CHARACTERIZATION OF PTFE USING ADVANCED THERMAL ANALYSIS TECHNIQUES

J. Blumm[1,2], A. Lindemann[1], M. Meyer[1], C. Strasser[1]
[1]NETZSCH-Gerätebau GmbH, Wittelsbacherstr. 42, 95100 Selb, Bavaria, Germany
[2]To whom correspondence should be addressed
e-mail: juergen.blumm@netzsch.com

1. Introduction

Polytetrafluoroethylene (PTFE) is a synthetic fluoropolymer originally discovered by Roy Plunkett of DuPont in 1938, used in numerous industrial applications. It is often referred to by its trademarked name, Teflon. It has a low friction coefficient and is therefore used as a non-stick coating for pans and other cookware. Compared to other polymers, PTFE generally has a high density (around 2.2 g/cm³) and high melting point (approximately 327°C) [1]. At atmospheric pressures, crystalline or partially crystalline polytetrafluoroethylene undergoes several phase changes from sub-ambient temperatures up to the melting point [2]. Below 19°C, a well-ordered hexagonal crystal structure is obtained. When heating to higher temperatures, the crystalline PTFE turns into a partially ordered hexagonal phase. Above 30°C, the material converts into a pseudo-hexagonal, very disordered phase. This phase is stable until the material reaches the melting region around 330°C. The transitions mentioned can easily be measured and analyzed by differential scanning calorimetry (DSC). A more thorough understanding of the processes and transitions, however, requires a more detailed thermal characterization of the material.

2. Experimental

Various thermal analysis techniques were employed for the characterization of PTFE supplied by ElringKlinger Kunststofftechnik GmbH, Heidenheim. For the thermal expansion measurements, a NETZSCH model DIL 402 C pushrod dilatometer was employed. The specific heat of the PTFE was measured using a NETZSCH model DSC 204 F1 *Phoenix* heat flux differential scanning calorimeter. The thermal diffusivity was measured employing a NETZSCH model LFA 457 *MicroFlash* laser flash apparatus. The system allows measurement of different thermophysical properties between -125°C and 1100°C (using two interchangeable furnaces). The viscoelastic properties were measured using a NETZSCH model DMA 242 C dynamic mechanical analyzer.

3. Results and Discussion

Presented in fig.1 are the measured linear thermal expansion and expansivity of PTFE. The expansivity or physical coefficient of thermal expansion is defined as the rate-of-expansion divided by the original sample length:

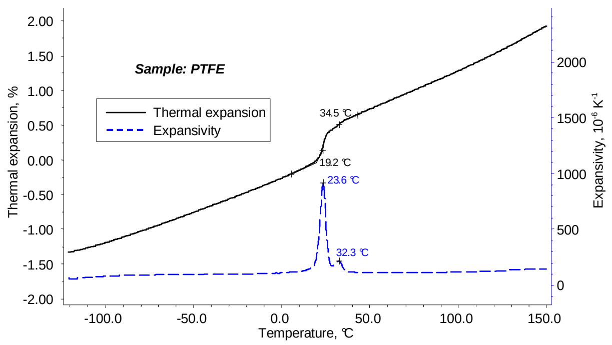

Fig. 1. Thermal Expansion and Expansivity of the PTFE Material

Starting at -130°C, the sample length increases over the entire temperature range with a slight increase in the rate-of-expansion versus temperature. Beginning at 19.2°C, two overlapped steps were detected in the thermal expansion curve. The two expansion steps are due to the solid-solid transitions [2]. From the well-ordered to the partially ordered phase, an expansion step of approximately 0.4% was measured. For the transition from the partially ordered to the very disordered phase above 35°C, a smaller step of approximately 0.1% was measured.

Depicted in fig. 2 is the apparent specific heat (specific heat and overlapped transition enthalpies) of the PTFE material. At low temperatures, the specific heat increases versus temperature as can be expected from the Debye-theory [3]. At 19.0°C (onset temperature), an endothermal peak overlaps the specific heat. The peak shows two separate maxima at 23.5°C and 31.6°C, indicating that two overlapped transitions occur in this temperature range. The structural changes are related with an entire enthalpy change of 7.76 J/g. Above the solid-solid phase change region, no significant phase transition was obtained in the measured specific heat until the melting range of the material was reached (240°C to 360°C, peak temperature at 337.2°C). The heat of fusion was measured to be 40.56 J/g.

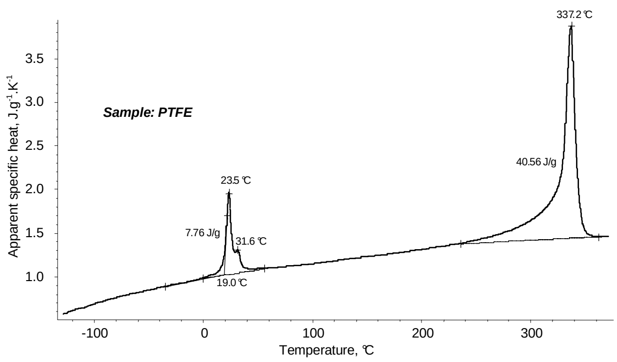

Fig. 2. Apparent Specific Heat of the PTFE Material

Presented in fig. 3 is the thermal diffusivity of the PTFE material versus temperature. As can be seen from the results, the thermal diffusivity decreases continuously with temperature outside the phase change region. This can be explained by solid state physics [3]. The temperature dependence of the thermal diffusivity above 25°C is small. Only a very weak step was measured around 125°C. This is the typical temperature range of the glass transition of the amorphous content inside the PTFE [4].

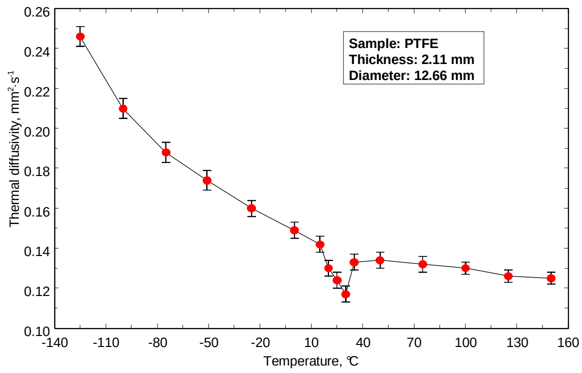

Fig. 3. Thermal Diffusivity of the PTFE Material

Fig. 4 shows the thermal conductivity of PTFE calculated from the measured results by multiplying the thermal diffusivity, specific heat and density. In the low-temperature range, the thermal conductivity is nearly constant. The values are around 0.32 W·m^{-1}·K^{-1}. At room temperature, significantly lower values (around 0.26 W·m^{-1}·K^{-1}) were found compared to the results prior to and after the phase change.

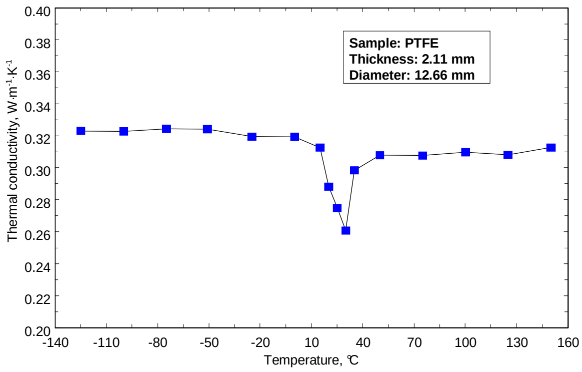

Fig. 4. Thermal Conductivity of the PTFE Material

Presented in fig. 5 are the mechanical properties (storage modulus *E'*, loss modulus *E''* and the ratio between these, the *tan δ*). A step in the storage modulus was measured at -123°C (onset temperature). This transition, which was not detected by the other methods employed is most probably due to a γ-relaxation [5]. Between 19°C (onset) and 39°C (end temperature), a further step of more than 50% can be seen in the storage modulus. At 110°C (onset), a further slope change can be seen in the storage modulus. This effect can be explained by the glass transition of the amorphous contents of the sample [5].

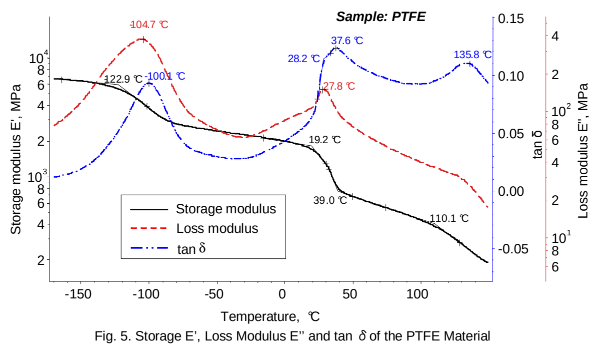

Fig. 5. Storage E', Loss Modulus E'' and tan δ of the PTFE Material

4. Conclusion

Various thermophysical and thermomechanical properties were measured on Polytetrafluoroethylene (PTFE) from -170°C to 370°C. Comparison of the different physical properties allows more detailed insight into the changes inside the material during the phase transitions around room temperature.

References

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