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Characterization of PTFE Using Advanced Thermal Analysis Techniques

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Abstract Polytetrafluoroethylene (PTFE) is a synthetic fluoropolymer used in numerous industrial applications. It is often referred to by its trademark name, Teflon. Thermal characterization of a PTFE material was carried out using various thermal analysis and thermophysical properties test techniques. The transformation energetics and specific heat were measured employing differential scanning calorimetry. The thermal expansion and the density changes were determined employing pushrod dilatometry. The viscoelastic properties (storage and loss modulus) were analyzed using dynamic mechanical analysis. The thermal diffusivity was measured using the laser flash technique. Combining thermal diffusivity data with specific heat and density allows calculation of the thermal conductivity of the polymer. Measurements were carried out from −125 °C up to 150 °C. Additionally, measurements of the mechanical properties were carried out down to −170 °C. The specific heat tests were conducted into the fully molten regions up to 370 °C.

Keywords Polytetrafluoroethylene · Specific heat · Thermal analysis · Thermal expansion · Thermophysical properties · Thermal conductivity · Thermal diffusivity

1 Introduction

Polytetrafluoroethylene (PTFE) is a synthetic fluoropolymer originally discovered by Roy Plunkett of DuPont in 1938. DuPont patented it in 1941 and registered the material as ‘Teflon.’ PTFE has an extremely low coefficient of friction and is used as a

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non-stick coating for pans and other cookware. Furthermore, it is used as a sealing material for reactive substances such as nuclear materials. Compared to other polymers, PTFE generally has a high density (around $2.2\,\mathrm{g\cdot cm^{-3}}$) and a high melting point (approximately 327 °C) [1]. PTFE has excellent insulating and dielectric properties. It is therefore a well-suited material for cable insulations or in microwave applications. Furthermore, it is chemically inert and therefore often used for containers and pipe work for reactive and corrosive chemicals (e.g., bottles for HF).

At atmospheric pressures, crystalline or partially crystalline PTFE 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, 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.

Presented in this work are measurements of different thermophysical and mechanical properties such as the specific heat, the thermal expansion and density change, the thermal diffusivity and thermal conductivity, and the viscoelastic properties (storage modulus, damping behavior) of a PTFE material. The material was supplied as large plates from ElringKlinger Kunststofftechnik GmbH of Heidenheim, Germany. The different samples for the various methods were prepared from the supplied plates.

2 Experimental

For the thermal expansion measurements on PTFE, a NETZSCH DIL 402 C pushrod dilatometer was employed [3]. The system was equipped with a liquid-nitrogen-cooled furnace allowing measurements from −180 °C up to 500 °C. The system was equipped with a fused silica sample holder and pushrod. The tests were carried out in a dynamic inert atmosphere (helium at a flow rate of $100\,\mathrm{ml\cdot min^{-1}}$) at a heating rate of $3\,\mathrm{K\cdot min^{-1}}$. The samples measured with the dilatometer were 10 mm long, 8 mm wide, and had a thickness of 2.11 mm. The measurements were performed in the length direction (10 mm). The tests were carried out in the solid region of the material between −130 °C and 150 °C. The influence of the sample holder on the measurement results was corrected employing software-based correction routines. From the measured thermal expansion, the expansivity, volumetric expansion, and density change were determined. The density was calculated from the measurement results using the thermal expansion data and a room temperature bulk density of $(2.161 \pm 0.015)\,\mathrm{g\cdot cm^{-3}}$. The room temperature bulk density was determined from a part of the original sample plate by measurements of mass and volume. The volume was determined from the dimensions of the sample. The uncertainty of dilatometer tests is generally in the range of 1 % [3].

The specific heat of the PTFE was measured using a NETZSCH Model DSC 204 F1 *Phoenix* heat flux differential scanning calorimeter. The system allows measurements between −180 °C and 700 °C. The samples tested with the DSC were approximately

5 mm in diameter and 1 mm thick. Aluminum crucibles with lids were used for the measurements. The measurements were carried out between −130 °C and 370°C. All tests were carried out in inert gas (nitrogen at $20\,\mathrm{ml \cdot min^{-1}}$) at heating rates of $10\,\mathrm{K \cdot min^{-1}}$. Evaluation of the specific heat was carried out employing the ratio method. Technical details regarding the instruments and evaluation technique can be found elsewhere [4]. The uncertainty of the method is specified as 3 % [4].

The thermal diffusivity was measured employing a NETZSCH Model LFA 457 *MicroFlash*™ laser flash apparatus [5,6]. The uncertainty of the system is better than 3 % [6]. The system allows the measurement of different thermophysical properties between −125 °C and 1100 °C (using two interchangeable furnaces). The tests were carried out between −125 °C and 150 °C in steps of 25 K, while the system was equipped with a liquid-nitrogen-cooled low-temperature furnace. The samples prepared for the laser flash technique (LFA) tests were disks of 12.66 mm in diameter and approximately 2 mm thick. The samples were coated with graphite on the front and back surfaces in order to avoid penetration of laser light through the sample and to improve the signal-to-noise ratio of the infrared detector signal.

Using the measurement results, the thermal conductivity was calculated according to

$$\lambda (T) = \rho (T)\, c_p (T)\, a (T). \tag{1}$$

The resulting thermal conductivity was analyzed in detail in the room temperature (phase-change) region.

The viscoelastic properties were measured using a NETZSCH Model DMA 242 C dynamic mechanical analyzer. The system allows tests between −170 °C and 600 °C in bending, compression, tension, shearing, and penetration modes. The tests were carried out using the three-point bending sample holder with a free bending length of 40 mm. The samples measured in the dynamic mechanical analysis (DMA) were 55 mm long, 10 mm wide, and 2.10 mm high. The measurements were carried out between −170 °C and 150 °C at a heating rate of $2\,\mathrm{K \cdot min^{-1}}$. Storage E' and loss modulus E'' as well as $\tan \delta$ (ratio between loss and storage modulus) were determined from the test results.

3 Results and Discussion

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

$$\text{expansivity} = \frac{1}{L_0} \frac{\mathrm{d}L}{\mathrm{d}T}. \tag{2}$$

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

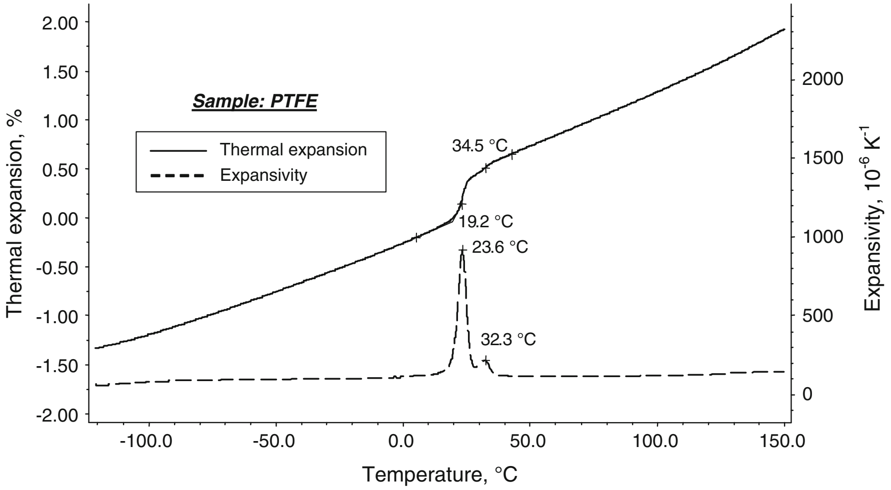

Fig. 1 Thermal expansion and expansivity of the PTFE material

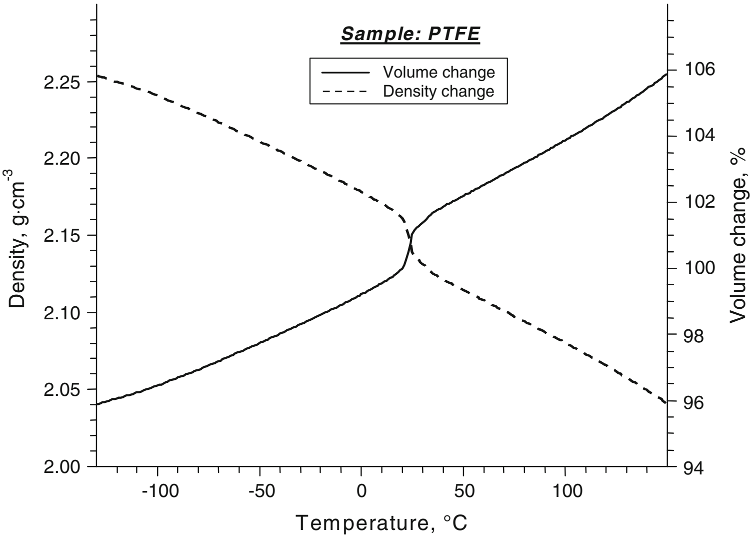

Fig. 2 Volumetric expansion and density change of the PTFE material

ordered phase, an expansion step of approximately 0.4 % was measured. For the transition from the partially ordered to the fully disordered phase above 35 °C, a smaller step of approximately 0.1 % was measured. Maxima in the expansivity were detected at 23.6 °C and 32.3 °C. These temperatures represent the points of the strongest expansion of the material during the phase transition. Above the phase-transition range, the thermal expansion continuously increases with an increasing rate-of-expansion.

Presented in Fig. 2 are the volume and density change of the PTFE material. The volume at room temperature was set to 100 %. The volume increases over the entire

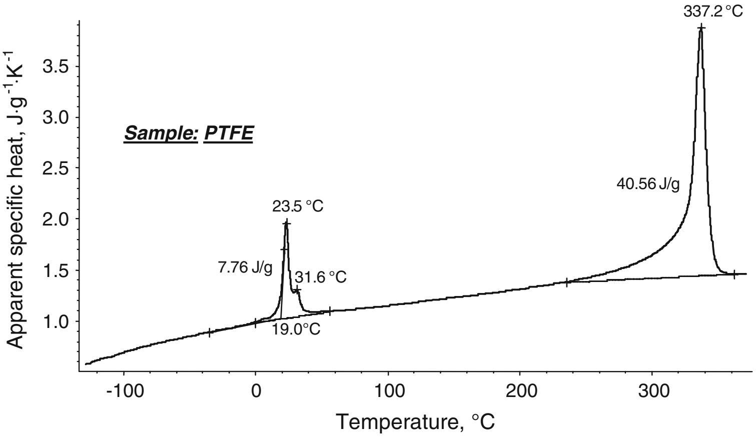

Fig. 3 Apparent specific heat of the PTFE material

temperature range. The steps in the measured thermal expansion, of course, show up in a similar way in the volume change. The density decreases from 2.254 $\mathrm{g \cdot cm^{-3}}$ at −130 °C to 2.041 $\mathrm{g \cdot cm^{-3}}$ at 150 °C. Of course, the upward steps in the volume cause a step downward in the density curve.

Depicted in Fig. 3 is the apparent specific heat (specific heat and overlapped transition enthalpies) of the PTFE material. At low temperatures, the specific heat increases with temperature as expected from the Debye theory [7]. 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 two transitions are due to the structural changes in the material (well-ordered to partially ordered hexagonal structure and partially ordered to disordered structure). The structural changes are related with a total enthalpy change of 7.76 $\mathrm{J \cdot g^{-1}}$. 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 $\mathrm{J \cdot g^{-1}}$.

Presented in Fig. 4 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 [7]. PTFE is a partially crystalline material. The heat transfer inside the material is dominated by phonon conduction (by the lattice structure). For such materials, the temperature dependence of the thermal diffusivity is mainly related to changes in the mean-free path length of the phonons. Due to more phonon–phonon interactions at higher temperatures, the mean-free path length gets shorter with increasing temperature and is proportional to T^{-1} [8]. Therefore, the thermal diffusivity shows a T^{-1} dependence as well. Around room temperature, significantly lower values were measured. This effect is most probably due to the structural changes in the material mentioned earlier. During the phase change, the material structure becomes more disordered, causing stronger scattering of the phonons and therefore a shorter mean-free path length. This results in a reduced thermal diffusivity. In any case, it must

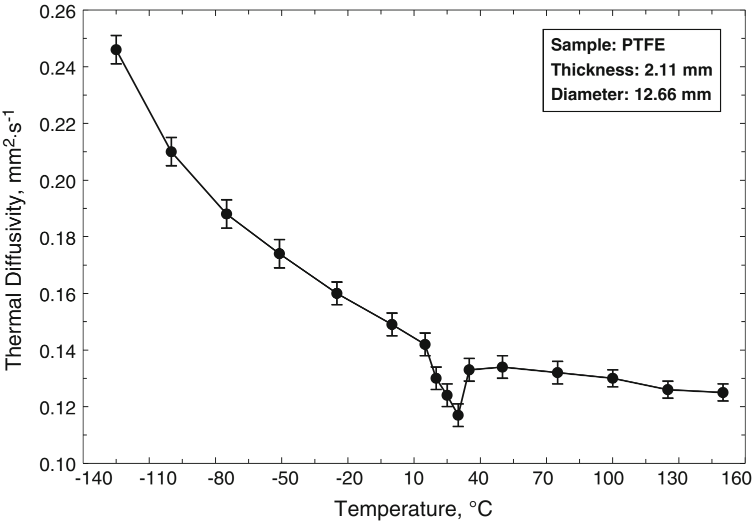

Fig. 4 Thermal diffusivity of the PTFE material

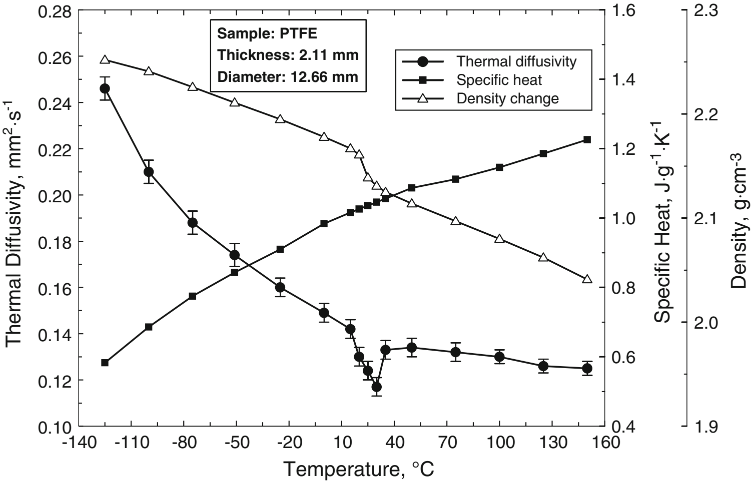

Fig. 5 Thermal diffusivity, specific heat, and density change of the PTFE material

be mentioned that the measurement of thermophysical properties in a phase-change region is critical, as the phase transition enthalpy can have an impact on the measurement and on the resulting data. In the fully disordered structure, the values are lower than in the ordered structure. 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 [9].

Depicted in Fig. 5 are the thermal diffusivity, specific heat, and density change of the PTFE material versus temperature. The enthalpy changes caused by phase

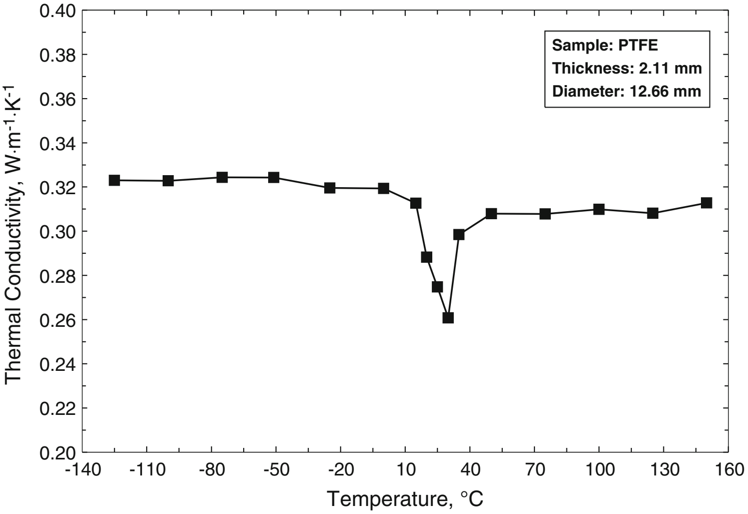

Fig. 6 Thermal conductivity of the PTFE material

transitions are removed from the specific heat results by a linear interpolation of the values measured before and after the phase transitions. It can clearly be seen that all measured thermophysical properties show a slight step or slope change in the temperature around room temperature. The strongest impacts of the structural changes on the measured result were detected in density and thermal diffusivity, which show significantly different behavior before, during, and after the phase change.

Figure 6 shows the thermal conductivity of the PTFE material calculated from the measured results as a product of the thermal diffusivity, specific heat, and density. In the low-temperature range, the thermal conductivity is nearly constant. The values are around $0.32\,\mathrm{W\cdot m^{-1}\cdot K^{-1}}$. At room temperature, significantly lower values (around $0.26\,\mathrm{W\cdot m^{-1}\cdot K^{-1}}$) were found compared to the results prior to and after the phase change. Obviously, the structural changes in the material reduce the thermal conductivity by more than 10 %. Above 35 °C, the thermal conductivity shows a slight increase versus temperature. Constant or slightly increasing thermal conductivities are typical for such partially crystalline polymer materials. No further transitions were measured in the temperature range above 100 °C. Typical literature values for the thermal conductivity of pure PTFE materials are around $0.25\,\mathrm{W\cdot m^{-1}\cdot K^{-1}}$ [10]. The results measured in this work are slightly higher (approximately 6 %) at room temperature and significantly higher at low or high temperatures. However, most of the literature data refer to tests carried out at room temperature and therefore in the phase-change region.

Presented in Fig. 7 are the measured mechanical properties (storage modulus E', loss modulus E'', and the ratio between these, $\tan\delta$) determined using a dynamic mechanical analyzer. A step in the storage modulus was measured at −123 °C (onset temperature). Peak temperatures in the loss modulus and in the $\tan\delta$ were at −105 °C and −100 °C, respectively. This transition, which was not detected by the other methods employed, is most probably due to a γ-relaxation. Such a transition is mentioned in the literature [11] and is most probably due to a structural change in the purely

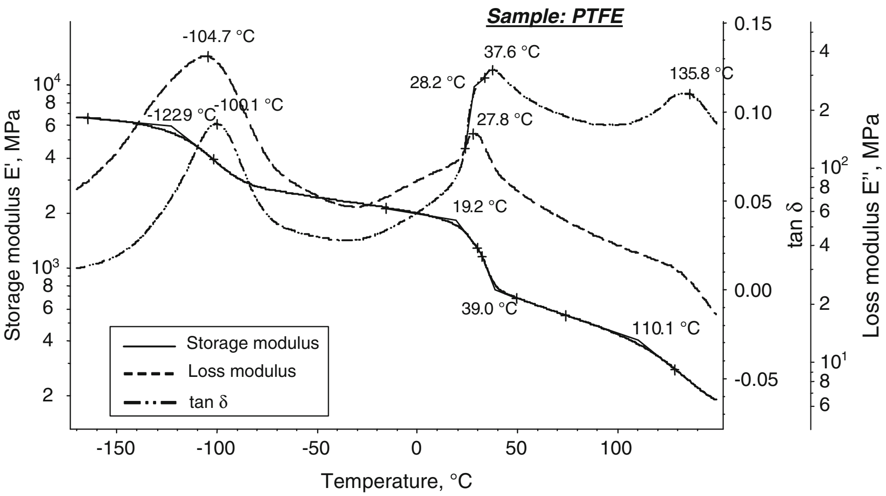

Fig. 7 Storage E', loss modulus E'', and tan δ of the PTFE material

amorphous region of the material. The transition causes a drop in the storage modulus of approximately 50 %. Between 19 °C (onset) and 39 °C (end temperature), a further step of more than 50 % can be seen in the storage modulus. The two-stage character of the transition shows up as a slope change during the step. However, the measured separation is not as clear as in the thermal expansion or specific heat results. The loss modulus shows a maximum at 28 °C. At 110 °C (onset), a further slope change can be seen in the storage modulus. Related to this, a peak is visible on the tan δ curve at 136 °C. This effect can be explained by the glass transition of the amorphous content of the sample [11].

4 Conclusion

Various thermophysical and thermomechanical properties were measured for 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. From the test results, it can be determined that the phase changes from the ordered to the disordered structures have significant impact on the material's mechanical strength. The influences on the thermal expansion and the thermal transport properties are less strong but can be clearly seen as well. Slope changes were detected in the thermal diffusivity in the phase-change region. The thermal conductivity is significantly lower in the phase-change region around room temperature, and shows only a slight temperature dependence outside the phase-change region.

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