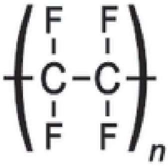
APPLICATION**NOTE**

# PTFE – A Fascinating Polymer Investigated by Advanced Thermal Analysis Techniques



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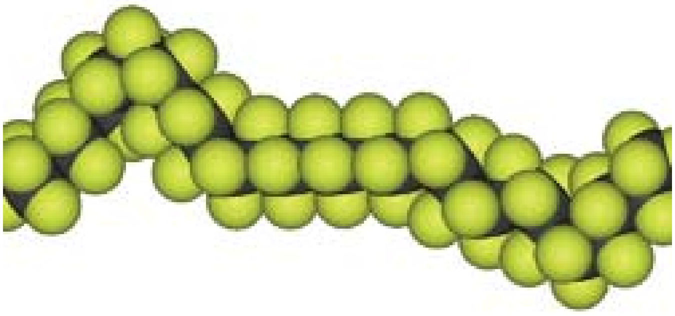
Dr. Markus Meyer



## Introduction

Polytetraflouroethylene (PTFE) is well known from its daily application as a non-sticking coating for frying pans and other cookware. PTFE is very unreactive and provides high chemical resistance. Due to these properties, it is not only used in medical applications but also in the industry like, for example, in containers and pipe work for corrosive and reactive chemicals. Also parts like bearings, bushings and gears, where sliding action is needed, are made of PTFE.

Thermal characterization of a PTFE material was realized using various thermal analysis and thermophysical property testing techniques. Measurements were carried out between -170°C and 700°C (depending on the method). The thermal expansion and density changes were determined by means of pushrod dilatometry (DIL, based on, e.g., ASTM E831, DIN 51045). Dynamic mechanical analysis (DMA) was used to analyze the visco-elastic properties (storage and loss modulus). The thermal diffusivity was measured with the laser flash technique (LFA, based on, e.g., ASTM E1461, DIN EN821. Combining thermal diffusivity data with specific heat and density allows for calculation of the thermal conductivity of the polymer. The decomposition behavior was studied using simultaneous thermal analysis (STA, based on, e.g., ASTM E1131, ASTM D3850, DIN 51006, ISO 11357, DIN 51004, DIN 51007, etc.). The evolved gases were analyzed by a mass spectrometer (QMS) and Fourier transform infrared spectroscopy (FT-IR).

PTFE exhibits several transitions over the entire temperature range. Below 19°C, a well ordered triclinic phase is obtained, whereas between 19°C and 30°C, PTFE forms a partially ordered hexagonal phase. Above 30°C and up to the melting point (328°C), the material shows a pseudo-hexagonal, very disordered phase. Further transitions can be found at -115°C and 131°C which can be attributed to the amorphous phase [1]. Some literature sources (e.g., [3], [4]) describe the phase transformation at 131°C as a glass transition.

## Polytetraflouroethylene = PTFE

- Better known as Teflon®*
- Discovered by Roy Plunkett in 1938
- Molecular formula: $C_nF_{2n+2}$
- Molecular mass: 100.02 g/mol
- Density: 2.2 g/cm³
- Melting point: 327°C

*Teflon® ist a registered trademark of E.I. DuPont de Nemours and Company.

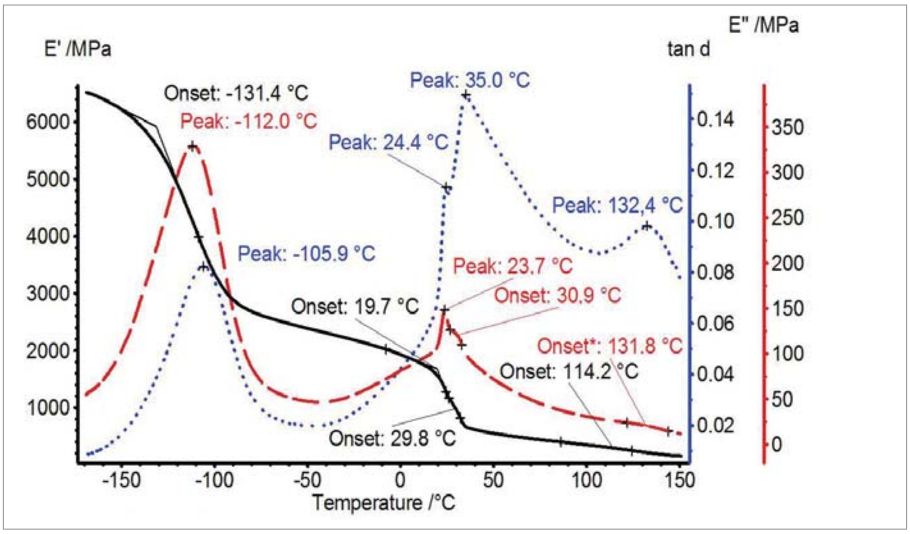
The PTFE analyzed in this work was supplied by ElringKlinger Kunststofftechnik GmbH, Heidenheim.

NGB · Application Note 024 · E · 01/13 · Technical specifications are subject to change.

## Test Results

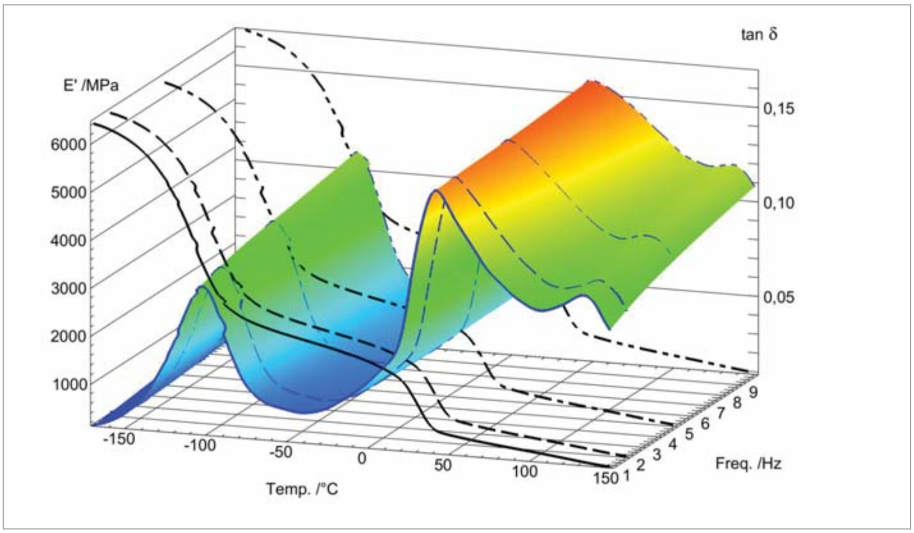
### *A) Viscoelastic Properties*

Figure 1 presents the determined mechanical properties E´, E´´ and tanδ. The step in storage modulus at -131°C can be attributed to the glass transition of the amorphous phase. Two solid-solid transitions can be seen between 20°C and 40°C. Another step in the E´ curve was observed at 115°C due to a solid-liquid transition of the amorphous phase [1], sometimes also characterized as glass transition [3], [4].



**1** Storage modulus E´ (black), loss modulus E´´ (red) and tanδ (blue) of the PTFE material at 1 Hz (DMA 242)

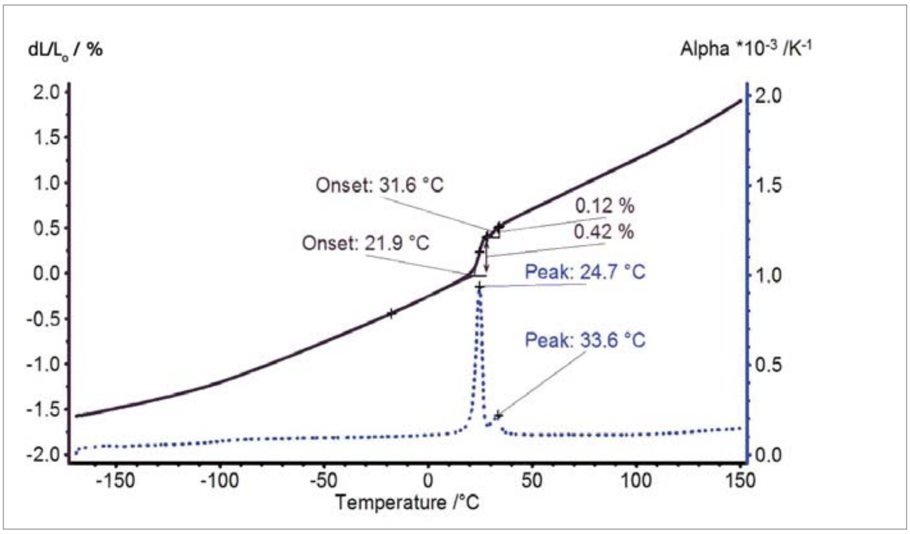
A 3-D plot of a multi-frequency measurement (1, 2, 5 and 10 Hz) is shown in figure 2. It can be seen that tanδ is increasing with frequency at a given temperature.



**2** 3-D plot of storage modulus E´ and tanδ at frequencies of 1, 2, 5 and 10 Hz (DMA 242)

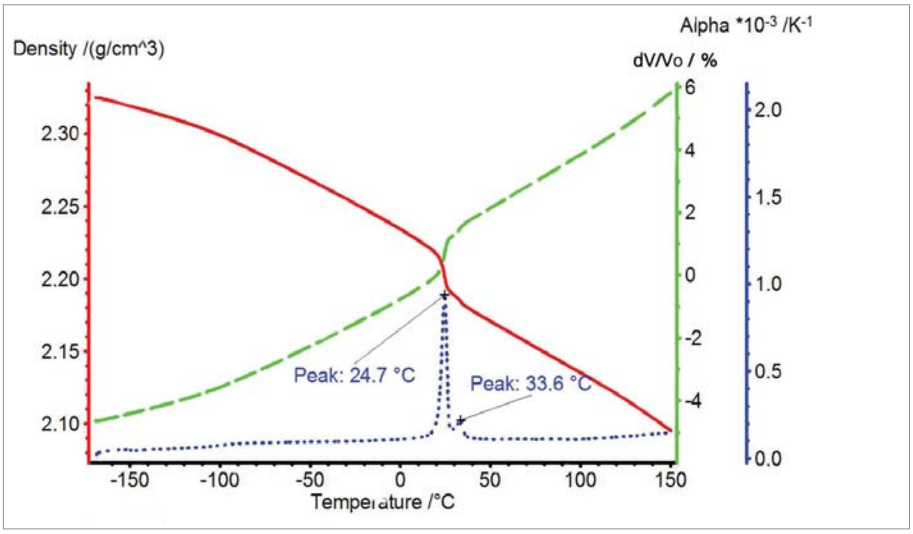
### B) Thermal Expansion, Density Change

PTFE expands with a constant rate of expansion between -170°C and 20°C (figure 3). A jump in the thermal expansion was detected at room temperature due to the solid-solid transition. Above the phase transition, the thermal expansion continuously increases with a slightly increasing expansion rate.



**3** Thermal expansion (solid line, black) and expansivity (dotted line, blue) of PTFE (DIL 402 C)

The volumetric expansion and density change of PTFE are depicted in figure 4. The solid-solid transition corresponds to a volume change of more than 1%.

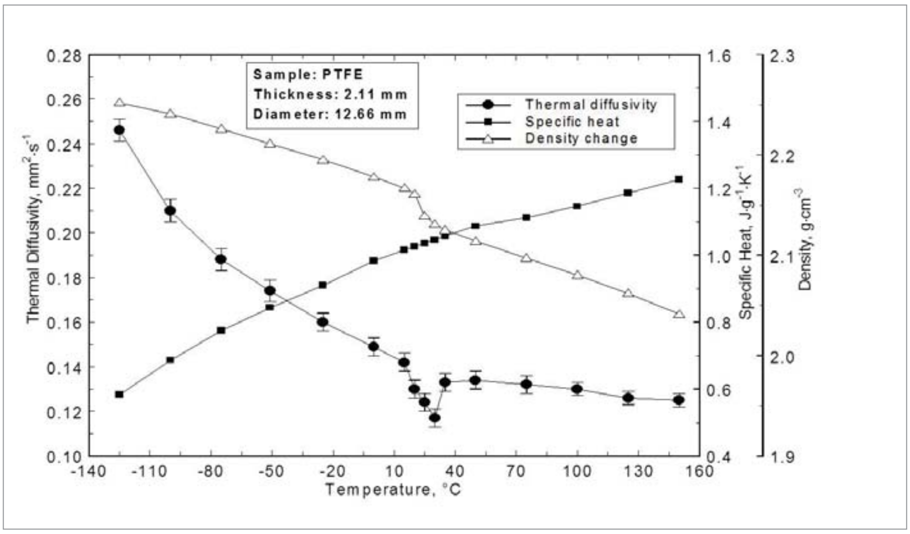


**4** Volumetric expansion (green curve), density change (red curve) and expansivity (blue curve) of PTFE (DIL 402 C)

## *C) Thermophysical Properties*

### Thermal Diffusivity, Density Change and Specific Heat

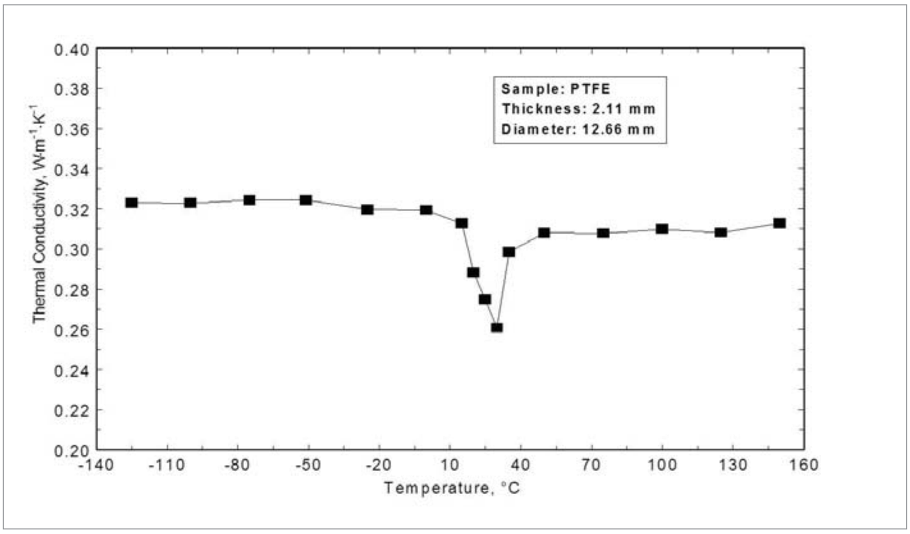
The thermal diffusivity, specific heat and density change of PTFE are displayed in figure 5. The diffusivity continuously decreases with temperature; this is expected from the solid-state physics for phonon conduction. The solid-solid transition at RT can clearly be identified whereas the other transitions at -131°C and at 115°C are not visible.



**5** Thermal diffusivity, specific heat and density change of PTFE (LFA 457 *MicroFlash*®, STA 449 ***F1*** *Jupiter*® and DIL 402 C)

### Thermal Conductivity

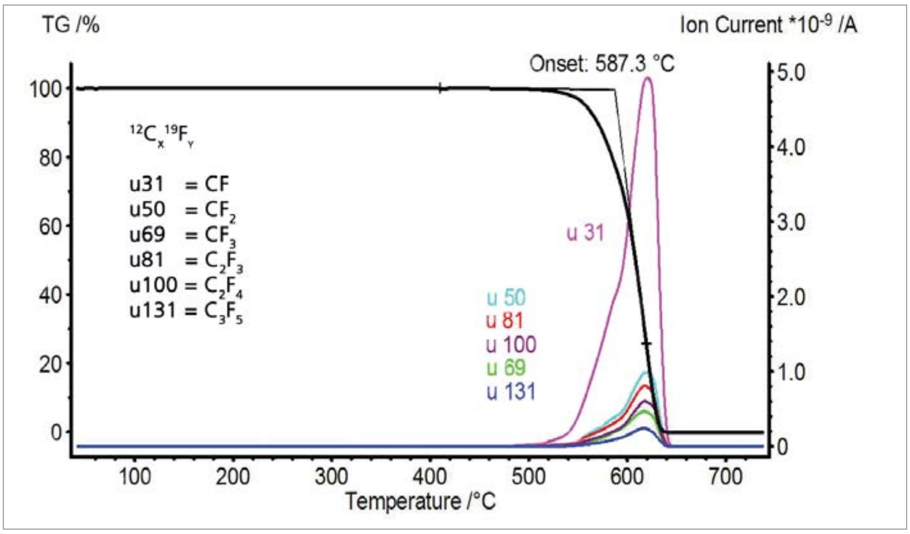
Figure 6 shows the thermal conductivity calculated by means of thermal diffusivity, specific heat and density. In the low-temperature range, the thermal conductivity is almost constant (0.32 $Wm^{-1}K^{-1}$). During the phase transition between 10°C and 40°C, the thermal conductivity decreases by more than 10% and even at higher temperatures – after the signal raised again – the thermal conductivity is significantly lower compared to the region prior to the phase change.



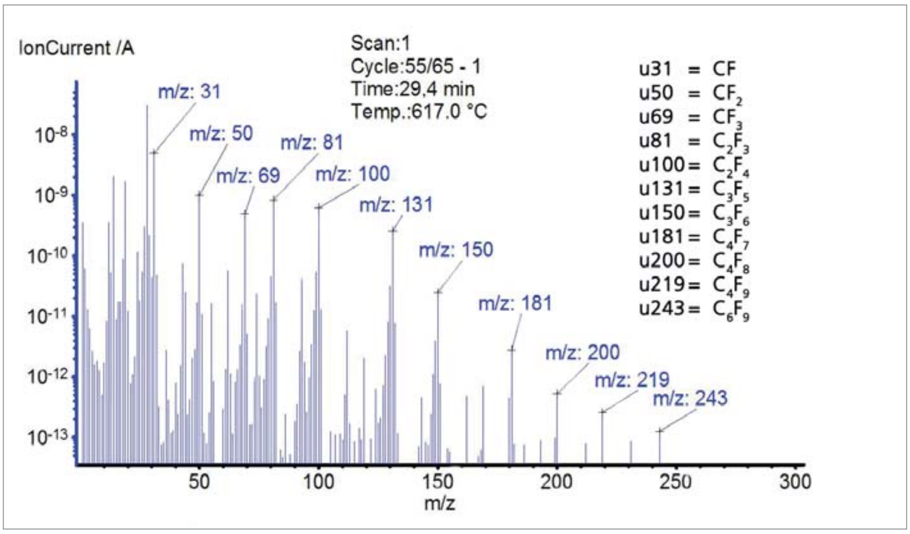
**6** Thermal conductivity of PTFE (LFA 457 *MicroFlash*®)

### *D) Thermal Decomposition, Gas Analysis*

The temperature-dependent mass changes and signals of the mass spectrometer are depicted in figures 7 and 8. PTFE shows no mass loss until the pyrolytic decomposition starts at 587°C. The mass spectrometer detected changing ion current intensities for mass numbers 31, 50, 69, 81, 100, 131, 150, 181, 200, 219 and 243. These mass numbers indicate typical fragments of PTFE. Polytetrafluoroethylene completely decomposes; no residual mass remains in the inert gas atmosphere.

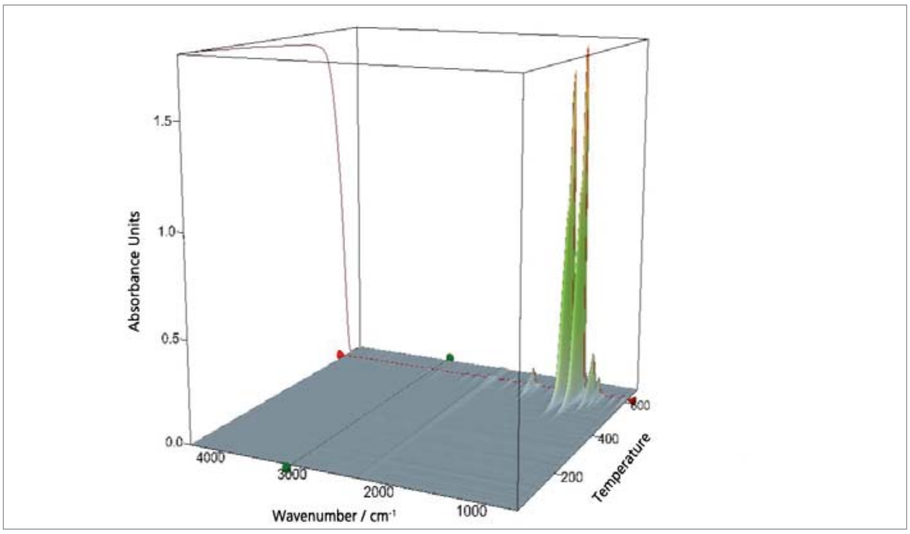


**7** Temperature-dependent mass change (TGA) and mass spectrometer signals (mass numbers 31, 50, 69, 81, 100 and 131) of PTFE (STA 449 ***F1*** *Jupiter*® - QMS 403 C *Aëolos*®)



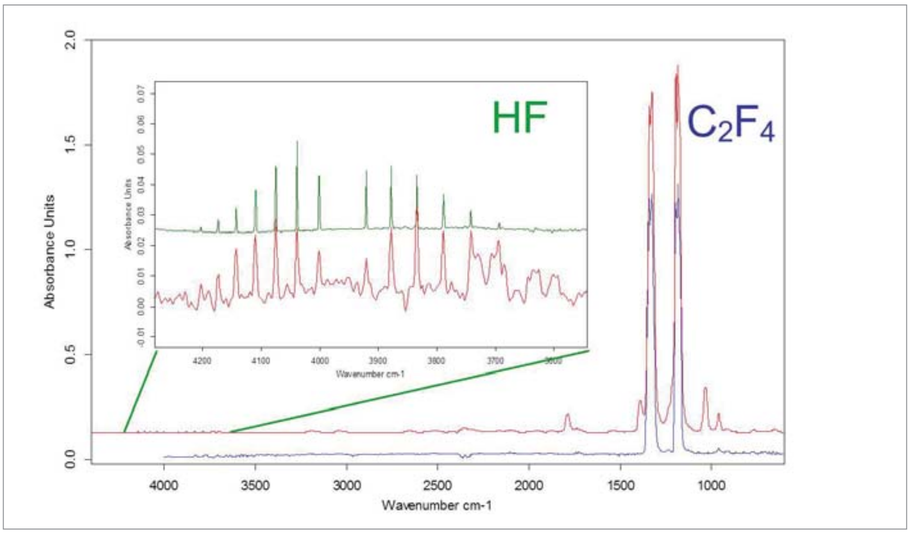
**8** Mass spectrum at 617°C for PTFE (QMS 403 C *Aëolos*®)

Simultaneously to the TGA-MS, an FT-IR measurement was performed. A collection of all detected IR-spectra is shown as a 3-dimensional cube in figure 9. Additionally, the TGA signal at the side face of the cube is additionally included.



**9** 3-D view of all detected IR-spectra versus temperature, including TGA results of PTFE (STA 449 ***F1*** *Jupiter*®-Bruker FT-IR TENSOR)

From this 3-D plot, single spectra at a temperature close to the maxima of the visible peaks were extracted (figure 10) and compared to library data. HF and tetrafluoroethylene were identified.



**10** Comparison of the extracted IR-spectra at 620°C (red curve) with the library spectra of tetrafluoroethylene (blue) and HF (green curve) for PTFE

## Conclusion

Various thermophysical and thermomechanical properties were tested to get a better understanding of PTFE. The solid-solid transition could be identified by all thermal analysis techniques employed. Only dynamic mechanical analysis was able to detect transitions related to the amorphous phase.

## Literature

[1] K. Hying, Analyse der viskoelastischen Eigenschaften von Polytetrafluorethylen im Bereich des β-Übergangs, Ph.D. thesis (RWTH Aachen, 2003)
[2] V. Villani, Thermochim. Acta, 162, 189 (1990)
[3] L. David, C. Sachot, G. Guenin and J. Perez, *Journal de Physique* III, Vol. 6, Dec 1996.
[4] J.D. Menczel, R.B. Prime, *Thermal Analysis of Polymers*, John Wiley & Sons, 2009.