Complete Thermal Characterization of PTFE – The Combination of DSC, DMA and Rotational Rheometry

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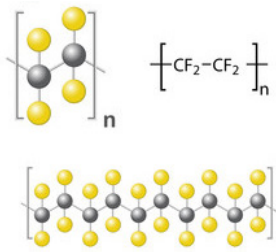
Introduction

PTFE (polytetrafluoroethylene) is a polymer commonly known as Teflon. It has a helical linear structure, in which the fluorine atoms surround the carbon atoms and build a protective layer (see structure below). This explains its exceptional properties in terms of thermal stability, insulation, chemical resistance, etc. [1].

The properties of PTFE are temperature-dependent and include those typical of semi-crystalline materials such as glass transition and melting. Moreover, its helical structure is thought to be responsible for the existence of crystal-crystal transitions around room temperature [2].

In the following, a PTFE sample was measured with DSC, DMA and rotational rheometry. These three methods go hand in hand: DSC provides information about the thermal properties of a material, DMA and rheometry offer the possibility to obtain (among others) the viscoelastic properties of the sample by evaluating the response to an oscillatory signal.



Some Definitions

DMA:
E*: Complex elastic modulus
E': Storage modulus, elastic contribution to E*
E": Loss modulus, viscous contribution to E*
tan δ: Loss factor

Rheometry:
G*: Complex shear modulus
G': Storage shear modulus, elastic contribution to G*
G": Loss shear modulus, viscous contribution to G*
δ: Phase angle

DSC (Differential Scanning Calorimetry) – Functional Principle

DSC is a technique in which the difference between the heat-flow rate into a sample crucible and that into a reference crucible is derived as a function of time and/or temperature. During such measurement, sample and reference are subjected to the same controlled temperature program and a specified atmosphere.

Result: The thermal characteristics are determined, e.g., melting, crystallization, glass transition, degree of crystallinity, cross-linking reactions (curing)[1].

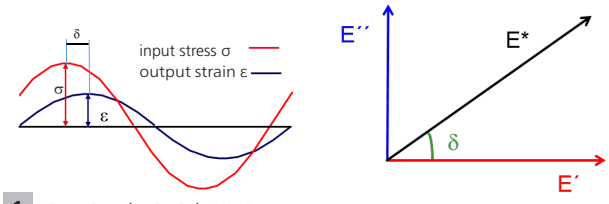
DMA (Dynamic-Mechanical Analysis) – Functional Principle

A sinusoidal force (stress σ, input) is applied to the sample resulting in a sinusoidal deformation (strain ε, output).

The response signal (strain, ε) is split into an "in-phase" and an "out-of-phase" part.

The "in-phase" part is related to the elastic properties (→ E´, storage modulus), the "out-phase" part to the viscous properties (→ E", loss modulus) of the viscoelastic material.

Result: The viscoelastic properties of the sample are determined, in particular its complex modulus E*[2].



1 Functional principle DMA

[1]More information on Differential Scanning Calorimetry at DSC

[2]More information on Dynamic-Mechanical Analysis at DMA

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Rotational Rheometer (Oscillation Measurement) – Fundamental Principle

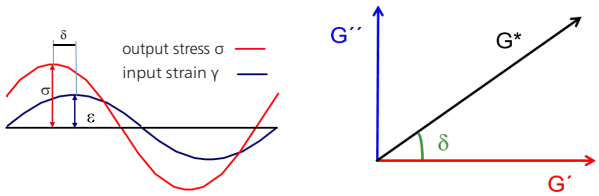
The upper geometry with a defined frequency f [Hz] (or ω [rad/s]) and amplitude [%] (or shear strain γ [%]).

The complex shear stress σ* [Pa] required for this oscillation is determined and is split into an "in-phase" and an "out-of-phase" part.

The "in-phase" part is related to the elastic properties (→ G´, storage shear modulus), the "out-phase" part to the viscous properties (→ G", loss shear modulus) of the visco-elastic material.

Result: The visco-elastic properties of the sample are determined, in particular its complex shear modulus G* and its complex shear viscosity η^* [Pa·s][3]:

$$\eta^* = \frac{G^*}{\omega}$$



2 Functional principle rotational rheometry

Table 1 summarizes the conditions of the three measurements.

Table 1 Test Conditions

Method	DSC	DMA	Rotational Rheometry
Crucible/geometry	*Concavus* (aluminum), closed with pierced lid	3-point-bending, 40 mm	Torsion
Sample mass/dimensions	11.88 mg	Length: 40 mm Width: 9.98 mm Height: 2.1 mm	Length: 42.5 mm Width: 10.01 mm Height: 2.09 mm
Temperature range	-70°C to 380°C	-170°C to 150°C	5°C to 150°C
Heating rate	10 K/min	2 K/min	1 K/min
Amplitude/shear strain	-	60 µm	4.10^{-3} %[4]
Frequency	-	1 Hz	1 Hz
Atmosphere	Nitrogen (100 ml/min)	Air, static	Nitrogen (2 l/min)

[3]More information on Rheometry can be found at RHEOMETERS

[4]A previous amplitude sweep test established an appropriate shear strain was applied ensuring the oscillatory measurements were non-destructive. During the complete frequency measurement, the strain remained in the linear visco-elastic range (LVER) of the material, where strain and stress are proportional.

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Figures 3 to 5 display the resulting curves of the DSC, DMA and rotational rheometer measurements.

Phase Transition in the Low-Temperature Range

The DMA measurement (figure 3) shows that the elastic modulus of the polymer amounts to almost 6500 MPa at -160°C. It decreases by more than half of its initial value during heating to -100°C. This strong decrease, associated with a peak at -110°C and -105°C in the curves of loss modulus E" (blue) and loss factor tan δ (green), respectively, is most probably due to a structural change in the purely amorphous region and is called γ-relaxation [3].

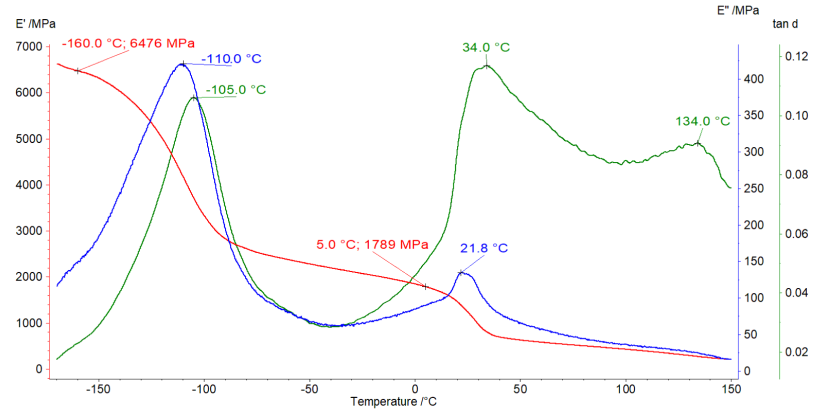
Crystal-Crystal Transitions around Room Temperature

The DSC measurement in figure 4 shows a peak at 21°C with a shoulder at 30°C. This is due to the two crystal-crystal transitions (from well-ordered to partially ordered hexagonal structure and from partially ordered to disordered structure) [4]. It corresponds to a drop in the E´ modulus, associated to a peak at 34°C in tan δ of the DMA measurement (figure 3).

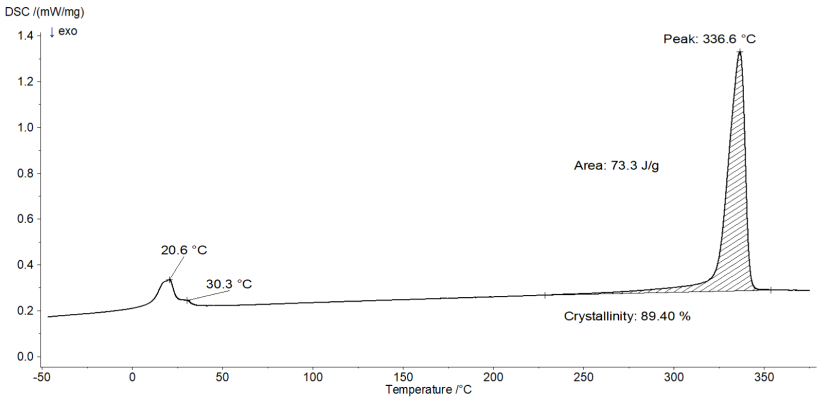
The measurement with the rotational rheometer is in agreement with these results (figure 5). The solid-solid transitions lead to a decrease of the G´ curve (red) as well as a double peak at 26-27°C and 33-34°C in the G" (blue) and in the δ curves (green).

Amorphous and Crystalline Regions: Glass Transition and Melting

An additional peak was detected at 134°C in the loss factor, tan δ, curve (figure 3) and at 127°C in the phase angle, δ, curve (figure 5). This corresponds to the glass transition of PTFE, during which the amorphous part of the polymer changes from a glassy to a rubbery state.



3 DMA measurement. Red: Storage modulus E´. Blue: Loss modulus. Green: Loss factor tan δ.



4 DSC measurement: The degree of crystallinity can be calculated from the measured melting enthalpy, divided by the enthalpy of a 100% purely amorphous PTFE material.

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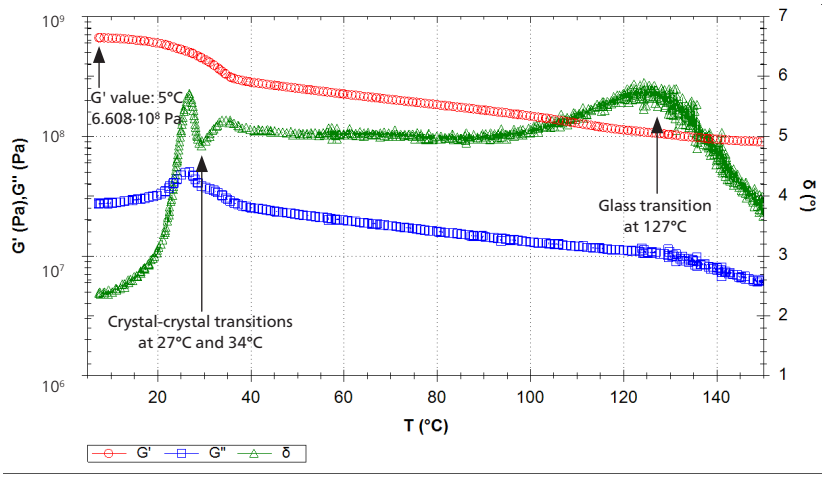
Furthermore, the endothermic peak detected at 337°C (figure 4) is due to the melting of the crystalline phase of PTFE [4]. The evaluation of the melting enthalpy (73 J/g) enables the determination of the degree of crystallinity of the material (see info box). This PTFE has a crystallinity of almost 90%. In turn, the amorphous phase amounts only 10% of the sample. This means that the amorphous part of the polymer is only weakly pronounced.

The degree of crystallinity of a semi-crystalline polymer is obtained as follows:

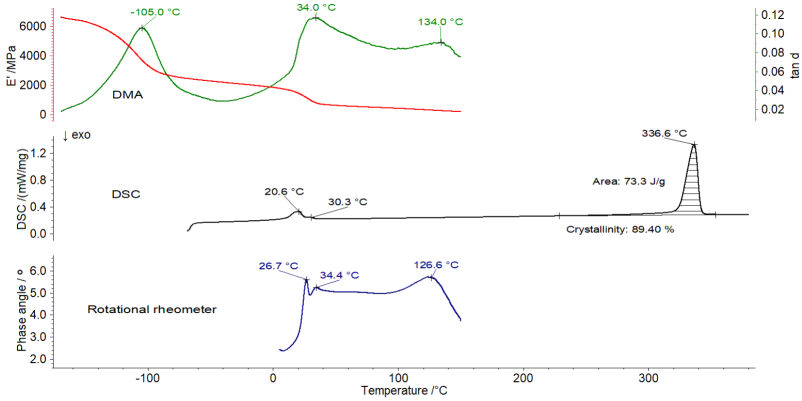
$$\text{Degree of crystallinity [\%]} = \frac{\text{enthalpy (melting peak)}}{\text{enthalpy (melting peak, 100\% crystalline)}} \cdot 100$$

The detection of this very weak glass transition is not possible with the DSC, but alternative methods of DMA and rotational rheometry may be more suitable where a peak relating to the glass transition temperature is very distinct in both curves of loss factor (peak temperature at 134°C) and phase angle (peak temperature at 127°C).

Figure 6 depicts the curves obtained with the three methods. In the temperature range up to 150°C, the loss factor of the DMA measurement as well as the phase angle of the rotational rheometer test clearly reveal the glass transition temperature of this highly crystalline PTFE sample.



5 Oscillation measurement with the rotational rheometer. Red: Elastic shear modulus G´. Blue: Viscous shear modulus G". Green: Phase angle δ.



6 DSC, DMA and rheometer measurements. Black: DSC. Red: Storage modulus E´ (DMA). Green: Loss factor tan δ (DMA). Blue: Phase angle δ (rotational rheometer).

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How to Link E′ and G′? Complex Methods – Simple Answer

As noticed previously (see [4] on page 2), the applied deformations were in the linear visco-elastic range of the material. In this case, the elastic modulus E' (DMA) and the elastic shear modulus G' are related by the following equation:

$$E' = 2 \cdot G' \cdot (1 + \nu)$$

where ν is Poisson's ratio and amounts to 0.42 for PTFE [5].

At 5°C → E´ = 1789 MPa
At 5°C → G´= 661 MPa
2 · G′ (1 + ν) = 1876 MPa

The measured value of E´ is in good agreement with the value calculated from the relationship between storage modulus and Poisson´s ratio.

Conclusion

DSC, DMA and rotational rheometry were performed on an unfilled PTFE material. All three methods identified the crystal-crystal transitions. The very weak glass transition was detected by means of DMA and rotational rheometry. In addition, a good correlation between elastic modulus measured in the DMA and elastic shear modulus via rheometry was found.

The γ-transition, melting and degree of crystallinity were also characterized.

The combination of results using different methods not only ensures the validity of the results, but also increases the knowledge of the thermal and mechanical properties of the material.

References

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