

## THERMAL CONDUCTIVITY OF PTFE AND PTFE COMPOSITES

Duncan M. Price

IPTME, Loughborough University, Loughborough, Leics. LE11 3TU, UK  
d.m.price@lboro.ac.uk

Mark Jarratt

Department of Physics, University of 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.

### INTRODUCTION

Polytetrafluoroethylene (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 outstanding 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 fabric and frying pans.

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.

### EXPERIMENTAL

#### Materials

Samples of PTFE and polymethylmethacrylate 3 mm thick sheet were supplied by ICI (UK). PTFE/glass fiber mats (some with added aluminum

powder) were obtained from Fothergill Tygaflor (UK). Thermogravimetry showed that the PTFE/glass fiber mats contained 60% by weight PTFE.

### Lee's 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 (2). This method, in its classical form, utilizes 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. A diagram of the apparatus is shown in figure 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 6W 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 discs 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 minute intervals and, as equilibrium was reached, readings were taken every 10-15 minutes. 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 apparatus had been stable to within  $\pm 0.1^\circ\text{C}$  for 30 minutes, a value for the thermal conductivity of the specimen ( $\lambda$ ) of thickness  $d$  and radius  $r$  was calculated from the following:

$$I = \frac{ed}{2\rho^2(T_B - T_A)} \left[ a_S \frac{T_A + T_B}{2} + 2a_A T_A \right] \quad (1)$$

where  $e$  is given by:

$$e = VI \left[ a_A T_A + a_S \frac{T_A + T_B}{2} + a_H \frac{T_B + T_C}{2} + a_B T_B + a_C T_C \right] \quad (2)$$

$a_A$ ,  $a_B$ ,  $a_C$ ,  $a_S$  and  $a_H$  are the exposed surface areas of **A**, **B**, **C** and the specimen and heater respectively. Areas  $a_A$  and  $a_C$  include the flat ends of the discs.  $T_A$ ,  $T_B$  and  $T_C$  are the temperatures of the discs **A**, **B** and **C** above ambient (ie. the true temperature of the disc minus the ambient temperature).  $V$  is the potential difference across the heater and  $I$  is the current which flows through it. The full derivation of Eq. (1) and (2) gave be found in the manual which accompanies the apparatus (3).

From the above it can be seen that working out  $\lambda$  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 six to two hours.

### 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 Reijnen 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; by applying a pure metal, placed 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 ( $\lambda$ ), thickness  $h$  and cross-sectional area  $A$  is given by:

$$I = \frac{h}{A} \cdot \frac{\Delta H_f(lit.)}{\Delta H_f(meas.)} \cdot S_{onset} \quad (3)$$

Where  $\Delta H_f(lit.)$  is the literature value for the heat of fusion of the metal,  $\Delta H_f(meas.)$  the measured value for the heat of fusion of the metal and  $S_{onset}$  is the slope of  $dH/dt$  vs.  $T$  for the onset of melting of the standard.

## **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  $\lambda$  for PMMA and PTFE (199 & 259 mW m<sup>-1</sup> °C<sup>-1</sup> respectively) to  $\pm 2.5\%$  in good agreement with the certified values (194 & 264 mW m<sup>-1</sup> °C<sup>-1</sup>) 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 ( $\approx 0.25$  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 may exist which compromise 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 aluminum powder. As one might expect, addition of a highly conductive metal filler improves heat transport through the film (11).

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 reduction in voids brought about by better contact of the polymer with the glass. In order to check 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 check the performance of the Lee's disk apparatus).

The crystallinity of bulk PTFE was measured by several different methods: X-ray diffraction (XRD (12), density and a DMA technique (13). Only the X-ray diffraction 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) from which the heat of fusion of 100% crystalline polymer can be estimated (48.9 J g<sup>-1</sup>). It should be recognized that this value relates to the specific sample studied, for example, Lau et. al. recommend a value of 80 J g<sup>-1</sup> for crystalline PTFE (14). There are widely varying values for the heat of fusion of PTFE to be found in the literature (15) – our result is simply used to assess the relative crystallinity of samples.

Samples of PTFE sheet of different crystallinity were prepared *in situ* in the DSC by cooling specimens at different rates. The heat of fusion of the sample was measured by re-heating the samples at the 10°C/min. 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 to concerns over the thermal stability of the sample. Prolonged exposure to elevated temperatures during was found to result in reduction of molecular weight of the specimen (from inspection of the crystallization exotherm) and yielded little improvement in 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°C) was used to determine the temperature gradient across the specimens and therefore the data to  $\lambda$  at this temperature. Whilst the data appears to fit a linear trend of increasing thermal conductivity with crystallinity 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  $\lambda$  with crystallinity whereas others detect an increase or decrease in this parameter with crystallinity. Kline (11) and Reese (20) discuss in detail the effect of crystallinity on  $\lambda$  for polymers, whereby changes in temperature can result a decrease or no change in this parameter with crystallinity. Our observation has, however, particular relevance to the use of PTFE/glass mats in its end-use application for food processing where the substrate is likely to near to 200°C.

## 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 and P. Parker; *Advanced Level Physics* (3<sup>rd</sup> 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 and J.C. Whitewell; *J. Appl. Polym. Sci.* **1968** 21 1800-1802.
5. J. Chiu and P.G. Fair; *Thermochim. Acta* **1979** 34 267-273.
6. Y. P. Khanna, T.J. Taylor and G. Chomyn; *Polym. Eng. Sci.* **1988** 28(16) 1034-1041.
7. G. Hakvoort and L.L. van Reijen; *Thermochim. Acta* **1985** 93 317-320.
8. J.H. Flynn and D.M. Levin; *Thermochim. Acta* **1988** 126 93-100.
9. S.M. Marcus and R.L. Blaine; *Thermochim. Acta* **1994** 243 231-239.
10. ISO 8301 (heat flow meter), ISO 8302 (guarded hot plate).
11. D.E. Kline; *J. Polym. Sci.* **1961** 50 441-450.
12. R. Scigala and A. Wlochowicz; *Acta. Polym.* **1989** 40(1) 15-19.
13. Y.P. Khanna; *J. Appl. Polym. Sci.* **1989** 37(9) 2719-2726.
14. S.F. Lau, H. Suzuki and B. Wunderlich; *J. Polym. Sci.: Polym. Phys. Ed.* **1984** 22 379-405.
15. H.W. Starkweather Jr., P. Zoller, G.A. Jones and A.J. Vega; *J. Polym. Sci.: Polym. Phys. Ed.* **1982** 20 751-761.
16. K-L Hsu, D.E. Kline and J.N. Tomlinson; *J. Appl. Polym. Sci.* **1965** 9 3567-3574.
17. M. Hattori; *Kol-Z* **1962** 185(1) 27-31.
18. K. Eiermann and K.H. Hellwage; *J. Polym. Sci.* **1962** 57 99-106.

19. T. Ozawa and K. Kanari; *Polym. Lett.* **1967** 5 767-770.  
 20. W. Resse; *J. Macromol. Sci.-Chem.* **1969** 3(7) 1257-1295.

Table 1. Thermal conductivity of PTFE and composites

Sample	$\lambda$ (mW m <sup>-1</sup> °C <sup>-1</sup> ) @ 50°C
Bulk PTFE	259±6
Unsintered PTFE/glass	198±5
Sintered PTFE/glass	222±6
Sintered PTFE/glass + 5% Al	244±6
Sintered PTFE/glass + 10% Al	267±7
Sintered PTFE/glass + 15% Al	262±7
Sintered PTFE/glass + 30% Al	271±7

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

Cooling rate (°C min <sup>-1</sup> )	$DH_f$ (J g <sup>-1</sup> )	Crystallinity (%)	$\lambda$ (mW m <sup>-1</sup> °C <sup>-1</sup> ) @ 232°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

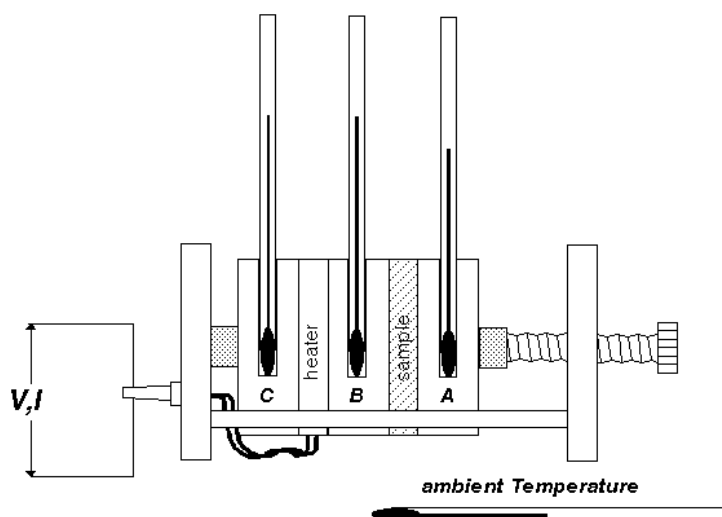


Figure 1. Lees' Disk Apparatus (schematic)