

Thermal conductivity of extruded polyethylene

D. Greig and M. Sahota

Department of Physics, University of Leeds, Leeds LS2 9JT, UK

(Received 31 October 1977)

The thermal conductivity of extruded polyethylene has been measured between 220 and 360K by a direct comparative method. For the material with the highest extrusion ratio the conductivity parallel to the extrusion direction, κ_{\parallel} , is 72 mW/cm K at room temperature and more or less constant over the complete temperature range. Between the same temperatures the conductivity perpendicular to the extrusion direction decreases with increasing T by about 50% with the anisotropy in the most highly extruded sample almost 30 at room temperature. The results on κ_{\parallel} cannot be explained by the Takayanagi model used in our earlier papers and further modifications to the model are required.

In a recent paper¹ on the low temperature thermal conductivity, κ , of highly extruded polyethylene we have shown that, above about 25K, there is a marked anisotropy in κ with the conductivity parallel to the extrusion direction, κ_{\parallel} , significantly greater than that in the perpendicular direction, κ_{\perp} . Furthermore, although at a given temperature κ_{\perp} is substantially independent of extrusion ratio, λ , κ_{\parallel} increases linearly with λ in all available specimens. For our most highly extruded sample, in which $\lambda \sim 25$, the conductivity ratio, $\kappa_{\parallel}/\kappa_{\perp}$, at 100K was 18.5. It is therefore clear that κ_{\parallel} in such specimens is substantially greater than the usual conductivity of polymers, and is, in fact, rather more akin to that of a concentrated metallic alloy.

Whether or not this phenomenon lends itself to applications must depend on whether this anisotropy is maintained to much higher temperatures. In this paper we therefore report measurements on the same specimens in a temperature range that includes room temperature. Because of the effects of radiation it is much more difficult to measure κ above 100K than at lower temperatures. We have therefore been unable to use the simple 'potentiometric' technique used in our previous papers¹⁻³, but have instead used the comparative sandwich method that is often used at these temperatures. In this, κ is obtained by comparing it with that of a standard material of known thermal conductivity. For this we chose isotropic polyethylene so that the conductivity of the extruded polyethylene can be compared directly with it. The values of κ in the temperature range 220 to 360K for the isotropic polyethylene of density 0.972 g/cm³ were interpolated from published data⁴ and are shown in Figure 1. For each experiment two 'standards' were used in the form of thin discs, each 18 mm diameter by 1 mm thick. Samples of extruded Rigidex 50, details of which are given in our earlier paper¹, were also machined into the form of 18 mm diameter discs, of thickness varying from 1 to 7.5 mm chosen so as to make their thermal resistance roughly equal to that of the 'standards'.

The apparatus used was a modified version of that described by Stuckes and Chasmar⁵. Briefly, the conduction path was formed by a copper rod 7 cm long x 18 mm diameter, cut across its diameter in three places to form a sandwich with the two 'standards' in the outer positions and the specimen under investigation in the middle. This assembly rested

on the base of a copper can, the temperature of which could be controlled to better than 0.1°C. A heater attached to the top of the copper rod generated a uniform heat flow through the sample and standards. The temperature differences across the sample and the two standards were measured using copper/constantan thermocouples soldered into the intervening copper blocks. A good thermal contact between the polyethylene and copper was achieved by exerting pressure onto the heater by using stiff springs. Thermal contact was further improved by using a very small amount of silicone vacuum grease. This combination of pressure and grease ensured a good thermal contact in the temperature range covered. By measuring samples of different thickness, it was found that the contact resistance due to silicone grease can be neglected. The overall advantage of this method is that by noting the temperature across the two standards, we can allow for the heat loss by radiation from the specimen.

The results are shown in Figure 1 with values of κ at

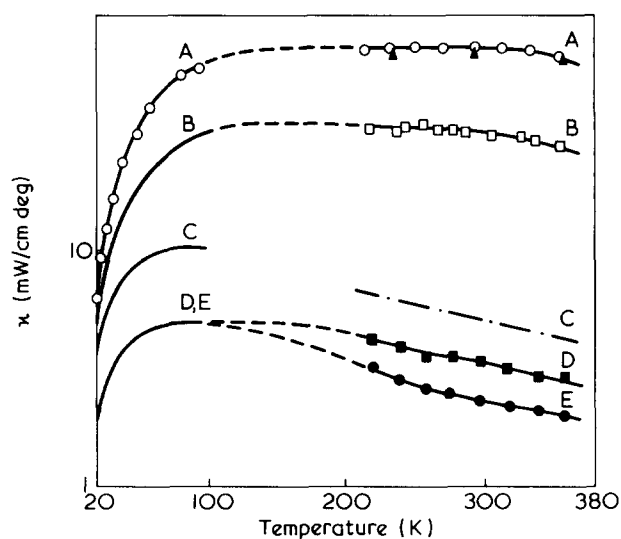


Figure 1 Temperature dependence of thermal conductivity. The various curves and points represent: A, κ_{\parallel} for $\lambda = 18$; B, κ_{\parallel} for $\lambda = 5.4$; D, κ_{\perp} for $\lambda = 5.4$; E, κ_{\perp} for $\lambda = 18$. Curves B, C, D, and E below 100K are from ref 1. (---), C, the 'standard' data, is from Eiermann⁴

Table 1 Experimental thermal conductivity of extruded polyethylene at selected temperatures (mW/cmK)

T(K)	5.4:1		18:1	
	κ_{\parallel}	κ_{\perp}	κ_{\parallel}	κ_{\perp}
220	34	4.3	70	3.1
240	34	4.0	71	2.9
260	33	3.8	72	2.7
280	33	3.6	72	2.5
300	32	3.4	72	2.4
320	31	3.2	71	2.3
340	29	3.1	69	2.2
360	28	2.9	66	2.0

selected temperatures given in Table 1. We note that measurements of κ_{\parallel} on two samples of different thicknesses of material with an extrusion ratio 18:1 are in agreement with each other to better than 5%. For measurements perpendicular to the extrusion direction data from two specimens agree to better than 1% and the points have not been shown separately. It can also be seen in Figure 1 that the measured curves extrapolate to the results obtained below 100K, most of which, apart from some new data on the specimen of highest extrusion ratio, were taken from our earlier paper¹.

The most important feature of the results is that the very marked anisotropy in κ found at liquid nitrogen temperatures is sustained over the complete range of measurements. Indeed, since, for the specimens of greatest extrusion ratio, λ , κ_{\perp} falls with increasing T while κ_{\parallel} is more or less constant, the anisotropy ratio $\kappa_{\parallel}/\kappa_{\perp}$ increases from 12 at 100K to 30 at room temperature. The other, more minor, feature is that κ_{\perp} is no longer independent of λ .

In our earlier papers^{3,6} we have established that the anisotropy of conductivity on extrusion is due, at low extrusion ratios, to the alignment of the molecular chain axes in crystalline regions. For higher extrusion ratios, on the other hand, this mechanism alone is insufficient to account for the continuing increase in κ_{\parallel} with λ , and it is necessary to postulate the development of bridges of high conductivity in the intercrystalline (amorphous) regions¹. Such behaviour is also reflected in the mechanical properties of polyethylene and we have used a modified Takayanagi model to explain this correlation and to make numerical estimates of $\kappa_{C\parallel}$, the crystalline conductivity parallel to the extrusion direction. In this very schematic model we have described the highly extruded polymer as an intercrystalline fraction, a , in series with the remaining crystalline fraction $(1 - a)$, with the intercrystalline region containing a small parallel volume fraction, b , of intercrystalline bridges. If these bridges have the same high conductivity, $\kappa_{C\parallel}$, as the bulk crystalline phase, then very approximately:

$$\kappa_{\parallel} \approx \frac{b}{a} \kappa_{C\parallel} \quad (1)$$

(see equation 2 of ref 1). As a is essentially independent of extrusion ratio, λ , our result was that the continuing increase in κ_{\parallel} with λ is simply a reflection of an increase in b , the number of intercrystalline bridges.

However, the present results indicate that this argument must be incomplete. Around room temperature the thermal conductivity of a crystalline solid is determined either by point defect scattering or by phonon-phonon U -processes,

both of which give a conductivity that falls as T rises. From Figure 1 we see that for the specimen of greatest extrusion ratio κ_{\parallel} is more or less independent of T and only begins to decrease slightly at much higher temperatures. This behaviour is a characteristic of amorphous polymers, for example, PMMA⁷, although the magnitude of their conductivities around 300K is only a few mW/cm K. For the present measurements of κ_{\parallel} it is therefore necessary to invoke the importance of crystalline conduction to explain the magnitude of the results, but the temperature dependence is such that the amorphous fraction must also play a dominant role. It is clear that such a combination of properties cannot be explained by equation (1). The problem can be resolved by proposing that the $\kappa_{C\parallel}$ used in equation (1) is not the same as in the bulk material. If schematically we consider that the intercrystalline bridge fraction is not continuous but contains a small fraction, x , of amorphous material of conductivity κ_A , then, on the assumption that $\kappa_{C\parallel} \gg \kappa_A$, $\kappa_{C\parallel}$ in equation (1) is replaced by κ_A/x and:

$$\kappa_{\parallel} \approx \frac{b}{ax} \kappa_A \quad (2)$$

In this way κ_A becomes the dominant conductivity and the temperature dependence of κ_{\parallel} follows that of amorphous material. As $a \sim 0.25$ (ref 1), the correct magnitude of κ_{\parallel} at 100K is obtained for the specimen of highest λ if $b/x \sim 13$. We note that although in the modified Takayanagi model (equation 1) it was necessary to keep $b < 0.1$ in order that κ_{\parallel} remains appreciably less than $\kappa_{C\parallel}$, this restriction is no longer necessary. The value of b can now be of the same order as a , and κ_{\parallel} is largely determined by the value of x .

We should also add that Davies, Gibson and Ward⁸ have recently re-examined results on the elastic properties of extruded polyethylene in the light of new X-ray data and have also shown the inadequacy of the modified Takayanagi model. They have adopted a statistical model of intercrystalline bridges to explain the mechanical behaviour. It is important to note that the present schematic model for thermal conductivity and their model for mechanical behaviour are consistent, although the controlling factors determining the high temperature behaviour are different for the two properties. Whereas the amorphous regions make a negligible contribution to the stiffness of these highly oriented polymers at high temperatures, the present results show that the behaviour of the amorphous regions determines the overall thermal conductivity of the material.

Finally we should comment again on the observation that the curves for κ_{\perp} separate above about 100K. In our earlier papers^{1,3} we have argued that the curves for κ_{\parallel} diverge at about 25K when, with increasing T , the wavelength of the dominant phonons becomes smaller than the structure. An equivalent explanation for κ_{\perp} would imply that the structure perpendicular to the extrusion direction is about 1/4 of the thickness of that in the parallel direction; that is about 50 Å. The fact that κ_{\perp} decreases with increasing λ suggests that, as the extrusion is increased, the structure is becoming more broken up.

ACKNOWLEDGEMENTS

We are most grateful to Professor I. M. Ward and his colleagues, particularly Dr A. G. Gibson and Dr G. R. Davies, for their constructive interest in this work and for supplying all the

specimens used. It is also a pleasure to record our thanks to SRC for their financial support of this project.

REFERENCES

- 1 Gibson, A. G., Greig, D., Sahota, M., Ward, I. M. and Choy, C. L. *J. Polym. Sci. (Polym. Lett. Edn)* 1977, **15**, 183
- 2 Burgess, S. and Greig, D. *J. Phys. (D)* 1974, **7**, 2051
- 3 Choy, C. L. and Greig, D. *J. Phys. (C)* 1977, **10**, 169
- 4 Eiermann, K. *Kolloid. Z. Z. Polym.* 1962, **180**, 163
- 5 Stuckes, A. D. and Chasmar, R. P. 'Report of Meeting on Semiconductors', Physical Society, London, 1956, p 119
- 6 Burgess, S. and Greig, D. *J. Phys. (C)* 1975, **8**, 1637
- 7 Reese, W. *J. Appl. Phys.* 1966, **37**, 3227
- 8 Davies, G. R., Gibson, A. G. and Ward, I. M. to be published