Journal of Thermal Analysis, Vol. 24 (1982) 3–8

THERMAL CONDUCTIVITIES OF POLYTETRAFLUOROETHYLENE AND POLYCHLOROTRIFLUOROETHYLENE BETWEEN 4.2 AND 20 K

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(Received May 5, 1981)

The thermal conductivities of bulk technical samples of polytetrafluoroethylene and polychlorotrifluoroethylene were measured in the temperature range 4.2–20 K by application of the steady-state method. An interpretation of the thermal conductivity data in terms of the available theoretical and empirical models is presented.

The technology of preparation of polymeric materials and their technical applications at room and low temperatures require a knowledge of the experimentally obtained thermal conductivity values. A number of papers and monographs [1–7] are devoted to thermal conductivity investigations of these materials operating under cryogenic conditions. However, there are not enough experimental data for the helium temperature case or, when they are available, they differ to a great extent.

In this paper we report the results of measurements of the thermal conductivities of bulk commercial samples of polytetrafluoroethylene (T_4) and polychlorotrifluoroethylene (T_3) within the temperature range 4.2–20 K. For these measurements a steady-state method with axial heat flux was applied, with the experimental equipment illustrated in Fig. 1.

A cylindrical polymeric sample (1) 10 mm in diameter and about 50 mm in length (measured at room temperature) was attached to the copper bottom (2) of the experimental insert (Fig. 1) by means of a heat-sink consisting of a thin-wall stainless steal tube (3) and two copper screw bushings (4 and 4'). The sample was enclosed in a perforated copper radiation shield (5) with 600 Ω – 0.050 mm constantan heating wire (6) on it. The shield was surrounded by a copper vacuum can (7) evacuated to about $0.133 \cdot 10^{-2}$ Pa at room temperature. Two 500 Ω constantan heaters H_1 and H_2 were wound and glued on the lower and upper ends of the sample. The lead connections of 0.050 mm constantan wire (8) were thermally anchored at liquid helium temperature. Two 300 Ω Allen Bradley carbon resistance thermometers R_1 and R_2 were inserted into two 1.8 mm holes drilled through the sample at a distance of about 1 cm from each end. The resistance thermometer R_2 was a gradient thermometer and was calibrated from 2.5 to 30 K against a germanium (NIG) substandard. The resistance thermometer R_1 was uncalibrated and maintained at constant temperature T_1 during the experiment by means of the heating wire H_1. One experimental measurement consists

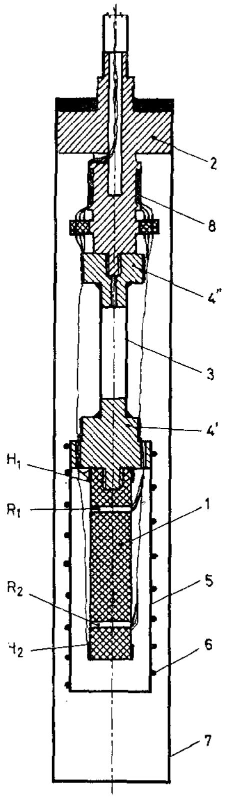

Fig. 1. Experimental insert for the thermal conductivity measurements: 1 — sample, 2 — copper bottom of insert, 3 — thin-wall stainless steel tube, 4' and 4" — copper screw bushings, 5 — perforated copper radiation shield, 6 — H_1 and H_2 — electrical heaters, 7 — copper vacuum can, 8 — lead connections, R_1 and R_2 — carbon resistance thermometers

in the following: first, we measure the temperature $T_{\mathrm{off}}(R_2) = T(R_1) = T_1$ without switching on the electrical heater H_2; second, we measure the temperature $T_{\mathrm{on}}(R_2) = T_2$ with power $\dot{Q}$ applied to the electrical heater H_2. If we postulate that

L = the distance between thermometers R_1 and R_2, S = the cross-sectional sample area, $\dot{Q}$ = the steady-state axial heat flux,

$(T_2 - T_1) = T_{\mathrm{off}}(R_2) - T_{\mathrm{on}}(R_2)$ = the thermal gradient of the sample, the thermal conductivity κ can be calculated from the well-known expression

$$\kappa = \frac{\dot{Q}L}{S(T_2 - T_1)} \tag{1}$$

where the temperature difference $(T_2 - T_1)$ was about 5% of the temperature $\frac{T_1 + T_2}{2}$. The reproducibility of the measurements was ±1.5%, and the total

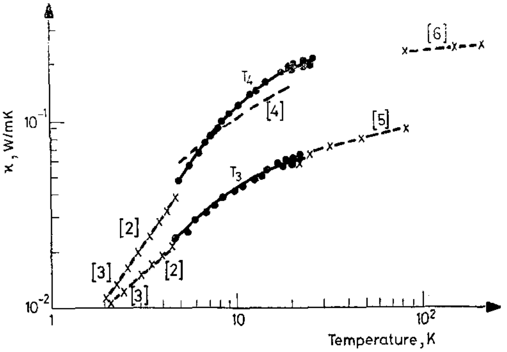

Fig. 2. Thermal conductivities of polytetrafluoroethylene (T_4) and polychlorotrifluoroethylene (T_3). .— our measurements; x— measurements from earlier papers [2–6]

absolute error was not more than 4% up to 20 K. All calculations were carried out by computer. In these calculations the correction for the thermal expansion of the sample was made.

The experimental difficulties (heat losses along the leads, extremely long equilibrium times, poor thermal contact between the specimen and cryostat, non-uniform heat flow) in the measurement of κ in disordered materials by an equilibrium method at low temperatures are discussed in ref. [10]. Our specimen geometry ($D = 10$ mm and $L = 50$ mm) was chosen to accord to this research work [10] and was acceptable with a view to a reasonable equilibrium time τ_1. The equilibrium time τ_1 for the presented experiments above 10 K was established in 1–2 hours for T_4 and 2–3 hours for T_3, which is in good agreement with Reese [8], Eq. (2):

$$\tau_1 = \frac{18.4\, C(T) L^2}{\pi^2 \kappa(T)} \text{ sec} \tag{2}$$

where L is the length of the sample, and $C(T)$ and $\kappa(T)$ are the experimental data for specific heat and thermal conductivity.

The data for the thermal conductivities of the polytetrafluoroethylene (T_4) and polychlorotrifluoroethylene (T_3) samples from our measurements (solid lines) and from the measurements of other authors (dashed lines) are shown in Fig. 2.

Following Chang and Jones [11], an empirical fit of the thermal conductivity data up to 9 K for T_4 and up to 6.7 K for T_3 was made (Eq. 3):

$$\kappa = \frac{k^2 \cdot T}{6\pi^2 \cdot \hbar} \cdot \frac{A}{a} \cdot \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} \cdot \frac{dx}{x^2 + (A/a\lambda_b)(\hbar\nu/kT)^2} \tag{3}$$

Expression (3) is derivable from standard transport theory assuming a Debye phonon distribution, considering only longitudinal phonons and allowing two scattering mechanisms: the "structure scattering" of Klemens [14, 15], who gives the mean free path for a phonon of wave vector q as $l_s = \frac{A}{a} \cdot q^2$, and the "frequency-independent scattering" with relaxation time $\tau_b = \frac{\lambda_b}{v}$. In Eq. (3)

κ is the thermal conductivity,
T is the absolute temperature,
$\hbar$ is Planck's constant divided by 2π
k is Boltzmann's constant,
$\frac{A}{a}$ is an experimentally determined parameter of dimensions m^{-1}: this inverse length relates to the length over which elastic properties are correlated with the amorphous material,
λ_b is the temperature-independent scattering length, and
v is the average sound velocity of longitudinal waves.

The first step of this analysis was to obtain graphically the constants $\frac{A}{a}$ and $\frac{v^2}{\lambda_b}$ for the longitudinal modes, utilizing the numerical values given by Colloway [12] for integral

$$\int\limits_0^\infty \frac{x^4 e^x dx}{(x^2 + y^2)(e^x - l)^2} \text{ in Eq. 3, where } y^2 = \frac{A}{a\lambda_b} \cdot \left(\frac{\hbar v}{kT}\right)^2.$$

The average sound velocities v for these materials were calculated using the Debye relationship [4] for specific heat at low temperatures

$$\frac{C(T)}{T^3} = \frac{2 \cdot \pi^2 \cdot k^4}{5\hbar^3 \cdot v^3} \tag{4}$$

where $C(T)$ are the experimental specific heat values taken from [13]. The average sound velocity v then gives λ_b. All quantities $\frac{A}{a}$, λ_b, v and ρ are shown in Table 1. The data obtained by Reese and Tucker [2] are also given in Table 1. Using a polarizing microscope, these authors observed a good correlation between the values of λ_b and the average sizes of crystalline regions. At higher temperature (over 4 K) the influence of the morphology of the sample on the mechanism of the heat transport has not been investigated.

In conclusion, the results of our thermal conductivity investigations confirm the application of the modified theoretical model of Chang and Jones [11], extended from about 4 K up to 9 K for T_4 and up to 6.7 K for T_3, where the temperature-dependence of the specific heat is $C(T) \sim T^{2.5}$ [13].

There is a fairly successful attempt to account for κ in the theoretical work of Morgan and Smith [9]. Their theory explains the behaviour of κ in terms of one

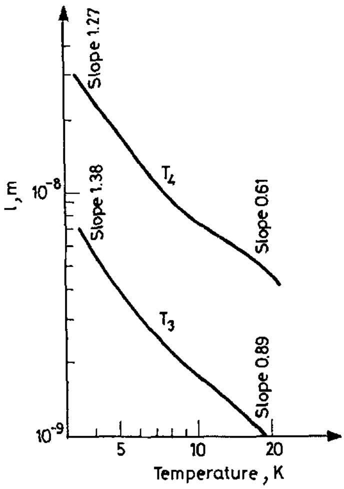

Fig. 3. Polytetrafluoroethylene (T_4) and polychlorotrifluoroethylene (T_3): total mean free path for scattering *vs* temperature

Table 1

Source	Material	Temperature range, K	A/a, m^{-1}	λ_b, m	v, m/sec	ϱ, kg/m^3
Our measurements	T_4	4.5–9	$9.26 . 10^{10}$	$0.73 . 10^{-6}$	$1.26 . 10^3$	—
	T_3	4.5–6.7	$3.92 . 10^{10}$	$1.05 . 10^{-6}$	$1.15 . 10^3$	—
Reese and Tucker [2]	T_4	1–4	$11.00 . 10^{10}$	$0.78 . 10^{-6}$	$1.07 . 10^3$	$2.160 . 10^3$
	T_3	1–4	$4.84 . 10^{10}$	—	$1.00 . 10^3$	$2.144 . 10^3$

adjustable parameter, the correlation length a(Å) for the fluctuations in the properties of the solid from point to point. This theory assumes a Debye model for the phonon spectrum. It can be applied to all disordered solids and besides, it is not dependent on details of morphology. For large values of a (1000–3000 Å) the thermal conductivity κ rises as T^n where n lies between 2 and 3. When a is reduced to 500–100 Å, κ begins to flatten, while for small values of a (15–5 Å) κ develops a plateau. It is possible to apply Morgan and Smith's analysis over the complete temperature range of our measurements, but this interpretation can only be claimed to be qualitative. The variation of n around 1 in the expression $\kappa \sim T^n$ for our measurements can be explained by a value of a between 100 and 500 Å. To explain the small value of n (0.43) above 13.5 K up to 20 K for T_4, an assumption of an additional scattering mechanism. Umklapp scattering of phonons with $\kappa_{add} \sim \exp(\theta_D/T)$, was made. This assumption was permissible for temperatures

$T < \theta_D$ ($T < \frac{\theta_D}{6}$ [15]), where the Debye temperature θ_D for T_4 is 102 K [13].

In Fig. 3 a total mean free path l for two polymers is presented. It is extracted from a kinetic approach first suggested by Debye and written as

$$\kappa(T) = \frac{1}{3} C(T)vl \tag{5}$$

where $C(T)$ and $\kappa(T)$ are experimental data for specific heat and thermal conductivity. The approach of the mean free path l to the dependence T^{-2} at lower temperatures confirms the result predicted by Klemens's theory.

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This work was done in the International Laboratory of High Magnetic Fields and Low Temperatures, Wrocław, Poland.

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ZUSAMMENFASSUNG — Die thermischen Leitfähigkeiten technischer Einzelproben von Polytetrafluoräthylen und Polychlortrifluoräthylen wurden im Temperaturbereich von 4.2 bis 20 K durch Einsatz der Festkörper-Methode gemessen. Eine Deutung der thermischen Leitfähigkeitsangaben wird anhand der zur Verfügung stehenden theoretischen und empirischen Modelle gegeben.

Резюме — Измерены удельные теплопроводности объемных технических образцов политетрафторэтилена и политрифторхлорэтилена в области температур 4.2—20 К с помощью метода стационарного состояния. Интерпретация полученных данных проведена на основе доступных теоретических и эмпирических моделей.