# Thermal conductivity of Tecamax® SRP from millikelvin temperatures to room temperature

Adam L. Woodcraft*,[1,2] Valentina Martelli,[3,4] and Guglielmo Ventura[3,5]

[1]*SUPA, Institute for Astronomy, University of Edinburgh, Blackford Hill, Edinburgh EH9 3HJ, UK*
[2]*UK Astronomy Technology Centre, Blackford Hill, Edinburgh EH9 3HJ, UK*
[3]*INFN, Section of Florence, Via G. Sansone 1, 50019 Sesto Fiorentino, Florence, Italy*
[4]*LENS, University of Florence, Via Nello Carrara 1, 50019 Sesto Fiorentino, Italy*
[5]*Department of Physics, University of Florence, Via G. Sansone 1, 50019 Sesto Fiorentino, Florence, Italy*
(Dated: November 17th, 2009)

Tecamax® SRP (self-reinforced polyphenylene) is a new commercially available amorphous polymer which is suitable for use at cryogenic temperatures. It has a high tensile strength (210 MPa at room temperature), resulting from the molecular structure of the polymer rather than by the addition of reinforcing materials. We have measured the thermal conductivity between 60 mK and 280 K. We find that the conductivity below 10 K is similar to, but lower than, most amorphous materials, and the material offers a good combination of low conductivity at low temperatures and high tensile strength. Our results suggest that the material may in fact have a small crystalline component, which may be a partial explanation for the low conductivity. Above 10 K, the temperature dependence of the conductivity is different from most amorphous materials. We are unaware of previous measurements of the thermal conductivity of this material, even at room temperature.
**Keywords:** Structural materials (A), Thermal conductivity (C), Instrumentation (D)

## 1 Introduction

In recent years, various new polymers have become commercially available, some of which are sold as being suitable for use at cryogenic temperatures. However, information from the manufacturers is generally limited to properties at room temperature, making it difficult to decide if they will be useful for a particular cryogenic application. One such material is Tecamax® SRP. This is a high tensile strength (210 MPa [1]) polymer manufactured by Ensinger[1] by extruding PrimoSpire® PR-120. PrimoSpire is an amorphous thermoplastic (self-reinforced polyphenylene, SRP) produced by Solvay[2]. High strength is obtained by a rigid-rod molecular structure, rather than by the addition of reinforcing materials such as carbon fibres, and it is claimed to be the world's stiffest and strongest unreinforced plastic [2]. Unlike many high strength polymers, it is relatively inexpensive. Other desirable properties include good mechanical performance at cryogenic temperatures.

While the high strength and good cryogenic performance suggest that this material should be useful for thermally isolating supports in cryostats, a knowledge of the thermal conductivity is required for most applications. We are not aware of previous thermal conductivity measurements on this material at *any* temperature; the section on (room temperature) thermal conductivity in the manufacturer's datasheet [1] is blank. We carried out measurements over the entire temperature range from 60 mK to 280 K.

*E-mail: adam.woodcraft@physics.org. Tel.: +44-870-765-1873; Fax: + 44-870-879-7873

[1] Ensinger Ltd., Pontyclun, Mid Glamorgan, United Kingdom

[2] Solvay Advanced Polymers, Alpharetta, GA 30005, USA

## 2 Experimental technique and measurements

The thermal conductivity was measured over the temperature ranges below and above 5 K in different cryostats, using samples with geometry optimised for the conductivity in each temperature range. In both cases, the thermal conductivity was measured along the extrusion direction. (While SRP is isotropic, the extrusion process is likely to introduce some anisotropy [3].) The same sample was used for all measurements, being cut down in size to change the geometry as required.

The experimental arrangements are shown in Fig. 1. The thermal contact at each end of the samples was made by a copper cup which was a tight fit around the sample at room temperature, and by a 4 mm copper screw which was screwed into the sample. We do not know the thermal contraction of Tecamax below room temperature. However, good thermal contact is assured by this scheme. If the Tecamax contracts more than the copper as it is cooled to cryogenic temperatures it will contract around the screw; if it contracts less, the cup will contract around the sample.

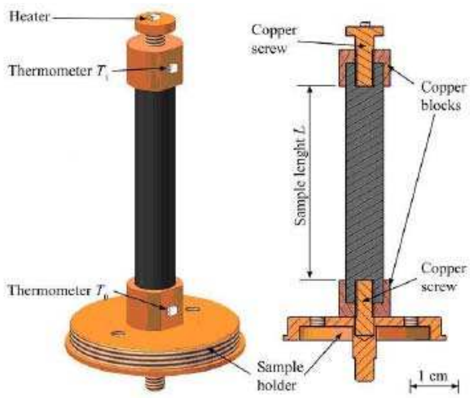


Figure 1: Set up for the measurements of the samples.

| Temperature (K) | Conductivity ($Wm^{-1}K^{-1}$) |
|---|---|
| 0.057 | $5.30 \times 10^5$ |
| 0.070 | $7.64 \times 10^5$ |
| 0.080 | 0.000100 |
| 0.100 | 0.000151 |
| 0.125 | 0.000230 |
| 0.150 | 0.000338 |
| 0.200 | 0.000576 |
| 0.250 | 0.000883 |
| 0.300 | 0.00123 |
| 0.400 | 0.00199 |
| 0.500 | 0.00280 |
| 0.600 | 0.00368 |
| 0.800 | 0.00520 |
| 1.00 | 0.00674 |
| 1.25 | 0.00838 |
| 1.50 | 0.0100 |
| 2.00 | 0.0115 |
| 2.50 | 0.0129 |
| 3.00 | 0.0138 |
| 3.50 | 0.0145 |
| 4.00 | 0.0154 |
| 5.00 | 0.0169 |
| 6.00 | 0.0185 |
| 7.00 | 0.0200 |
| 8.00 | 0.0225 |
| 9.00 | 0.0252 |
| 10.0 | 0.0288 |
| 11.0 | 0.0343 |
| 12.0 | 0.0391 |
| 13.0 | 0.0466 |
| 14.0 | 0.0579 |
| 16.0 | 0.0750 |
| 18.0 | 0.0834 |
| 20.0 | 0.0880 |
| 25.0 | 0.0961 |
| 30.0 | 0.101 |
| 40.0 | 0.111 |
| 50.0 | 0.116 |
| 60.0 | 0.125 |
| 70.0 | 0.135 |
| 80.0 | 0.145 |
| 90.0 | 0.155 |
| 100 | 0.166 |
| 125 | 0.198 |
| 150 | 0.236 |
| 175 | 0.276 |
| 200 | 0.327 |
| 250 | 0.431 |
| 282 | 0.492 |

Table I: Measured conductivity of Tecamax (the measured values are interpolated to a set of temperatures at fixed intervals).

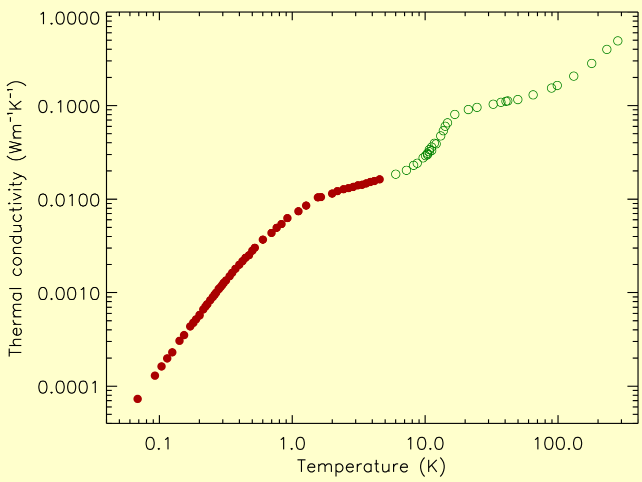


Figure 2: The measured thermal conductivity of Tecamax, in the low (•) and high (○) temperature ranges.

SMD (surface mount device) NiCr heaters were used to heat both samples. Each sample had a thermometer mounted at both ends. The high temperature sample used Cernox thermometers, while the low temperature sample used Cernox thermometers for temperatures above 2 K and $RuO_2$ thermometers for lower temperatures. The heaters and thermometers were mounted on the copper blocks. The electrical connections to the heaters and to the thermometers were made with 25 µm NbTi wires for the low temperature sample and 50 µm manganin wires for the high temperature sample.

The thermometers on the low temperature sample were calibrated by means of an SRD 1000 (Superconductive Reference Device) and a NBS SRM 767a fixed point device [4–6]. The thermometers on the high temperature sample were calibrated using a commercial secondary calibrated thermometer, with an expected accuracy of 1%. This was checked at the following temperatures (boiling points were corrected for pressure dependance):

- 4.2 K: Helium boiling point
- 9.21 K: Niobium transition in the SRM 767a fixed point device
- 77.35 K: Nitrogen boiling point
- 273.16 K: Triple point of a water cell

All thermometers were measured with an AVS 47 AC resistance bridge.

The low temperature sample was a cylinder with effective length (i.e. the length over which the temperature gradient is measured) $L = (41.85 \pm 0.05)$ mm, radius $r = (4.1 \pm 0.01)$ mm and geometrical factor $g = A/L = (1.26 \pm 0.02)$ mm (where $A$ is the area of the sample). The high temperature sample was a cylinder with effective length $L = 5.75 \pm 0.03$ mm and radius $r = 4.00 \pm 0.01$ mm, giving a geometrical factor $g = 8.74 \pm 0.09$ mm.

### 2.1 Low temperature measurements

For the measurements below 5 K, the copper block at the bottom of the sample was screwed onto a copper sample holder in thermal contact with the mixing chamber of a conventional liquid helium cooled dilution refrigerator. A copper shield, in thermal contact with the mixing chamber of the dilution refrigerator, surrounded the experiment. Power for the heaters was supplied with a four wire I - V source meter (Keithley 2601). The NbTi wires leading to the heaters and thermometers were electrically connected by tiny crimped Cu tubes. At the ends of the NbTi wires a four lead connection was adopted.

The thermal conductivity was measured by the longitudinal steady heat flow method. A known power $P$ was supplied to one end of the sample to establish a difference of temperature $T_1 - T_0$ along the sample. The thermal conductivity, $\kappa(T)$ was obtained by differentiation of the integrated power (at constant

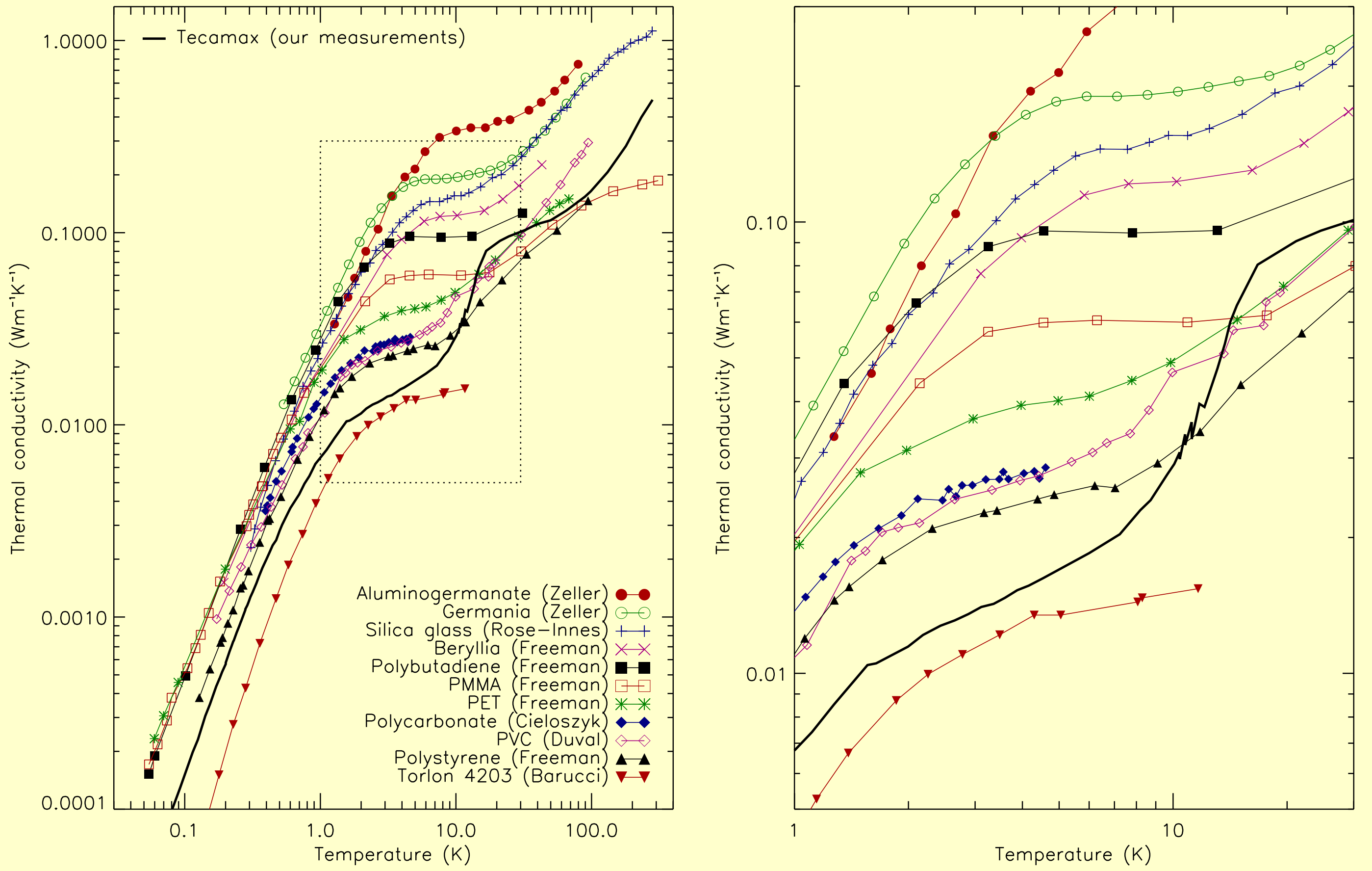


Figure 3: Measured results for Tecamax (solid line), compared with other amorphous materials: aluminogermanate glass (•) [7], germania (○) [7], silica glass (+) [8], beryllia (×) [9], polybutadiene (■) [9], PMMA (□) [9], PET (∗) [9], polycarbonate (♦) [10], PVC (◇) [11], polystyrene (▲) [9] and Torlon 4203 (▼) [12, 13]; to avoid obscuring other datapoints, the conductivity of Torlon is only shown up to 13 K. The right hand graph shows the section of the left hand graph enclosed by a dotted line. The conductivity of most amorphous materials does not change significantly from sample to sample, and therefore the single measurements shown here can be taken to be representative of each material.

$T_0$),

$$P(T_1) = \frac{A}{L}\int_{T_0}^{T_1} \kappa(T)dT, \tag{1}$$

where $A$ and $L$ are the sample section and length respectively.

To check that the contact thermal resistances could be neglected, a second measurement was carried out with a different geometrical factor (approximately twice that of the initial sample). Within the experimental error, the same values of thermal conductivity were obtained in the overlapping temperature range.

There are three main contributions to the relative error in $k(T)$:

– the power supplied to the sample: we estimate that the relative error of $P$ is of the order of $\sim 0.1\%$;
– the measurement of the geometrical factor $g = A/L$. The error in the measurements of $g$ is estimated to be less than 1%;
– the uncertainty in the temperature, $dT$, due to the accuracy of the thermometers in this temperature range. A conservative value of $(dT)/T$ is $\sim 2\%$ for $T > 1K$ and $\sim 1\%$ for $T < 1K$.

Taking into account these contributions, the maximum relative error in $k(T)$ is about 3%.

## 2.2 High temperature measurements

The measurements above 5 K were made in a cryostat based around a pulse tube cooler. The pressure in the vacuum vessel was maintained at about $10^{-4}$ Pa. As with the low temperature range, the thermal conductivity was measured by a steady state technique. However, instead of mounting the sample directly onto the cold head of the cooler, it was mounted on a copper platform whose temperature could be controlled by a heater. All copper components were gold plated to reduce emissivity, and thus blackbody radiation.

A cylindrical thermal shield (length 22 mm, inner diameter 12 mm and thickness 1.5 mm) closely fitted the sample, and was itself enclosed by an outer shield. Both shields were constructed from gold plated copper, and were maintained at the same temperature as the cold end of the sample.

For a range of platform temperatures, power ($P$) was supplied to the sample heater to create a temperature gradient $\Delta T$ along the sample of approximately 2% of the sample temperature. The thermal conductance at a temperature $T$ was evaluated from

$$\kappa(T) = \frac{P}{g\Delta T}, \tag{2}$$

with the temperature $T$ taken as the mean temperature of the sample.

Calculating the error budget in this temperature range is more

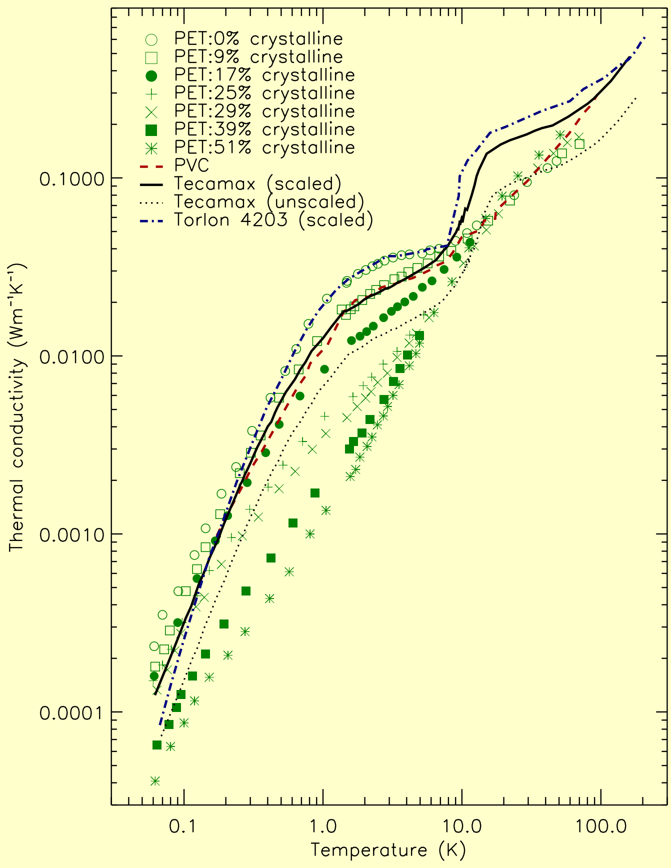


Figure 4: The thermal conductivity of PET of varying degrees of crystallinity (as shown in the key) [14, 15] and PVC of 12% crystallinity (dashed line) [11]. Our measurements on Tecamax are superimposed, both unscaled (dotted line) and with the temperature and conductivity scaled by the appropriate factors to bring them into agreement with the PET 9% crystalline results below approximately 10 K (solid line). The conductivity of Torlon 4203 [12, 13] is also shown, scaled in a similar manner (dot dashed line). Since the graph is plotted with logarithmic axes, this scaling corresponds to displacing the curve along the two axes.

involved than at lower temperatures since the effects of thermal radiation must be taken into consideration. The calculation is the same as for previous measurements [13] on Torlon over a similar temperature range, in which very good agreement was found between the measured room temperature conductivity and the value supplied by the manufacturer. Rather than repeating the details here, we refer the reader to our previous paper (sections 3.2 and 3.4 in Ref. [13]), in which we calculate that the maximum relative error in conductivity, considering all error sources, is 5%.

## 3 Results and discussion

The measured conductivity is shown in Fig. 2 and Table I. The measurements made in the two temperature ranges appear to be in good agreement. We compare our results with the thermal conductivity of other amorphous materials in Fig. 3. It has been well established for a number of years that the thermal conductivity $\kappa$ of totally amorphous solids exhibits a "universal" behaviour at low temperatures. At temperature $T < 1$ K, a temperature dependence of $\kappa \propto T^n$ is seen, with $n$ ranging from 1.8 to 2, for reasons that are not fully understood [9]. The conductivity in this region shows very small variation between materials. Above 1 K, $\kappa$ shows a decreasing slope, with a "plateau" usually located somewhere between 2 and 30 K in which the conductivity is approximately constant. Here, the variation between materials is much larger.

Our measurements show similar behaviour to other amorphous materials, with the existence of a plateau supported by measurements in both temperature ranges. The conductivity below 1 K is similar to, but lower than, most amorphous materials, and below 300 mK can be represented by $\kappa(T) = (12.6 \pm 0.2)10^{-3}T^{(1.92\pm0.01)}$, where $\kappa$ is conductivity (in $\mathrm{Wm^{-1}K^{-1}}$) and $T$ is temperature (in K). While various materials have lower conductivities than Tecamax below 1 K, we are only aware of one fully amorphous material, Torlon 4203, with significantly lower conductivity [12] in this temperature range.[3] This is another high strength amorphous polymer which is used at cryogenic temperatures.

The conductivity in the plateau region is lower than any other material we know of except, again, Torlon 4203. Moreover, the conductivity rises noticeably in the plateau. Such a conductivity rise seems to be associated with the presence of a crystalline component in other amorphous materials. The behaviour of such semi-crystalline polymers has been demonstrated clearly in a set of measurements on PET (polyethylene terephthalate) [14, 15], which unlike most polymers can be prepared with a large range of crystallinities. These results are shown in Fig. 4, along with the PVC measurements from Fig. 3. Our Tecamax results are also shown, scaled in both temperature and conductivity to give the best agreement with the PET results in and below the plateau. Such scaling has been shown to be valid for fully amorphous materials [9], though the reasoning does not necessarily apply to semi-crystalline materials. The Tecamax results are similar to both the 9% crystalline PET sample, and the 12% crystalline PVC sample. Tecamax is described by the manufacturer as fully amorphous. From our measurements, we cannot definitely state that this is not true. However, the results could be explained by some degree of crystallinity. We also show the conductivity of Torlon 4203, scaled as with the Tecamax results. Here, there is very good agreement with the fully amorphous PET sample, suggesting that the Torlon is also fully amorphous.

It is clear from Figs. 3 and 4 that the conductivity of Tecamax and Torlon 4203 above 10 K does *not* follow the normal pattern for amorphous materials, with the results suggesting a second plateau above 10 K. We are not aware of any other materials exhibiting this behaviour. Since the Torlon measurements were also made by us, the reader may be concerned that this unusual behaviour is actually an experimental error. We believe that this is not the case for the following reasons. Firstly, the Torlon measurements above 4.2 K were made in a different cryostat to the Tecamax measurements, using a different thermometer type (carbon instead of Cernox). Moreover, they were calibrated against a different standard thermometer. Finally, we have made measurements on other materials with similar con-

[3] Somewhat lower values are reported for various amorphous materials in Ref. [18]. However, they are derived indirectly from measurements across joints incorporating these materials, and thus may suffer from considerable systematic error.

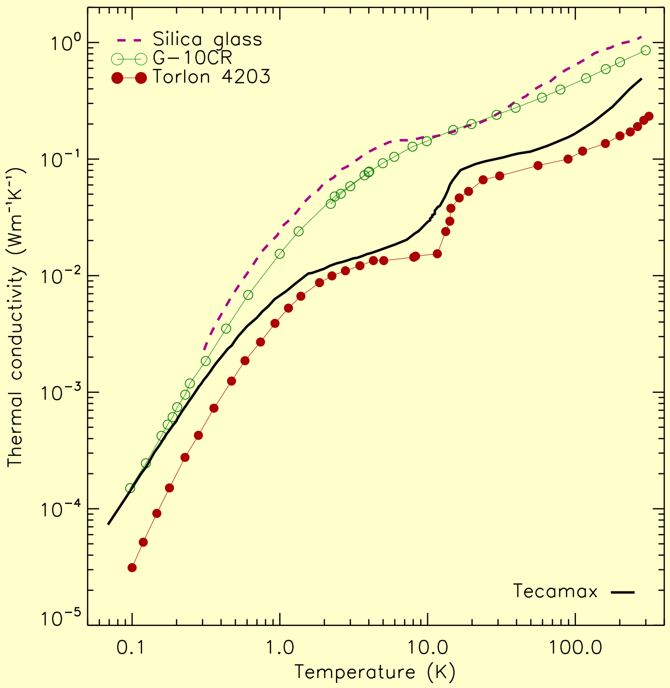


Figure 5: Measured results on Tecamax (solid line), compared with the conductivity of Torlon 4203 (•) [12, 13] and G-10CR (○) [16, 17]. The conductivity of silica glass from Fig. 3 is also shown (dashed line).

ductivity which did not show this second plateau. We cannot suggest a physical explanation for this behaviour, but note that it may be a property of high strength polymers. It is also interesting, but possibly not significant, that at the highest temperatures the scaled conductivity of both Tecamax and Torlon 4203 appear to be in good agreement with each other, and with an extrapolation of the conductivity of PVC.

In Fig. 5, the (unscaled) conductivity of Tecamax and Torlon 4203 is shown and compared with G-10CR, as an example of a polymer which obtains high tensile strength (around 430 MPa) by fibre reinforcement. While the conductivity is similar at the lowest temperatures, Tecamax and Torlon 4203 are much better insulators at higher temperatures.

At room temperature (280 K), we find a conductivity of 0.49 $\mathrm{Wm^{-1}K^{-1}}$ for Tecamax. To our knowledge, this is the first measurement of the conductivity of this material at room temperature.

## 4 Conclusions

We find that the thermal conductivity of Tecamax below 10 K is similar to most other amorphous materials. The conductivity is proportional to $T^{1.9}$ below 300 mK; above this the variation of conductivity with temperature becomes shallower, leading to a plateau. However, the conductivity is lower than most other amorphous materials, especially in the 1 – 10 K temperature range. It therefore offers a good combination of low conductivity at low temperatures and high tensile strength. The conductivity in the plateau has a significant temperature dependence, suggesting that the material may in fact have a small crystalline component; this may be a partial explanation for the low conductivity.

Above 10 K, the conductivity shows unusual behaviour, with a second plateau being apparent. The only other material we are aware of that shows this behaviour is Torlon 4203, another high strength amorphous polymer. We are unaware of previous measurements of the thermal conductivity of Tecamax, even at room temperature.


## Acknowledgements

We would like to thank Adam Gray for help in compiling the properties of materials used for comparison.



[1] "Product Information: Tecamax SRP - extreme strength without fibre reinforcement", Ensinger Ltd., Pontyclun, Mid Glamorgan, United Kingdom

[2] "More remarkable PrimoSpire™ self-reinforced polyphenylene", Solvay Advanced Polymers, LLC, Alpharetta, Georgia USA

[3] Choy CL, Greig D. The low temperature thermal conductivity of isotropic and oriented polymers. Journal of Physics C: Solid State Physics 1977;10:169.

[4] Bosch, WA et al., Status Report on the Development of a Superconductive Reference Device for Precision Thermometry below 1 K, in Proceedings of the 8th International Symposium on Temperature and Thermal Measurements in Industry and Science TEMPMEKO 2001, VDE Verlag, Berlin 2001, 397-401

[5] Schottl S et al., Evaluation of SRD1000 Superconductive Reference Devices, J. Low Temp. Phys. 2005;138(3-4):941-946

[6] Schooley JF, Soulen Jr. RJ, Evans Jr. GA. Preparation and Use of Superconductive Fixed Point Devices, SRM 767, NBS Special Publication 260-44, Washington, DC, National Bureau of Standards 1972;1-35

[7] Zeller RC, Pohl RO. Thermal conductivity and specific heat of noncrystalline solids. Phys. Rev. B 1971;4:2029.

[8] Rose-Innes AC. Low temperature laboratory techniques. English Universities Press, 1973.

[9] Freeman JJ, Anderson AC. Thermal conductivity of amorphous solids. Phys. Rev. B 1986;34:5684.

[10] Cieloszyk GS, Cruz MT, Salinger GL. Thermal properties of dielectric solids below 4 K. I. Polycarbonate. Cryogenics 1973; 13:718.

[11] E Duval TA, Boukenter A, Varrel B, et al. Low-energy excitations in polyvinyl chloride: Raman scattering and thermal properties. Journal of Non-Crystalline Solids 1995;190:258.

[12] Ventura G, Bianchini G, Gottardi E, et al Thermal expansion and thermal conductivity of Torlon at low temperatures Cryogenics 1999;39:481.

[13] Barucci M, Olivieri E, Pasca E, et al. Thermal conductivity of Torlon between 4.2 and 300 K. Cryogenics 2005;45:295.

[14] Greig D, Sahota MS. The thermal conductivity of an amorphous material below 1 K - variation with degree of crystallinity. Journal of Physics C: Solid State Physics 1983;16:L1051.

[15] Greig D. Low temperature thermal conductivity of polymers. Cryogenics 1988;28:243.

[16] Walker FJ, Anderson AC. Thermal conductivity and specific heat of a glass-epoxy composite at temperatures below 4 K. Review of Scientific Instruments 1981;52:471.

[17] Fickett FR, Reed RP, Dalder ENC. Structures, insulators and conductors for large superconducting magnets. Journal of Nuclear Materials 1979;85 & 86:353.

[18] Anderson AC, Peterson RE. Selection of a thermal bonding agent for temperatures below 1K. Cryogenics 1970;10:430.