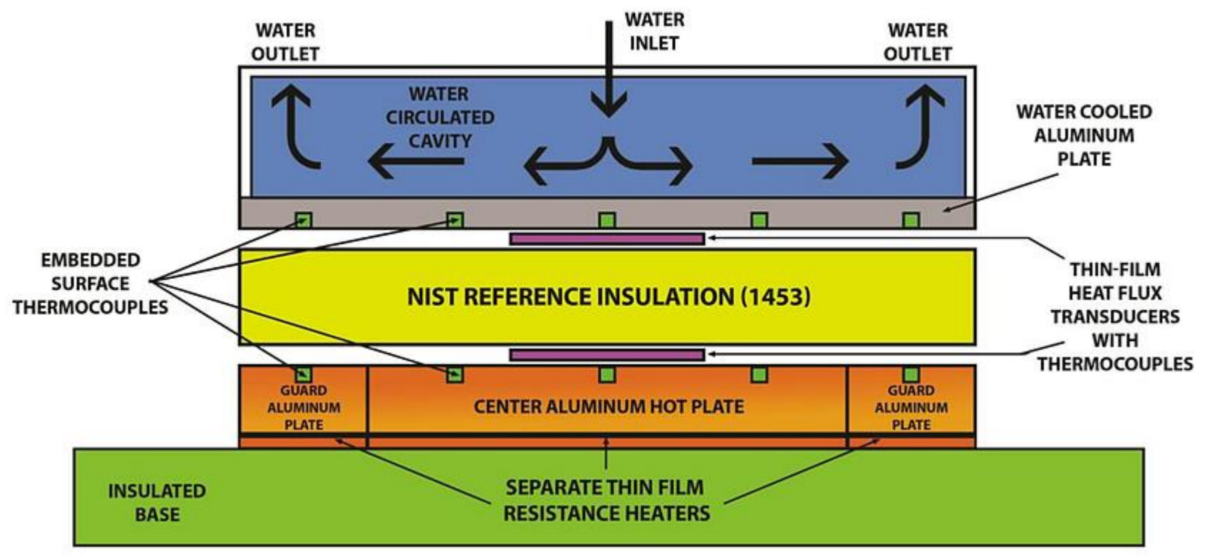
Takes few days or weeks to a measurement due to steady state challenges

Very particular about sample dimensions and need 2 samples
100mm thickness and 300 mm dia.
0.003 to 2W/m.k
-150 to 300/600ºC

Calcium Silicate, Expanded glass granulates, fibre glass insulations

ISO8302

Insulations
Bigger footprint

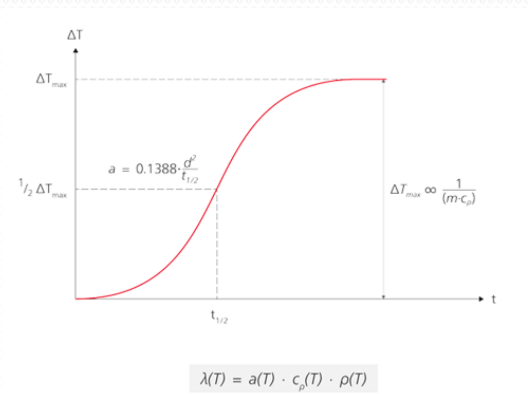


LASER FLASH DEVICE:

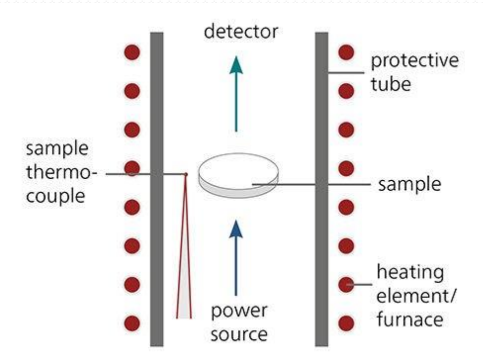
The lower surface of a plane parallel sample is first heated by a short energy pulse. The resulting temperature change on the upper surface of the sample is then measured with an infrared detector. The typical course of the signals is presented in figure 2 (red curve). The higher the sample's thermal diffusivity, the steeper the signal increase.

Solids,
Composites
Very high temperatures
graphite, metals
Silicon Nitrides etc

Half time $t_{1/2}$, time value at half signal height) and sample thickness (d), the thermal diffusivity (a) and finally the thermal conductivity (λ) is derived by **λ = a.Cp. P 0.1W/m.K onwards.**



Density and Specific heat are Compulsory



Flash Technique

LCGC
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TRANSIENT

- ModifiedTPS
- TPS
- TLS

Effusivity- Why should I bother about this?

Thermal Effusivity is used to describe heat transition behavior of two objects, when the two objects are contacted to each other. When the two materials have the same thermal Effusivity, the heat transition behavior will equal to a unique object as if there are no junction between the two objects.

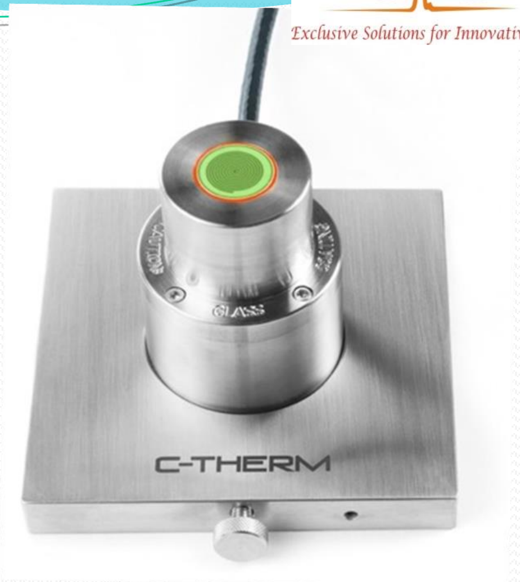
A typical example is the human skin. When we touch different materials for a period, we will have different feelings. We feel cool with some materials, and feel warm with some others. Let's say, hand on a metal pipe in the park, we feel cool, and a cotton cloth is warm. To the physical measurement, the metal pipe has higher thermal Effusivity and the cotton cloth is lower. Thermal Effusivity is a unit which can express the real physical amount, instead of the feeling of 'cooler' or 'warmer'.

$\sqrt{K\rho c_p}$, gives Effusivity

Air	6
Rubber	518
Human Skin	1360
Silver	23688

https://theconversation.com/cool-touch-shirts-can-make-you-feel-cool-on-hot-days-but-which-materials-work-best-144475

MTPS (Modified TPS) or MTPS



Single sided

Fastest Measurement , Negating convention issues

Almost any geometry samples

Any sort of sample state (liquids/solids/powders/paste)
Anisotropic and isotropic handling

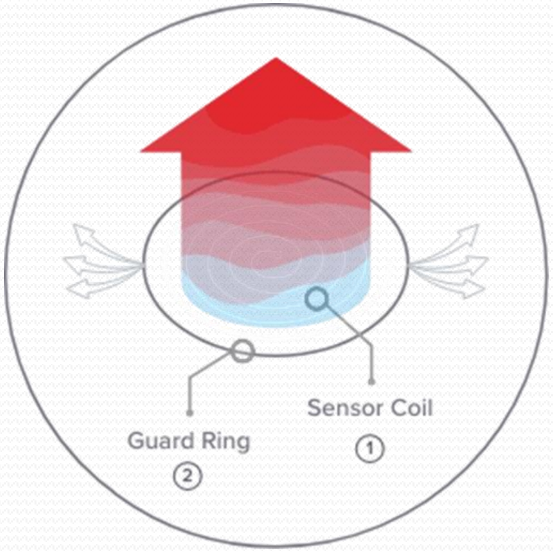
0.03W/m.K onwards and upto 500W/m.K

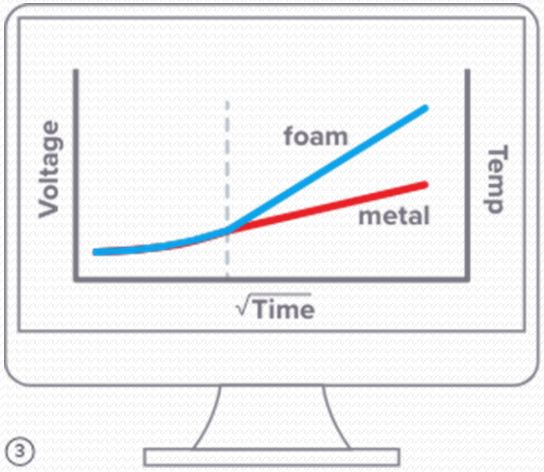
Need of a contact agent to reduce contact resistance

In addition to Conductivity this gets Effusivity too
Thermal Effusivity, is a value to describe the behavior of the heat storing or dissipating capability of materials.
It is the square root of the product of the material's thermal conductivity and its volumetric heat capacity: $\sqrt{K\rho c_p}$

How this works

Current is applied in electrically heating main sensor coil.
A guard ring surrounds the primary sensor coil to support a one-dimensional heat transfer into the sample.
The voltage drop is calibrated to monitor the change in temperature over time. The sample's thermal conductivity is inversely proportional to the rate of increase in the temperature. Slope is much steep for low conducting and vice versa.





TRANSIENT PLANE-SOURCE (TPS)

Double-Sided Sensor

Greatest flexibility over experimental parameters (timing & power)

No contact agent required, except powders, two identical sample blocks needed

Specific sample dimensions a pre requisite depending on the sensor diameter, mostly demand two identical samples

0.05 to 2000W/m.K

Does report Cp too and thermal diffusivity too.

Conforms to ISO standard 22007-2

How TPS technology works?

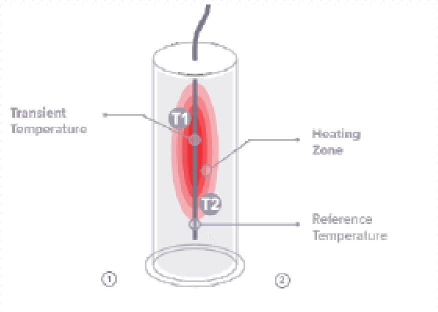
Planar, double-sided spiral sensor placed within the sample or between two solid blocks of sample

Constant heat flux applied

Temperature measured over time

Analysis of temperature-time data gives thermal conductivity and diffusivity

TLS Needle: (Transient Line Source)



Method for testing semi-solids, high viscous liquids

How this works?

An electrically heated needle is inserted into a material. The heat flows out radially from the needle into the sample.

0.1 to 0.6 W/m.K

An internal platinum wire is heated electrically – providing a known amount of heat per unit length.

The temperatures are measured at locations T1 (located in the middle of the heating wire) and T2 (located at the tip of the needle).

The rate of increase in delta temperature difference as a function of logarithmic time is then used to calculate the thermal conductivity of the sample. The slope of the line is inversely proportional to the thermal conductivity of the sample. The temperature will rise more steeply when lower thermal conductivity materials (e.g. powders) are tested.

Conforms to ASTM D5334, D5930 and IEEE 442.

TLS NEEDLE

Sheathed in stainless steel, the TLS Needle sensor offers maximum robustness in thermal conductivity testing of polymer melts and aggregate samples.
Conforms to ASTM D5334 and D5930.

ANISOTROPIC/ISOTROPIC – Remark

Isotropy is uniformity in all directions, in other words, direction independent
Anisotropy is exactly opposite, meaning such materials are heavily
Dependent on direction of measurement.

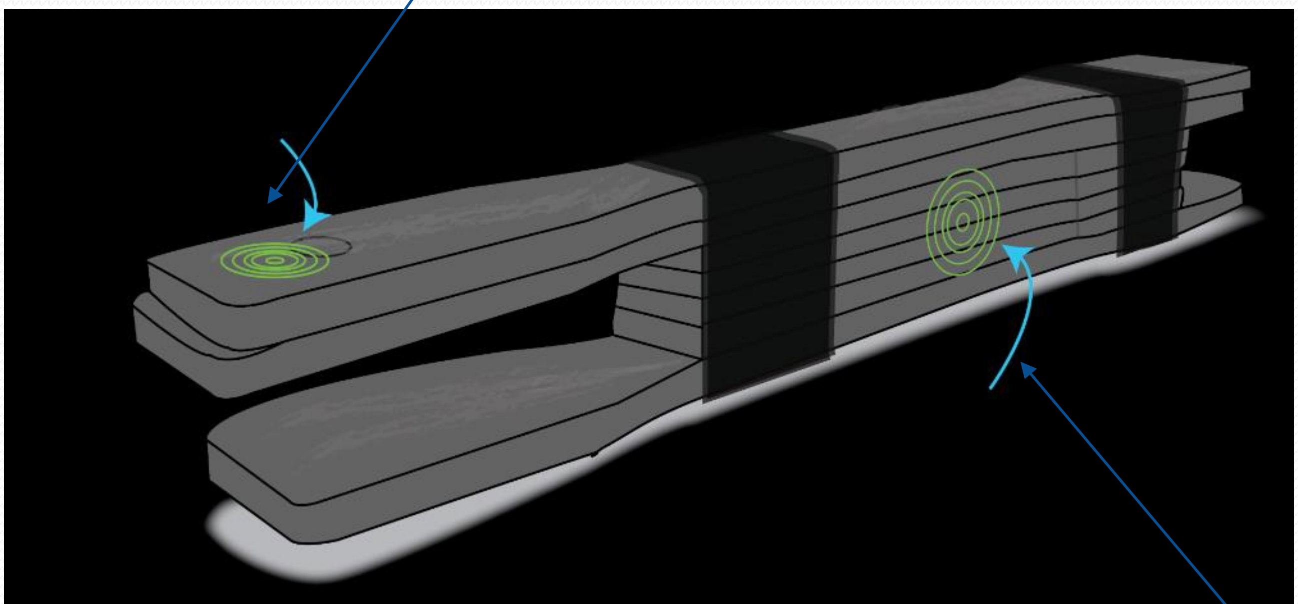
The MTPS and TPS Technology offer excellent help to handle
Such materials and generate data with high repeatability.

Direction dependency

ISOTROPIC	ANINSOTROPIC
METALS	WOOD
GLASS	COMPOSITES
	GRAPHITE
	Rocks

https://ctherm.com/resources/webinars/conductive-polymers-characterizing-thermal-properties

Through plane



In plane

Test Method	Modified Transient Plane Source	Transient Plane Source	Transient Line Source
Recommended Applications	Aerogels, Automotive, Batteries, Composites, Insulation, Explosives, Geological, Liquids, Metals, Nanomaterials, Metal Hydrides, Nuclear, Phase Change Materials (PCMs), Polymers, Rubber, Thermal Interface Materials (TIMs), Thermoelectrics	Cement/Concrete, Porous Ceramics, Polymers (Not suitable for open-celled foams or fluids)	Polymer Melts, Semi-Solids, Soil (Not suitable for lower viscosity fluids due to convection)
Thermal Conductivity Range	0 to 500 W/mK	0.03 to 2000 W/mK	0.1 to 6 W/mK
Thermal Diffusivity Range	0 to 300 mm^2/s*	0.01 to 1200 mm^2/s	N/A
Heat Capacity Range	Up to 5 MJ/m^3K*	0.1 to 5 MJ/m^3K*	N/A
Thermal Effusivity Range	5 to 40,000 $Ws^{1/2}/m^2K$	N/A	N/A
Temperature Range	-50 °C to 200 °C With option to extend to 500 °C	-50 °C to 300 °C	-55 °C to 200 °C

Parameter	GHP	HFM	LFA	MTPS	TPS
Materials	INSULATIONS	INSULATIONS	Conducting	Wider range	Conducting
TC range	Limited to 2W/m.K	Limited to 2W/m.K	Upto 2000W/m.K	0.03 to 500W/m.K	Upto 2000
Samples geometry etc	Sample specific - 2	Sample specific	Sample specific	No limitation on sample dimensions	Sample specific -2
Principle	Steady state	Steady state	Transient	Modified Transient	Transient
Duration	Takes weeks	Takes longer time	Takes longer	Fastest	User controllable
Standards	Conforms to ISO	Conforms to ISO	Conforms to DIN	ASTM	ISO
Liquids, powders	NO	NO, Limitations	NO Limitations	Yes, versatile	No
Temp range	-150 to +600	Mean temp upto 90.C	-125 to +2000.C	-75 to +500.C	-75 to +300.C
Price* indicative	In excess of 200K Euros	65K Euros	65 to 200K Euros	65 to 90K euros	30K euros

SELECTION DRIVERS

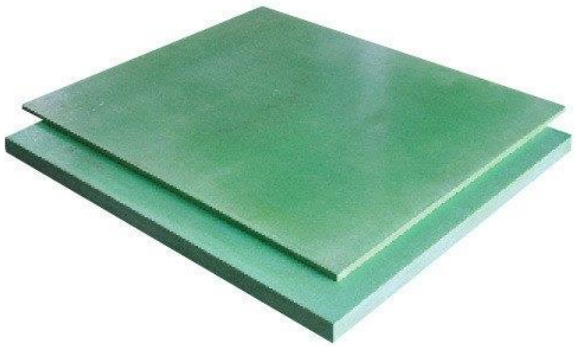
1. Temperature range
2. Sample nature (liquids/solids/powders etc)
3. Need to conform to Standards
4. Affordability and cost considerations

GF/CF/Epoxy composites- their thermal conductivity study:

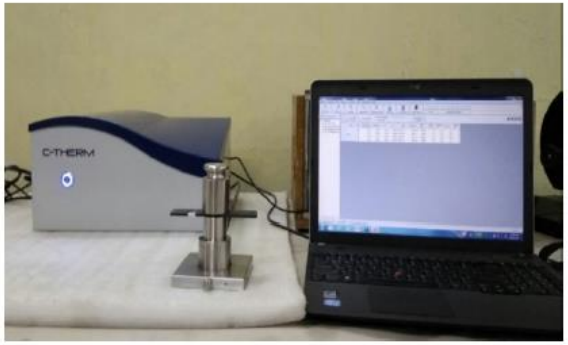
- ❑ GFER , CFER composite system,
- ❑ by hand layup and vacuum bagging method
- ❑ 200 GSM . 0º - 90º orientation

- ❑ Base: Liquid Diglycidyl Ether of Bisphenol-A
- ❑ Hardener: acid based Anhydride

- ✓ Goal to prepare a new material that possesses higher strength to weight ratio



Set up Info:
TCI MTPS sensor ,
100 mm Length and 5mm thick, flat samples.
500 g standard weight used to improve contact



S. No	Type of Fiber in the composite	Specimen No	Thermal conductivity (W/m. K)
1	Carbon Fiber (CF)	CF1	0.455
2		CF2	0.462
3		CF3	0.471
6	Glass Fiber (GF)	GF1	0.420
7		GF2	0.415
8		GF3	0.422

Composite reinforced with CF having better tensile and flexural strength (UTM)
Both GF and CF reinforcements have almost similar K value, user can decide
Based on cost perspective, but most importantly this high K value helps in faster dissipation of heat in high voltage electrical systems, which is added advantage

A ceramic is any of the various hard, brittle, heat-resistant and corrosion-resistant materials made by shaping and then firing a nonmetallic mineral, such as clay, at a high temperature. Common examples are earthenware, porcelain, and brick

SUMMARY

- ✓ Composites and their importance in ever changing Material World
- ✓ Role of thermal analysis especially DSC/TGA in evaluations
- ✓ Thermal conductivity as another important parameter can successfully be employed for assessment and right choices given the boundaries
- ✓ Techniques such as DMA and TMA are more qualitative and oriented towards mechanical properties, expensive as compared to others

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Thank you!