Thermal conductivity of PTFE and PTFE composites

Duncan M. Price[a],[*], Mark Jarratt[b]

[a]IPTME, Loughborough University, Loughborough, Leics, LE11 3TU, UK
[b]Department of Physics, University of Warwick, Warwick, Coventry CV4 7AL, UK

Abstract

The thermal conductivity of polytetrafluoroethylene (PTFE) was studied using an instrumented thermal conductivity apparatus (Lees' disk) and by DSC. The former method was used to study the effect of incorporating fillers into a PTFE/glass fiber fabric used for conveyor belts in food processing. The effect of crystallinity on thermal conductivity was investigated and different methods of crystallinity determination were compared. The incorporation of aluminum flakes improved heat transport through the composites. The thermal conductivity of PTFE with different levels of crystallinity was measured at 232 °C and shown to increase linearly with this parameter.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Composites; Crystallinity; Lees' disk; Polytetrafluoroethylene; Thermal conductivity

1. Introduction

Polytetrafluoroethlylene (PTFE) exhibits useful properties over the widest temperature range of any known polymer. At one end of the temperature scale, the polymer possesses unusual toughness at cryogenic temperatures. PTFE also has an usually high virgin crystalline melting point (342 °C), extremely high shear viscosity (10^{11} Poise at 380 °C) in the melt and good thermal stability. The polymer is insoluble in all common solvents and is highly resistant to chemical attack. Its combination of electrical properties is outstanding with high dielectric strength and extremely low dielectric loss. The polymer is uniquely non-adhesive and anti-frictional.

These factors mean that although PTFE is expensive and difficult to process, it has many uses ranging from bearings and gaskets to breathable fabrics and cooking utensils.

Of particular interest in this study are PTFE-impregnated glass fiber fabrics which are prepared by dip coating glass fiber fabric with an aqueous dispersion of polymer, drying and then sintering the PTFE to achieve good adhesion and homogeneity. The end product is used in applications such as tunnel oven conveyor belts (in particular for the food industry) and architectural coverings where the unique properties of PTFE are required. This paper discusses aspects of a wider ranging project to provide fundamental information about these materials relevant to the manufacturing and end use [1]. To this end, techniques were developed to measure the thermal conductivity and crystallinity of PTFE and PTFE/glass composites so as to study their inter-relationship.

---

* Corresponding author. Tel.: +44-1509-223332;
fax: +44-1509-223332.
E-mail address: duncanprice@uk2.net (D.M. Price).

2. Experimental

2.1. Materials

Samples of PTFE and polymethylmethacrylate in the form of 3 mm thick sheet were supplied by ICI (UK). PTFE/glass fiber mats (some with added aluminum powder) were obtained from Fothergill Tygaflor (UK). Gravimetric analysis of the materials showed that the PTFE/glass fiber mats contained 60% by weight PTFE.

2.2. Lees' disk thermal conductivity apparatus

The apparatus used was a modification of the standard Lees' disk method for the measurement of thermal conductivity by the absolute plane parallel plate technique. Explanations of this technique can be found in various physics textbooks (e.g. [2]). This method, in its classical form, utilises a steam chest to provide a temperature of 100 °C on one side of the sample and subsequently cooling measurements in order to calculate the heat flow through the sample. However, the equipment used for this work employed electrical heating without the need for cooling measurements [3]. A diagram of the apparatus is shown in Fig. 1 and is widely used in school physics classes. This consists of three copper plates (A–C) drilled to accept liquid-in-glass thermometers and a 6 W

electrical plate heater of the same diameter as the copper plates (Griffin & George Ltd., Wembley, Middlesex, UK).

The sample to be studied was cut to the same diameter as the copper plates (41 mm) and to a thickness of approximately 3 mm. Several sheets of PTFE/glass fiber mats were used to build up the required thickness and liberally coated with petroleum jelly to facilitate good thermal contact. The specimen was then placed between copper plates A and B. The heater was sandwiched between plates B and C and, after tightening the clamp screw to hold all the disks together, the power to the heater was switched on. The whole assembly was placed in an enclosure to minimize the effects of draughts and a fourth thermometer was placed within the enclosure, fairly close to the apparatus, to measure the ambient temperature. At the beginning of each determination, the power from a stabilized dc supply was turned on full until the average temperature of the sample (i.e. the mean of the temperature of plates A and B) reached the desired value. The power was then adjusted to allow the temperatures of the plates to stabilize. This took several hours, throughout which time readings were taken at 30 min intervals and, as equilibrium was reached, readings were taken every 10–15 min. At these times, in addition to the four temperature readings, the current and voltage applied to the heater was monitored. When the temperature of all parts of the
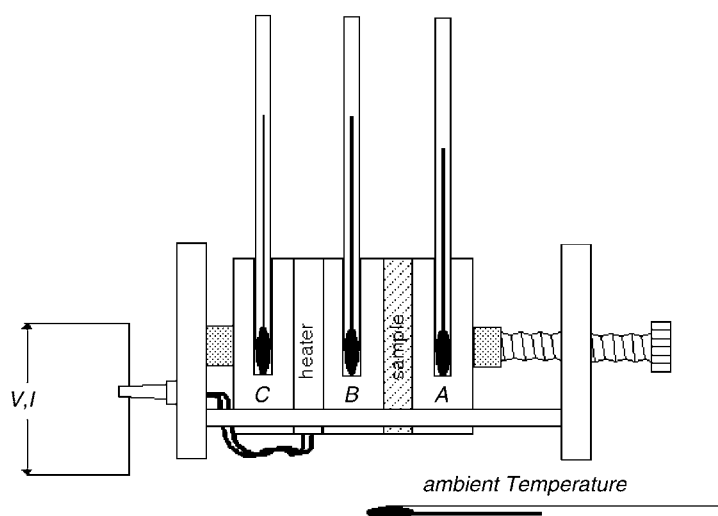

Fig. 1. Lees' disk apparatus (schematic).

apparatus had been stable to within $\pm 0.1\,^{\circ}\mathrm{C}$ for 30 min, a value for the thermal conductivity of the specimen (λ) of thickness d and radius r was calculated using Eq. (10) derived in Section 3.

2.3. Differential scanning calorimetry

DSC measurements were made using a TA Instruments 910 DSC under nitrogen. The instrument was calibrated for temperature and heat flow response according to the melting points and heats of fusion of pure gallium, indium, tin and bismuth. Synthetic sapphire was used as a reference material for heat capacity determinations.

Several papers describe the use of differential scanning calorimeters to measure thermal conductivity [4–9]. An advantage of using DSC is that the specific heat capacity of the sample can be measured with the same instrument and hence, if its density is known, the thermal diffusivity of the sample ($\lambda/\rho C_p$) can be found. For this work, we used the method of Hakvoort and van Reijen, whereby both the temperature and heat flow into the base of the sample are measured [7]. The temperature of the top surface of the sample cannot be measured directly, but by placing a pure metal on top of the sample, the temperature of that side of the sample is defined during melting of the metal. This limits the temperatures at which determinations can be made to that of readily available melting point standards. The thermal conductivity of the specimen (λ), thickness h and cross-sectional area of a is given by

$$\lambda = \frac{h}{a} \frac{\Delta H_f\,(\mathrm{lit})}{\Delta H_f\,(\mathrm{meas})} S_{\mathrm{onset}} \tag{1}$$

where ΔH_f (lit) is the literature value for the heat of fusion of the metal, ΔH_f (meas) the measured value for the heat of fusion of the metal and S_{onset} is the slope of $\mathrm{d}H/\mathrm{d}t$ versus T for the onset of melting of the standard.

3. Theory of operation of Lees' disk apparatus [3]

The heat transfer between an object and its surroundings depends on the exposed surface area of the object and the temperature difference between the object and its surroundings. Let e joules of energy be emitted from the exposed area of surface (measured in m^2) $\mathrm{s}^{-1}\,^{\circ}\mathrm{C}^{-1}$ above ambient temperature.

Assume that this is the same for disks A, B, C and the specimen.

The temperature of the specimen (T_S) is the mean temperature of disks A and B. The total heat emitted from the apparatus is

$$H = ea_A T_A = ea_S \frac{T_A + T_B}{2} + ea_B T_B + ea_C T_C \tag{2}$$

where a_A, a_B, a_C, a_S and a_H are the exposed surface areas of A, B, C, the specimen and heater, respectively. Areas a_A and a_C include the flat ends of the disks. T_A, T_B and T_C are the temperatures of the disks A, B and C above ambient (i.e. the true temperature of the disk minus the ambient temperature). The heat (H) supplied by the electrical heater is given by

$$H = VI \tag{3}$$

where V is the potential difference across the heater and I is the current which flows through it.

From Eqs. (2) and (3)

$$e = VI \left(a_A T_A + a_S \frac{T_A + T_B}{2} + a_B T_B + a_C T_C \right) \tag{4}$$

From the standard equation for conduction of heat through an object, the heat flowing through the specimen S is

$$h_S = \lambda \pi r^2 \frac{T_B - T_A}{d} \tag{5}$$

where r is its radius, d its thickness and λ the thermal conductivity of the specimen.

All of the heat entering S from B is that which is emitted by S and A together

$$h_{BS} = ea_S \frac{T_A + T_B}{2} + ea_A T_A \tag{6}$$

The heat leaving S for A is that which is emitted by A alone

$$h_{SA} = ea_A T_A \tag{7}$$

The mean of these two is

$$h_S = \frac{e}{2} \left(a_S \frac{T_A + T_B}{2} + 2a_A T_A \right) \tag{8}$$

Thus from (2) and (8)

$$\lambda \pi r^2 \frac{T_B - T_A}{d} = \frac{e}{2} \left(a_S \frac{T_A + T_B}{2} + 2a_A T_A \right) \tag{9}$$

Substituting the value for e in Eq. (1) into Eq. (9) gives

$$\lambda = \frac{ed}{2\pi r^2 (T_B - T_A)} \left(a_S \frac{T_A + T_B}{2} + 2 a_A T_A \right) \qquad (10)$$

which is the quantity we wish to measure.

From the above it can be seen that working out λ for each sample by hand would be very laborious. These calculations were therefore, performed using a computer program which could accept data manually or take input directly from a six channel data logger (DataHog SDL2850, Skye Instruments, Llandrindod Wells, Powys, UK). This measured the four temperatures using K-type thermocouples and the power supplied to the heater via two channels (0–10 V for heater voltage) and (0–1 V for the heater current via the voltage drop across a $1\,\Omega$ resistor). Following introduction of the data logger, the time taken to obtain a reliable value for the thermal conductivity of specimen was reduced from 6 to 2 h.

4. Results and discussion

The accuracy of the Lees' disk method for determining thermal conductivity was checked by sending test samples to the National Physical Laboratory, Teddington, Middlesex, UK for measurement using a 76 mm diameter guarded hot plate apparatus whose calibration was traceable to national standards. The tests were carried out according to national and European standards [10] and the specimens were returned for testing on the apparatus described above. At 50 °C, we obtained λ for PMMA and PTFE (199 and 259 mW m^{-1} °C^{-1}, respectively) to $\pm 2.5\%$ in good agreement with the certified values (194 and 264 mW m^{-1} °C^{-1}) from NPL who claim a similar level of precision.

Samples of unsintered and sintered PTFE/glass mats supplied by the manufacturer were tested using the Lees' disk method. These were only available as thin (≈ 0.25 mm) sheets, so that ten, or more, sheets had to be used in order to build up the required specimen thickness. Petroleum jelly was applied to the surface of each sheet to ensure good thermal contact between them, nevertheless, air gaps might have been present thereby compromising the accuracy of the method. Table 1 shows the results for sintered and unsintered PTFE/glass mats in addition to measurements made on sheets containing added aluminum

Table 1
Thermal conductivity of PTFE and composites

Sample	λ (mW m^{-1} °C^{-1}) at 50 °C
Bulk PTFE	259 ± 6
Unsintered PTFE/glass	198 ± 5
Sintered PTFE/glass	222 ± 6
Sintered PTFE/glass + 5% Al[a]	244 ± 6
Sintered PTFE/glass + 10% Al[a]	267 ± 7
Sintered PTFE/glass + 15% Al[a]	262 ± 7
Sintered PTFE/glass + 30% Al[a]	271 ± 7

[a] The aluminum was in addition to the PTFE present (60% w/w PTFE, 40% w/w glass). For example, the material containing 30% Al is composed of 30/130 (w/w) Al, 60/130 (w/w) PTFE and 40/130 (w/w) glass.

powder. As one might expect, addition of a highly conductive metal filler improves heat transport through the sheets [11], although there does appear to be a diminishing improvement in heat transfer as more aluminum is incorporated.

Comparison of data for unsintered and sintered PTFE/glass mats indicated that sintering improved the thermal conductivity of the specimen. This may have been due to changes in crystallinity of the PTFE or, more likely, to a reduction in voids brought about by better contact of the polymer with the glass. In order to investigate the effect of crystallinity of PTFE on its thermal conductivity, measurements were made on samples of bulk PTFE (the same sample that was used to establish the performance of the Lee's disk apparatus).

The crystallinity of the bulk PTFE was measured by several different methods: X-ray diffraction (XRD [12]), density and dynamic mechanical analysis (DMA [13]). Only the XRD method is an absolute measure of crystallinity, but the values obtained (75.0% XRD, 65.7% density & 62% DMA) are in reasonable agreement—the presence of voids within the sample might explain the reason that XRD gave the highest value. The heat of fusion of this sample was then determined by DSC (37.4 J g^{-1}). This would indicate a the heat of fusion of 100% crystalline polymer of 48.9 J g^{-1}. Lau et al. [14] recommend a value of 80 J g^{-1} for crystalline PTFE; there are widely varying values for the heat of fusion of PTFE to be found in [15]. It should therefore be recognized that our value relates to the specific sample studied and this result is simply used to assess the relative crystallinity of samples.

Table 2
Effect of cooling rate on crystallinity and thermal conductivity of PTFE

Cooling rate ($^{\circ}$C min^{-1})	ΔH_f (J g^{-1})	Crystallinity (%)	λ (mW m^{-1} $^{\circ}$C^{-1}) at 232 $^{\circ}$C
As received	37.4	75 ± 2	300 ± 12
1	37.9	76 ± 2	298 ± 12
2.5	35.6	71 ± 2	292 ± 12
5	34.0	68 ± 2	287 ± 11
10	32.8	66 ± 2	286 ± 11
20	31.5	63 ± 2	283 ± 11
40	30.2	61 ± 2	279 ± 11

Samples of PFTE sheet of different crystallinity were prepared in situ in the DSC by cooling specimens at different rates from the melt. The heat of fusion of the sample was measured by re-heating the samples at 10 $^{\circ}$C min^{-1}. A slower cooling rate results in a more crystalline specimen. The highest cooling rate reflects the maximum controllable capacity of the DSC and the slowest rate is limited by concerns over the thermal stability of the sample. Prolonged exposure to elevated temperatures during cooling was found to result in reduction of molecular weight of the specimen (as judged by inspection of the crystallization exotherm) and yielded little improvement in the measured crystallinity. Table 2 shows the variation in crystallinity and thermal conductivity with sample preparation conditions.

Using Hakvoort's DSC method for measuring thermal conductivity, tin (T_m, 232 $^{\circ}$C) was employed to determine the temperature gradient across the specimens and therefore, the data for λ refer to this temperature. While the data appear to fit a linear trend of increasing thermal conductivity with crystallinity (Fig. 2), this only has operational significance for the single measurement temperature used. The results of earlier workers give contradicting conclusions [16–19]; some workers find no change in λ with crystallinity, whereas others detect an increase or decrease in this parameter. This effect of crystallinity on λ for
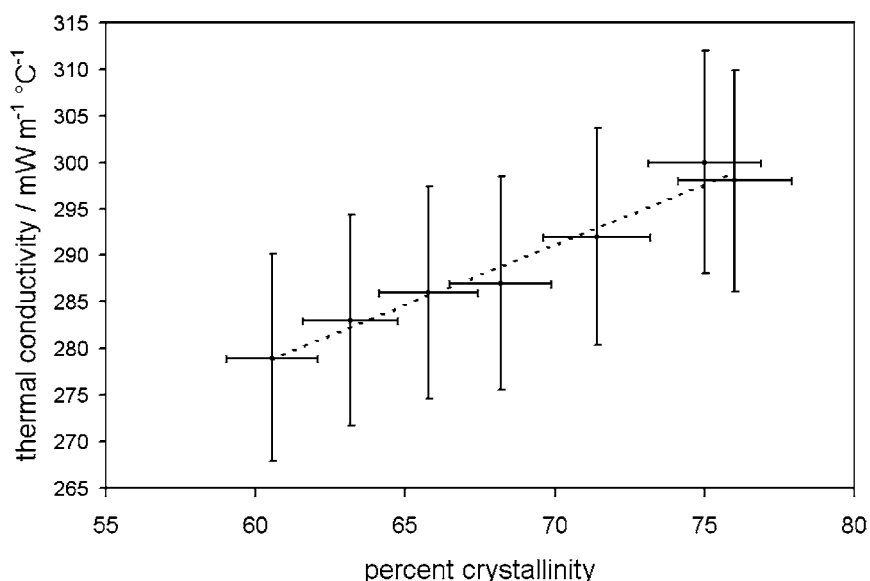

Fig. 2. Graph of thermal conductivity of PTFE vs. crystallinity measured at 232 $^{\circ}$C, broken line shows linear fit to data (slope: 1.3007 mW m^{-1} ($^{\circ}$C%)$^{-1}$; intercept: 200.08 mW m^{-1} $^{\circ}$C^{-1}; R^2: 0.9688).

polymers has been discussed in detail by Kline and Reese [11,20]. Changes in temperature can result in a decrease or no change in this parameter with crystallinity. Our observation has, however, particular relevance to the use of PTFE/glass mat in its end-use application for food processing, where the substrate is likely to near to 200 °C.

5. Conclusions

A simple and accurate apparatus for the determination of thermal conductivity was built and used to investigate the effect of processing and composition on the heat transport behavior of PTFE/glass fiber mats. Ancillary measurements indicated that the thermal conductivity of PTFE increased with increasing crystallinity at 232 °C.

References

[1] M. Jarratt, MSc Dissertation, University of Warwick, 1993.
[2] M. Nelkon, P. Parker, Advanced Level Physics, 3rd Edition, Heinman, London, 1988, pp. 336–338.
[3] Lees' Conductivity Apparatus (Electrical Method) LL44-590 I.S. 1122/7302, Griffin & George Ltd., Wembley, Middlesex, UK.
[4] W.P. Brennan, B. Miller, J.C. Whitewell, J. Appl. Polym. Sci. 21 (1968) 1800.
[5] J. Chiu, P.G. Fair, Thermochim. Acta 34 (1979) 267.
[6] Y.P. Khanna, T.J. Taylor, G. Chomyn, Polym. Eng. Sci. 28 (1988) 1034.
[7] G. Hakvoort, L.L. van Reijen, Thermochim. Acta 93 (1985) 317.
[8] J.H. Flynn, D.M. Levin, Thermochim. Acta 126 (1988) 93.
[9] S.M. Marcus, R.L. Blaine, Thermochim. Acta 243 (1994) 231.
[10] ISO 8301 (heat flow meter), ISO 8302 (guarded hot plate).
[11] D.E. Kline, J. Polym. Sci. 50 (1961) 441.
[12] R. Ścigała, A. Włochowicz, Acta. Polym. 40 (1989) 15.
[13] Y.P. Khanna, J. Appl. Polym. Sci. 37 (1989) 2719.
[14] S.F. Lau, H. Suzuki, B. Wunderlich, J. Polym. Sci: Polym. Phys. Ed. 22 (1984) 379.
[15] H.W. Starkweather Jr., P. Zoller, G.A. Jones, A.J. Vega, J. Polym. Sci: Polym. Phys. Ed. 20 (1982) 751.
[16] K.-L. Hsu, D.E. Kline, J.N. Tomlinson, J. Appl. Polym. Sci. 9 (1965) 3567.
[17] M. Hattori, Kol-Z 185 (1962) 27.
[18] K. Eiermann, K.H. Hellwage, J. Polym. Sci. 57 (1962) 99.
[19] T. Ozawa, K. Kanari, Polym. Lett. 5 (1967) 767.
[20] W. Resse, J. Macromol. Sci. Chem. 3 (1969) 1257.