

POLYMERS AND PLASTICS CHARACTERIZATION

THERMAL ANALYSIS , CALORIMETRY & GAS SORPTION SOLUTIONS

TRANSITIONS •
THERMAL STABILITY •
COMPOSITIONAL ANALYSIS •
RESEARCH & DEVELOPMENT •



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As a polymers and plastics developer, supplier or user, you need to check, understand and even guarantee their properties. These properties need to suit the polymers' and allow them to be processable and manufactured with efficiency and low cost. Polymers also need to have constant composition and quality.

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COMMON POLYMERS & PLASTICS - STUDIES & SOLUTIONS

This brochure presents some of our solutions in this field and we encourage you to contact us for more information.

Composition analysis is especially key for quality control of a polymer based material. It includes thermoplastics and thermoset, rubbers, or elastomer based materials. You can apply our TGA solutions to plasticizers/oil, polymer, carbon black filler, white filler contents. The characterization of polymers is a key step for their development to ensure they meet the desired specifications. We provide calorimetry and microcalorimetry solutions allowing the characterization from vacuum up to high pressure of their thermodynamic properties (heat capacity, ...), their transitions (melting, crystallization, glass transition, ...) and the characteristic temperatures of polymers in solution (including LCST - lower critical solubility temperature - or CMT - critical micelle temperature).

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Research & Development

Compositional analysis

You need to have control over the properties of polymers. It is this is for instance important both for their processing and use. But these properties change with the polymer structure. We provide DSC solution to characterize the temperatures of structure change.

Transitions

In every situation where a polymer material may be exposed to high temperatures, it is beneficial to test its thermal stability. You can use TGA or STA to find the temperature and steps of decomposition or transition, under different atmospheres.

Your polymers may face the most common cause of chemical aging: oxidation. The stability against oxidation can be studied using DSC. A longer Oxidation Induction Time means a better stability. Effect of antioxidants can be compared.

Thermal Stability

"The DSC allows us to check the authenticity of plastics. The SETLINE DSC is adapted to our technologies, we manage to make our measurements, to very easily exploit results. We are very satisfied with our SETLINE DSC, due to its precision and the ease of use of the CALISTO software "

> *Mame MBODJI, Materials Engineer PRP Creation - PLASTIC BOTTLE & PACKAGING SOLUTIONS – FRANCE*

THE KEP TECHNOLOGIES ADVANTAGE

KEP Technologies is addressing it's offerings to the market of polymers and plastics by making available the widest and most versatile choice of solutions. Now you can consult with one company, KEP Technologies, to address your challenges across the broadest number of polymer/plastic studies on the market.

Each solution embodies our "Reimagine Material Characterization" value proposition **EXPERIMENTAL** by delivering the three core customer CONTROL benefits of Experimental Control, Instrument Versatility and Quality Results. We believe solutions that provide these benefits will deliver the highest value to our customers. In addition to our core customer benefits, we are able to provide customized solutions by harnessing the engineering and project management of our highly skilled organization. OUALITY **INSTRUMENT** RESULTS VERSATILITY

CUSTOMIZED SOLUTIONS

Modular design allows for upgraded and tailored functionality Access to all previous non-proprietary custom requests Open access to our engineering development team

TRANSITIONS

INSTRUMENT



SPECIFICATIONS

Temperature range (°C)	-170 to 700
Programmable heating rate (°C/min)	0.01 to 100
Enthalpy accuracy / precision* (%)	+/- 0.3 / 0.50
Temperature accuracy / precision* (°C)	+/- 0.07 / 0.15
DSC measurement range (mW)	+/- 6 000
Atmosphere	Inert gas, air, High-pressure crucibles up to 500 bar at 600°C
Autosampler	SETLINE DSC+ version featuring a 59 position autosampler

* Based on indium melting tests

Determination of Crystallinity of PET by DSC

INTRODUCTION

PolyEthylene Terephtalate (PET) is a polyester widely employed in daily life (e.g. in water bottles, texile fibers, credit cards). The crystallinity is a very important characteristic because it is directly related to the properties of the polymer (e.g. toughness, clarity, stability). It is defined as the ratio between the crystalline and amorphous phases in the polymer. DSC is one of the main analytical techniques to determine the crystallinity ratio in a semicristalline polymer.

EXPERIMENT

Sample:

PolyEthylene Terephtalate (PET) pellet Experimental conditions:

• Atmosphere: Nitrogen, atmospheric pressure

• Sample mass: About 25 mg in a 100µl aluminium crucible

Experimental procedure:

The temperature is programmed from 35°C up to 300°C at 10 °C.min-1

RESULTS AND CONCLUSION

The DSC heating curve of the PET presents three main events:

- A glass transition that characterizes the initial amorphous phase of PET
- An exotherm that corresponds to the crystallization of the amorphous phase, also called cold crystallization
- An endotherm that corresponds to the melting of the initial crystalline phase and also to the melting of the crystalline

form, coming from the cold crystallization. PET Crystallinity is measured according to the following equation:



with:

 $\begin{array}{l} \bullet \ \Delta H_{m} heat \ of \ PET \ melting \\ \bullet \ \Delta H_{c} \ heat \ of \ PET \ cold \ crystallization \\ \bullet \ \Delta H_{m}^{\ 0} \ heat \ of \ melting \ (100\% \ crystalline \ PET) \ (140.1 \ J/g). \end{array}$

Crystallinity in this case : 4.8%



TRANSITIONS

INSTRUMENT



SPECIFICATIONS

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Characterization of glass transitions of different polymers by DSC

INTRODUCTION

Glass transition is the reversible transition of an amorphous or semi-crystalline polymer between its glassy and rubbery state. This transition is characterized by a modification of the polymer's physical properties such as viscosity, thermal expansion or heat capacity. It is thus a very important feature of a given polymer for its final application. The glass transition temperature (Tg) is easily determined by DSC. The ISO11357-2 standard describes the experimental Tg determination for polymers.

EXPERIMENT

Samples:

- PolyVinyl Chloride (PVC)
- PolyStyrene (PS)
- Poly Styrene/AcryloNitrile (SAN)
- PolyEtherEtherKetone (PEEK)
- PolyEther Sulfone (PES)
- Experimental conditions:

Atmosphere: Nitrogen, atmospheric pressure Sample mass: About 25 mg in a 100 μl sealed aluminum crucible

Experimental procedure:

The temperature is programmed from room temperature up to 300°C at 10°C.min-1.

RESULTS AND CONCLUSION

At the glass transition temperature, a shift of the DSC signal can be observed. It is due to the sudden change of heat capacity of the polymer at Tg. The signal shift is proportional to the heat capacity variation (Δ Cp). The temperature and the shift depend on the type of polymer. The peak frequently observed at the end of the shift is linked to the structural relaxation of the polymer. This peak depends on the thermal history of the polymer.

The large exothermic event observed with polyetheretherketone is linked to the recrystallization of the amorphous part of the polymer.

In this study, PES has the highest Tg (226°C) and PVC has the lowest (88°C).



THERMAL STABILITY



SPECIFICATIONS

Temperature range (°C)	-170 to 700
Programmable heating rate (°C/min)	0.01 to 100
Enthalpy accuracy / precision* (%)	+/- 0.3 / 0.50
Temperature accuracy / precision* (°C)	+/- 0.07 / 0.15
DSC measurement range (mW)	+/- 6 000
Atmosphere	Inert gas, air, High-pressure crucibles up to 500 bar at 600°C
Autosampler	SETLINE DSC+ version featuring a 59 position autosampler

* Based on indium melting tests

Oxidation Induction Time (OIT) of polyethylene by DSC

INTRODUCTION

Oxidation induction time (OIT) is defined as the time that takes oxidation of a sample to occur under oxygen at a given temperature. Applied to polymers, this measurement enables the evaluation of its oxidative stability.

As an example, the process of aging of water pipes submitted to chlorinated water could be forecasted by performing OIT analysis.

The OIT measurement is defined in the ISO11357-6 standard.

EXPERIMENT

Sample:

Fragment of Polyethylene (PE) Experimental conditions:

Atmosphere: Oxygen 20 ml/min,

atmospheric pressure

• Sample mass: 15 mg in a 30µl aluminum crucible

Experimental procedure:

RT : 220°C at 50°C/min under N2 Isotherm at 220°C under O2 until the end of oxidation

RESULTS AND CONCLUSION

During the heating ramp the melting of polyethylene is observed.

When the isotherm step is reached, the N2 gas is switched to O2 and an exothermic event occurs after a period of time: this corresponds to the beginning of the polyethylene oxidation.

The time between the introduction of oxygen and the oxidation event (measured at the peak onset) is the OIT, equal in this case to 95.6 min.





SPECIFICATIONS

Temperature range (°C)	room temperature to 1600
Isothermal and temperature scanning (°C/min)	0.01 to 100
Sample volume (ml)	up to 1 in TGA
Evolved gas analyzers (ETIR_MS_GCMS_MS_ETIR_or ETIR-GCMS) for performing qualitative	

Evolved gas analyzers (FTIR, MS, GCMS, MS-FTIR, or FTIR-GCMS) for performing qualitative and quantitative gas characterization

Analysis of Polyoxymethylene by TG-DSC + FTIR

INTRODUCTION

One interesting feature of THEMYS ONE STA is the possibility to connect its gas exhaust to a FTIR spectrometer in order to identify the vapours evolving from the sample and to monitor the level of each identified vapour.

EXPERIMENT

The following experimental procedure has to be used:

- Sample : Polyoxymethylene
- Crucible : Platinum
- Mass: 41.37mg
- Atmosphere : Argon 60ml/min

• Experimental procedure : The temperature is programmed from ambient up to 600°C at 10 °C/min.

RESULTS AND CONCLUSION

The Heat Flow curve presents two endothermic effects. The low temperature peak (with a maximum at 187.2°C) may correspond to melting because it isn't related to any mass loss signal. While the higher temperature peak (with two maxima at 355.3°C and 378.9°C) corresponds to the decomposition of Polyoxymethylene and is related to the main mass loss of 98.82%. Finally, the last mass loss of 1.18% is due to a second decomposition. From the FTIR spectra it is possible to draw the variation of intensity associated to the specific absorption band for carbon monoxide (2000-2200cm-1), formaldehyde (2600-3100cm-1) which are decomposition products of POM and tetrafluoroethylene (1100-1400cm-1). The release of this last compound is probably not linked with the degradation of the macromolecular chain, but with the presence of an additive or a residue of the preparation of the polymer in the final material.





SPECIFICATIONS

Temperature range (°C)	RT* to 1 100
Programmable heating rate (°C/min)	0.01 to 50
Temperature accuracy (°C)	+/- 1
Temperature precision (°C)	+/- 0.3
Atmosphere	Inert (N2, Ar, He**) or oxidative (Air, O2)
Mass Variation range (mg)	+/- 20 / +/- 200
Weighing accuracy (%)	0.03***
Weighing precision (%)	0.03***

*Room Temperature

** The maximum experimental temperature is 900°C under helium

*** 5 measurements using a 20mg certified reference material

Thermal stability of O-ring materials by TGA

INTRODUCTION

Many polymers can be used as seals, adhesives, and flexible parts. Thermal stability is a key parameter for selecting the most suitable polymer among the potential candidates to manufacture gaskets and O-rings. The resistance against temperature of four different O-ring materials were compared using SETLINE TGA: NBR (Nitrile Butadiene Rubber), EPDM (Ethylene Propylene diene Monomer), PTFE (Polytetrafluoroethylene) and FPM (Fluorinated rubber).

EXPERIMENT

SETLINE TGA was used for the experiments. For each material, a sample amount of 30 mg ± 2 mg was weighed and inserted in an alumina crucible.

The following profile was then applied:

- Heating from 30°C to 700°C at 10K/minute
- Atmosphere: nitrogen flow at a rate of 30 ml/ min

A blank experiment with an empty alumina crucible was run using the same experimental conditions. The obtained signals were used to subtract the contribution of buoyancy effects from the tests with samples.

Note: although blank experiment subtraction is a common good practice in TGA, the contribution of this correction is below 0.005% on the final mass loss results of that series of experiments.

RESULTS AND CONCLUSION

NBR and EPDM begin to decompose at around 210°C. At 700°C, their respective mass loss is 54.67% and 55.41%.

Concerning FPM, its thermal stability is better than NBR and EPDM with a decomposition temperature observed at around 270°C.

PTFE is the most stable, with a decomposition starting at around 480°C. However, it has a higher decomposition

rate than the three other elastomers and reaches a mass loss of 99.97% at the end of the heating.



COMPOSITIONAL ANALYSIS

INSTRUMENT



SPECIFICATIONS

Temperature range (°C)	RT* to 1 100
Programmable heating rate (°C/min)	0.01 to 50
Temperature accuracy (°C)	+/- 1
Temperature precision (°C)	+/- 0.3
Atmosphere	Inert (N2, Ar, He**) or oxidative (Air, O2)
Mass Variation range (mg)	+/- 20 / +/- 200
Weighing accuracy (%)	0.03***
Weighing precision (%)	0.03***

*Room Temperature

** The maximum experimental temperature is 900°C under helium

*** 5 measurements using a 20mg certified reference material

Compositional analysis of rubber from pneumatic tires

INTRODUCTION

TGA is frequently used to determine the content of polymers, rubbers, elastomers, and related materials with regards to their plasticizers/oil, polymer content, carbon black filler content, white filler content, and residual content.

Indeed, as TGA measures the elastomer's weight loss under programmed temperature and atmosphere conditions, it provides an indication of its composition and of its thermal stability.

EXPERIMENT

SETLINE TGA was used to determine the amounts of organics (oil, polymer), carbon black and ash (filler) in a rubber sample extracted from a tire. The test was performed firstly under nitrogen to decompose the organic matter and then under oxygen to burn the carbon content.

The following experimental procedure was used in the presented example:

- A small piece (15 mg) of the tire elastomer sample was placed into an alumina crucible
- A nitrogen flow rate (30 ml/min) was applied
- The sample was heated from 50°C to 350°C at 20°C/min
- It was stabilized at 350°C during 30 minutes
- It was heated from 350°C to 600°C at 20°C/min
- It was cooled down to 400°C at 20°C/min
- Nitrogen was switched with air (30 ml/min)
- The sample was heated from 400°C to 800°C at 20°C/min

RESULTS AND CONCLUSION

For the investigated tire material, three mass losses were observed, all corresponding to the decomposition of a fraction of the rubber. The remaining mass at the end of the experiment corresponds to the ash content (including fillers) of the sample: 4.4%.

Setline TGA is very well adapted for the investigation of the decomposition of polymeric materials and especially for their compositional analyses.

Temperature range	Atmosphere	Decomposing fraction	Content
50°C to 350°C	Nitrogen	Plasticizer, oil, and wax	30.58%
350°C to 600°C	Nitrogen	Elastomer	32.97%
400°C to 800°C	Air	Carbon black	32.05%



COMPOSITIONAL ANALYSIS

INSTRUMENT



SPECIFICATIONS

Temperature range (°C)	RT* to 1 100
Programmable heating rate (°C/min)	0.01 to 50
Temperature accuracy (°C)	+/- 1
Temperature precision (°C)	+/- 0.3
Atmosphere	Inert (N2, Ar, He**) or oxidative (Air, O2)
Mass Variation range (mg)	+/- 20 / +/- 200
Weighing accuracy (%)	0.03***
Weighing precision (%)	0.03***

*Room Temperature

** The maximum experimental temperature is 900°C under helium

*** 5 measurements using a 20mg certified reference material

Graphite content of a reinforced polymer by TGA

INTRODUCTION

Graphite or carbon fibers reinforced polymers strongly improve the physical properties of composite materials like their strength, thickness or thermal expansion. That is why they are used in the aerospace, transportation, sport or chemical industries.

TGA is a quality control / quality assurance tool used to check the graphite or carbon fibers content of reinforced composites. It is a key feature of a composite material as it affects its mechanical and physical properties.

Here, we report the analysis of a graphitereinforced PTFE (polytetrafluoroethylene) with the SETLINE TGA.

EXPERIMENT

The method consists in applying two heating cycles on the material:

First heating cycle: pyrolysis of the polymer matrix

• First heating cycle (pyrolysis of the polymer matrix) : heating from 30°C up to 1100°C at 10°C/min, under N2 at 30ml/min

• Second heating cycle (combustion of the graphite or fiber) : heating from 30°C up to 1100°C at 10°C/min, under Air at 30ml/min

RESULTS AND CONCLUSION

During the first heating cycle under nitrogen, a mass loss of 84.51% can be observed due to the pyrolysis of PTFE.

The second heating cycle under air shows a mass loss of 14.13% due to the combustion of the carbon content in the sample.

The pyrolysis of PTFE leads a mass loss near 100% of its initial mass (see ANS020 for more details). It means that the mass loss observed during the second heating cycle is equal to the graphite content in the composite: 14.13%.





SPECIFICATIONS

Temperature range (°C)	Ambient to 830°C -120 to 200 °C (with cooling accessory)
Temperature accuracy (°C)	+/- 0.05*
Temperature precision (°C)	+/- 0.15*
Programmable temperature scaning rate (°C/min)	0.01 to 30
Enthalpy accuracy (%)	+/- 0.8*
Calorimetric precision (%)	+/- 0.4*
Crucible or cells volume (ml)	Up to 0.32 depending on the chosen design and material (alu- minium, incoloy, graphite, alumina, platinum, etc)
Pressure (bar [psi])	400 [5,800] (measured and controlled); 500 [7,250] (resistant)

* Based on indium melting tests

Heat capacity of elastomers

INTRODUCTION

Elastomers show an important variation of their heat capacity near the glass transition. The knowledge of the heat capacity before and after transition is of a great utility for the uses and applications of the compounds.

In DSC methods, heat capacity (Cp) is proportional to thermal power evolved when the sample is heated Two runs are necessary in order to determine precisely Cp : the first one with empty cells (sample and reference), the second one using the same cells, with the sample. The difference between the curves of the two runs characterizes the heat capacity of the sample.

EXPERIMENT

RESULTS AND CONCLUSION

• Samples : natural rubber (156.7 mg) polychloroprene (230.8 mg)

• Crucible : Aluminum

- Heating mode : Scanning 5°C/min
- Use of the subambient cooling accessory

The mean values of specific heat before and after the glass transition are the following (in cal.g-1.°C-1) :

	Before Tg	After Tg
Natural rubber	0.240	0.360
Polychloroprene	0.190	0.300

The variation of heat capacity due to glass transition is 0.12 cal.g-1.°C-1 for natural rubber and 0.11 cal.g-1.°C-1 for polychloroprene.



RESEARCH & DEVELOPMENT

MICROCALVET

HIGHEST HEAT MEASUREMENT ACCURACY

Calvet 3D sensor based on Peltier elements with Joule effect calibration.

MODIFIABLE TEMPERATURE CONDITIONS

for increased flexibility and replication of real life conditions

CONVENIENT INTERCHANGEABLE CRUCIBLES AND CELLS

to perform even the most demanding experiments using one instrument :

• high pressure (1000bar) and high vacuum, pressure measurement and control

mixing experiment

EXTERNAL COUPLING CAPABILITY

Designed to increase your research options including manometry, BET instrumentation, gas analyzers, humidity controllers and gas panels

SPECIFICATIONS

Temperature range (°C)	-45 to 120
Isothermal and temperature scanning (°C/min)	0.001 to 2
Pressure, measured and controlled (bar [psi])	400 [5,800] 1 000 [14,600]
Cell and crucible volumes (ml)	up to 1

High pressure characterization of polymers

INTRODUCTION

When an elastomer is cooled below its glass transition temperature (Tg), it loses its elasticity and becomes brittle.

For elastomer O-rings, that are used for sealing purpose, Tg thus corresponds to a lower limit of use. Problems arise when they are used in high pressures systems, as their Tg may be shifted to higher temperatures.

The MICROCALVET, with its high pressure capability, is the most suited to investigate the Tg dependence vs. pressure as it allows purely isobaric temperature scanning experiments.

EXPERIMENT

Elastomer O-ring were heated between -40°C and 20°C at a rate of 1K/min under nitrogen pressures of 1, 100, and 400 bar.

RESULTS AND CONCLUSION

Glass transition temperature (Tg) can be determined at each pressure thanks to the heat capacity change of the elastomer. It is noticed that Tg increases with pressure, with a shift of about 10°C between 1 bar and 400 bar.

As a first approach, the evolution of Tg is described by a linear equation on the tested pressure range with a R2 value of 1.



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MICROCALVE ULTRA

HIGHEST HEAT MEASUREMENT ACCURACY

Calvet 3D sensor based on Peltier elements with Joule effect calibration

MODIFIABLE TEMPERATURE CONDITIONS

for increased flexibility and replication of real life conditions between -20 and 170°C

CONVENIENT INTERCHANGEABLE CRUCIBLES AND CELLS

to perform even the most demanding experiments using one instrument :

• high pressure (up to 400 bar) and high vacuum, pressure measurement and control

mixing experiment

EXTERNAL COUPLING CAPABILITY

designed to increase your research options including manometry, BET instrumentation, gas analyzers, humidity controllers and gas panels

SPECIFICATIONS

Temperature range (°C)	-20 to 170
Programmable temperature scanning rate (°C/min)	0.001 to 1.2
Cells volume (ml)	Up to 1 (standard cell)
Pressure measured and controlled (bar [psi])	400 [5,800]

Transition behavior of hydrophobically modified N-isopropylacrylamide copolymer solution

INTRODUCTION

Poly(N-isopropylacrylamide) (PNIPAAm) aqueous solutions presents a sharp transition around 32-34°C which is close to the body temperature. This characteristic has been exploited for the application in temperature sensitive nonviral vector for gene delivery.

Temperature induces a transition from coil to globule of copolymer backbone in solution, but the hydrophobic core of micelles is not affected. The author writes "...for PNI9.68VL1 solution, common DSC cannot provide calorimetry data with acceptable signal noise ratio. Herein, we employed μ SC to track the subtle transition with high sensitivity."

EXPERIMENT

The following solutions have been analyzed : (a) : PNI9.68VL1 (52.0 mg/ml) (b) : PNI9.68VL1 (231 mg/ml) (c) : PNIPAAm (52.0 mg/ml) (d) : PNIPAAm (288.3 mg/ml) Temperature was programmed from 5°C to 50°C at 1K/min.

RESULTS AND CONCLUSION

The curves show endothermic peaks where the onset temperatures for both PNI9.68VL1 and PNIPAAm slightly decrease when the concentration is raised.

Explanation and interpretation are given in the article.





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