Prototype 2:
Phase change temperature reference samples

Lead Partner: CNRS (Centre National de la Recherche Scientifique), France

The goal of these reference samples is the calibration of SThM probes for the measurement of the melting temperature (T_m), glass transition (T_g) or softening (T_{soft}) of polymeric materials.

Key Benefits

- *Compatible with most of the commercially available AFMs.*
- *Sample of well-known melting temperature*

Sample Specification

The sample set includes four bulk highly semi-crystalline polymeric materials (polycaprolactone (PCL), low-density polyethylene (LDPE), polyoxymethylene (POM) and polyethylene terephthalate (PET)) with clearly defined melting temperature T_m between 50 ºC to 250 ºC. The materials, sample codes and providers of the tested specimens and T_m measured by NPL and LNE are given in Table 1.

Table 1: *T_m for the reference samples*.*

Samples		**Provider of raw material**	**Melting point (°C) provider**	**Melting point (°C) NPL**	**Melting point (°C) LNE**
Sample code	**Material**				
S-TM-cal6	**PCL**	Sigma-Aldrich	55	62.1	--
S-TM-cal7	**LDPE**	Goodfellow	116	109.9	110.7
S-TM-cal8	**POM**	Radiospares	175	168.1	--
S-TM-cal9	**PET**	Goodfellow	235	250.4	248.1
Characterization technique		No information on the method used		Differential scanning calorimetry (DSC) using the heat flux plate measurement principle. **	

* The characterization of samples has been performed by two NMIs who are members of project Consortium: NPL and LNE.
**Three repeat tests were conducted for each specimen under Nitrogen at a heating rate of 10 °C/min. The repeatability for the melting temperature for NPL is 2 °C. Expanded uncertainty (k=2) associated to melting temperature estimated by LNE equal to 2°C.

Reference samples are individual samples (See Figure 1): one sample of each selected bulk highly semicrystalline polymeric material. They are available as unmounted pieces to be mounted by the microscopist. Samples (excepted S-TM-cal7: LDPE) were cut and machined from stock rods. The samples of low density polyethylene (S-TM-cal7) were obtained from rods (of 7.8 mm diameter) moulded from LDPE granules. Sample surfaces of interest and to be used are of about 1 mm² and were prepared using ultramicrotomy (cryogenic cutting depending on material at Centre Technologique des Microstructures (CTμ), Lyon, France) to produce flat defect-free surface. Roughness parameters of each samples were measured using AFM in intermittent contact mode and are given in Table 2.

Figure 1: *Optical picture of the S-TM-Cal 8 and 9 samples.*

Table 2: *Rms roughness of the reference samples measured on 1x1 µm² by CMI.*

Samples		**Rms (nm)**
Sample code	**Material**	
S-TM-cal6	**PCL**	12
S-TM-cal7	**LDPE**	17
S-TM-cal8	**POM**	12
S-TM-cal9	**PET**	10

Cleaning and storage

Cleaning is possible using dry air. Keep upper surface intact: avoid touching prepared surface. Rubbing with soft tissues, or any other firm physical contact, or the use of solvents such as acetone or alcohol will damage the surface of the reference sample. It is recommended to store these samples under low humidity/dry air, dust free environment out of direct sunlight.

Applications

- Nano-TA calibration
- T_m, T_g and T_{soft} measurements of polymeric materials.

Other information

Samples		Thermal properties at 23°C					Modulus at room temperature (? °C)				
Sample code	Material	Thermal conductivity	Density	Specific heat	Thermal diffusivity	Thermal conductivity	Average modulus E (GPa)		Uncertainty of modulus E (GPa)		Goodfellow Young modulus (GPa)
			($kg \cdot m^{-3}$)	($J \cdot kg^{-1} \cdot K^{-1}$)	(10^{-6} $m^2 \cdot s^{-1}$)	($W \cdot m^{-1} \cdot K^{-1}$)	Centre	Edge	Centre	Edge	
S-TM-cal6	PCL	0.2	*No specimen provided*				--	--	--	--	--
S-TM-cal7	LDPE	0.33	*No specimen provided*				0.4	0.4	0.1	0.1	0.3
S-TM-cal8	POM	0.22-0.24	1400	1430	-	-	2.5	2.5	0.4	0.6	3.0
S-TM-cal9	PET	0.15-0.4	1390	1130	0.169	0.265	2.5	2.6	0.3	0.5	2.0-4.0
Characterization technique / involved and measuring partner Uncertainty associated to measurands			Indirect method (measurement methods described in 2.1) / LNE The relative expanded uncertainties (k=2) associated to thermal diffusivity, specific heat and density measurements have been estimated respectively equal to 4 %, 3 % and 1 %. The expanded uncertainty associated to the determination of thermal conductivity is estimated to 5 %.				Nanoindentation / NPL Values for the modulus were obtained by calculating the mean and the uncertainty of 10 identical indentation experiments conducted at positions 50 µm apart on the specimen surface. For each specimen one series of indentations was conducted at the centre of the specimen and another at the edge of the specimen. The uniformity of the modulus at the centre and the edge of each of the specimens indicates that the mechanical properties of the specimens are homogeneous.				Uniaxial tensile testing /Raw materail provider nanoindentation and uniaxial tensile testing are extremely different techniques.

Contact details

CNRS_Centre d'Energétique et de Thermique de Lyon
Email: severine.gomes@insa-lyon.fr
Web: www.cethil.insa-lyon.fr