

## 5.1 Introduction

Fibre density plays a direct part in affecting the weight of fabrics, so that glass fabrics, with a fibre density of  $2.56 \text{ g/cm}^3$ , will tend to be heavy, whereas those of polyethylene, with a density of  $0.92 \text{ g/cm}^3$ , will be light. It is also a useful parameter in fibre identification and occurs incidentally in many parts of textile physics.

The definitions are straightforward: density is the mass of unit volume and is usually expressed in grams per cubic centimetre ( $\text{g/cm}^3$ )<sup>1</sup>. For some purposes, it is more convenient to use specific volume, which is the reciprocal of density and is expressed in cubic centimetres per gram ( $\text{cm}^3/\text{g}$ ).

## 5.2 Measurement

The mass of a specimen is easily determined by weighing it on a balance, but the determination of volume involves difficulties of definition and experimental problems. Any mass of fibres, whether disorganised raw material or organised into yarn or fabric, includes a large proportion of air as well as the fibres. Consequently, measurement of its overall volume gives no information on fibre volume. There is an additional complication with hollow fibres.

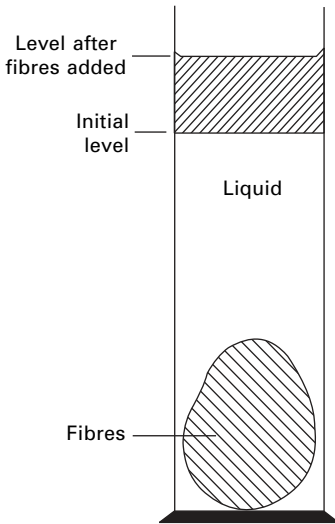
All measurements of volume, or of density directly, therefore depend on immersing the material in a fluid that will displace all the air from around the fibres. The simplest form of this method is shown in Fig. 5.1. The displacement of the level of liquid in a measuring cylinder equals the volume of the added fibres.

Two fundamental sources of error are immediately obvious. Firstly, the liquid may not displace all the air, particularly from crevices in the fibre surface. This means that the measured volume will be too high and the density too low. Secondly, the liquid may be absorbed by the fibres, which results in a smaller displacement of the liquid level. This would give too low a volume and too high a density.

It is now generally accepted that the best values of density are obtained with a large number of organic liquids (such as nitrobenzene, olive oil, toluene, benzene and

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<sup>1</sup>The consistent SI unit is  $\text{kg/m}^3$ ;  $1 \text{ g/cm}^3 = 10^3 \text{ kg/m}^3$  (i.e. 1 tonne per cubic metre).



5.1 Fibre volume by displacement of liquid.

carbon tetrachloride), which give the same results. Hermans [1] has put forward the arguments in favour of this and pointed out that it is extremely unlikely that the same values would be obtained if errors were involved. He has confirmed that these liquids do not penetrate into the fibre material but do envelop the fibre and fill any lumens or other true pores in native fibres. The earlier preference of Davidson [2] for the higher value of density obtained on immersion in helium was rejected, partly because of the evidence in favour of other values, but also because there was some evidence that helium was absorbed by the cellulose.

The experimental method indicated above, although sound in principle, would not be very accurate in practice. Some of the other standard methods, such as the use of a density bottle, or weighing a specimen immersed in a liquid, need a fairly large mass of material, from which it is difficult to exclude air completely. For single fibres, or small bundles of fibres, flotation methods are preferred. For example, Abbott and Goodings [3] found that, if chopped-up fibres were placed in a liquid (or a mixture of liquids) of the same density as the fibres, and then centrifuged in a tube, they remained as a uniform cloud; if the densities were different, they accumulated into a single group, which floated if the fibre density was the lower and sank if it was the greater. By a process of trial and error, the correct density can be found.

A more rapid adaptation of this method is the density gradient tube. This is a long tube containing a heavy liquid (e.g. pentachlorethane,  $1.7 \text{ g/cm}^3$ ) at the bottom, a light liquid (e.g. xylol,  $0.9 \text{ g/cm}^3$ ) at the top, and a continuously varying mixture of the two between them. If fibres are dropped in, they sink to the point at which the fibre density equals the liquid density and remain suspended there. Calibration of the tube may be provided either by means of pieces of different materials of known densities floating at their appropriate levels or by hollow glass spheres of varying mean density. The fibre density can be found by interpolation between the known densities on either side of the position at which the fibres come to rest. Methods of

setting up density gradient tubes and precautions to be adopted in their use are described by Preston and Nimkar [4], Stock and Scofield [5] and Austin and Roberts [6].

De Vries and Weijland [7] have described a method of measuring density by weighing fibres on a cantilever microbalance, first in air and then submerged in a suitable liquid. Neelakantan and Patel [8] have described improvements on the displacement and flotation methods.

### 5.3 Results

Typical values of the densities and specific volumes of fibres used in general textiles, dry and at 65% r.h., are given in Table 5.1. It will be seen that most of these fibres have a density slightly greater than that of water. Table 5.2 gives densities of some high-modulus fibres, used in composites and specialist applications, and Table 5.3 gives densities of some chemically and thermally resistant fibres. Some fibres, such as cotton and to a much greater extent kapok, do contain internal void spaces, which will lower the overall density to a value of about  $1.35 \text{ g/cm}^3$  in cotton.

The density of fibres varies when they absorb water, as is shown in Fig. 5.2. The increase in density on the addition of water, which has a density less than that of the fibres, means that there is a net contraction. The reasons for this are discussed later in connection with the swelling of fibres (see Section 12.1.6).

### 5.4 Density and order

Density measurement is commonly used as a means of estimating the degree of order, or crystallinity, of fibres. The necessary relation was given earlier as equation (1.3):

Table 5.1 Densities of some general-purpose textile fibres [4, 9–11]

Fibre	Density ( $\text{g/cm}^3$ , $\text{Mg/m}^3$ )		Specific volume ( $\text{cm}^3/\text{g}$ )	
	dry	65% r.h.	dry	65% r.h.
Cotton (lumen filled)	1.55	1.52	0.64	0.66
Viscose rayon	1.52	1.49	0.66	0.67
Secondary acetate, triacetate	1.31	1.32	0.76	0.76
Wool	1.30	1.31	0.77	0.76
Silk	1.34	1.34	0.75	0.75
Regenerated protein (casein)	1.30	1.30	0.77	0.77
Alginate		1.75		0.57
Nylon 6.6, nylon 6	1.14	1.14	0.88	0.88
Polyester (PET)	1.39	1.39	0.72	0.72
Acrylic (PAN)	1.19	1.19	0.84	0.84
Polyethylene (high density)	0.95	0.95	1.05	1.05
Polypropylene	0.91	0.91	1.09	1.09
Modacrylic ( <i>Dynel</i> )	1.29	1.29	0.78	0.78
Modacrylic ( <i>Teklan</i> )		1.34		0.75
Polyvinyl chloride (PVC)		1.40		0.71
Polylactic acid (PLA)		1.25		0.80
Glass	2.5	2.5	0.40	0.40

Table 5.2 Densities of some high-modulus fibres [12]

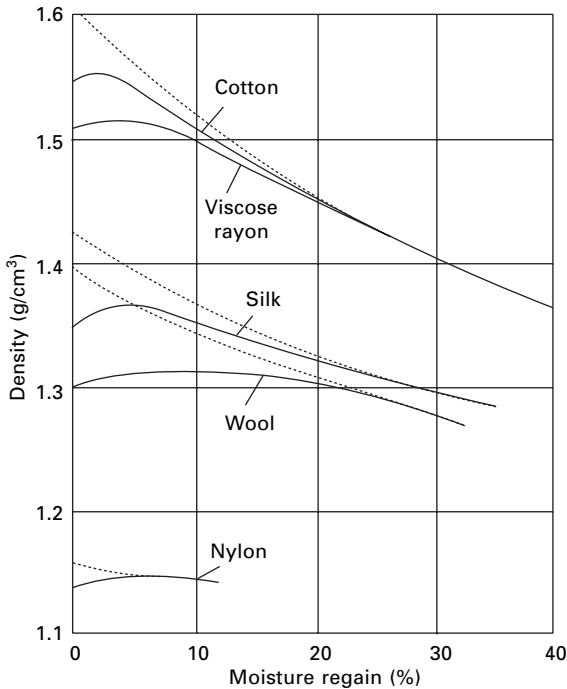
Fibre	Density (g/cm <sup>3</sup> , Mg/m <sup>3</sup> )	Specific volume (cm <sup>3</sup> /g)
Para-aramid ( <i>Kevlar</i> , <i>Twaron</i> )	1.44	0.69
Aramid ( <i>Technora</i> )	1.39	0.72
High-modulus polyethylene (HMPE)	0.97	1.03
LCP fibre ( <i>Vectran</i> )	1.40	0.71
PBO ( <i>Zylon</i> )	1.56	0.64
PIPD ( <i>M5</i> )	1.70	0.59
Carbon	1.8–2.0	0.56–0.55
Silicon carbide based	2.4–2.75	0.42–0.36
Silicon carbide near stoichiometric	3.0	0.33
Alumina	3.6–3.9	0.28–0.26
Alumina/silica	2.7–3.4	0.37–0.29
Alumina/zirconia	4.1	0.24
Steel	7.85	0.13

Table 5.3 Densities of some chemically and thermally resistant fibres [12]

Fibre	Density (g/cm <sup>3</sup> , Mg/m <sup>3</sup> )	Specific volume (cm <sup>3</sup> /g)
Polyvinylidene chloride (PVDC)	1.60	0.63
Polytetrafluoroethylene (PTFE)	2.2	0.45
Polyetheretherketone (PEEK)	1.30	0.77
Polyphenylene sulphide (PPS)	1.37	0.73
Meta-aramid ( <i>Nomex</i> )	1.46	0.68
Melamine-formaldehyde ( <i>Basofil</i> )	1.4	0.71
Novoloid, phenol-aldehyde ( <i>Kynol</i> )	1.27	0.79
Polyimide ( <i>P84</i> )	1.41	0.71
Polyamide-imide ( <i>Kermel</i> )	1.34	0.75
Polybenzimidazole (PBI)	1.43	0.70
Semi-carbon (oxidised acrylic)	1.35–1.4	0.74–0.71

$$\text{degree of order} = \frac{\rho - \rho_{\text{am}}}{\rho_{\text{cr}} - \rho_{\text{am}}} \quad (5.1)$$

The fibre density,  $\rho$ , is measured by the methods described above. The crystal density,  $\rho_{\text{cr}}$ , can be calculated from the dimensions of the unit cell, determined from the X-ray-diffraction pattern, and the molecular weight. Difficulty arises in the estimation of the amorphous density,  $\rho_{\text{am}}$ . In some instances, the material can be obtained in the amorphous state, for example, by the rapid quenching of undrawn polyester fibres. In other cases, the value must be obtained by extrapolation or by estimation from analogous compounds or the contribution of the constituent groups [18].



5.2 Variation of density with moisture regain for cotton [13], viscose rayon [14], silk [15], wool [16] and nylon [17].

## 5.5 References

1. P. H. Hermans. *Physics and Chemistry of Cellulose Fibres*, Elsevier, Amsterdam, Netherlands, 1949, pp. 197 *et seq.*
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## 6.1 Introduction

This chapter deals with basic thermal properties of fibres. Thermal transitions and the associated changes in structure and properties are covered in [Chapter 18](#), which includes an account of heat setting of fibres. For simple solid materials, the thermal properties consist of the thermal conductivity, specific heat and its variation with temperature, the coefficient of thermal expansion, the melting point, and the latent heat of melting. In fibres, many of these properties have not been studied in great detail because the relevant practical effects are influenced much more by other factors. The thermal conductivity of a textile fabric depends to a much greater extent on the air entrapped within it than on the fibre conductivity. Dimensional changes in fabrics due to reversible swelling on moisture absorption are much larger than those due to reversible thermal expansion. For moisture-absorbing fibres, the heat of absorption resulting from changes in moisture regain, rather than the thermal capacity, contributes the largest share of the uptake or loss of heat by a textile material when the ambient conditions change.

## 6.2 Thermal parameters

### 6.2.1 Specific heat of fibres

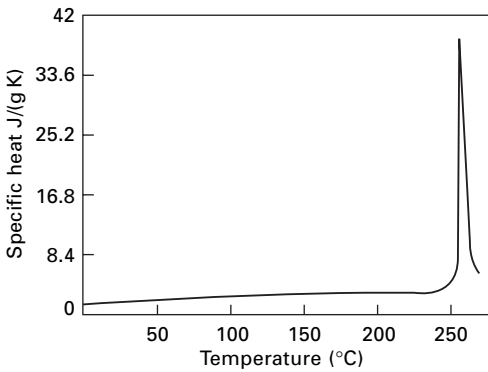
Various workers have measured the specific heat of dry fibres at room temperature, and some typical values are given in [Table 6.1](#).

Dole and his associates [3–8] have measured the variation of specific heats of several polymers with temperature, in a search for transition effects in the structure. [Figure 6.1](#) shows results for nylon. The high values of specific heat found at about 260 °C are due to the melting of the nylon. Since this is spread over a range of temperature, the heat does not appear as a latent heat of fusion at a single temperature but contributes to the heat change over the whole melting range. By integration of the area under the peak, values of latent heat of fusion of about 150 J/g are found, though the values vary with the history of the fibre. This gives rise to high values of the apparent specific heat. Some evidence was also found of a small latent heat associated with a change in structure at about 165 °C.

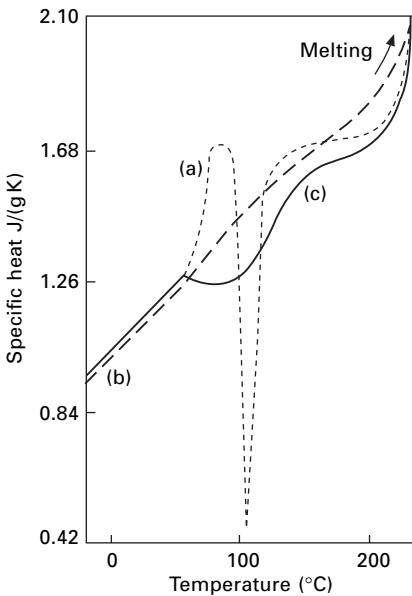
[Figure 6.2](#) shows some results for polyethylene terephthalate (*Dacron*) in various forms. The sharp rise at about 70 °C is associated with a second-order transition in

Table 6.1 Specific heat of dry fibres

Fibre	Specific heat J/(g K)
Cotton [1]	1.22–1.35
Rayon [1]	1.35–1.59
Wool [2]	1.36
Silk [2]	1.38
Nylon 6 [3]	1.43
Nylon 6.6 [1]	1.46
Polyester (PET) [1]	1.03
Asbestos [2]	1.05
Glass [2]	0.80



6.1 Specific heat of drawn nylon filament [4].



6.2 Specific heat of *Dacron* polyester [5]: (a) undrawn; (b) annealed undrawn; (c) commercially drawn fibres.

the structure, and the minimum at about 100 °C with increasing crystallisation, resulting in an evolution of heat. Both of these effects can be eliminated by annealing the fibres. A maximum, occurring at about 250 °C, is associated with melting accompanied by the absorption of the latent heat of fusion.

*Teflon* (polytetrafluoroethylene) is interesting, since there are two first-order transitions, with latent heats estimated to be 8.4 and 1.7 J/g, at 20 and 28 °C, respectively. This means that the specific heat apparently rises to very high values near room temperature, as is shown in Fig. 6.3. The transition at 20 °C is believed to be due to a change from a fully crystalline form with three-dimensional order to a structure with a lower degree of order [9].

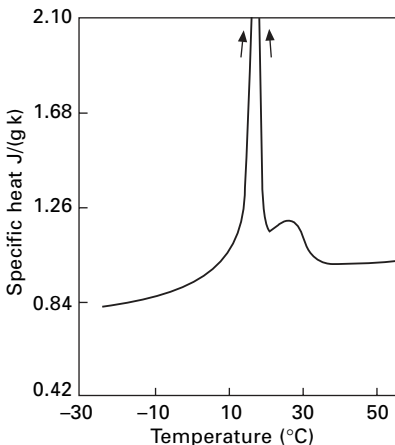
The absorption of water, which as a liquid has a specific heat of 4.2 J/(g K), would be expected to increase the specific heat of fibres. For changes in temperature at constant regain, a simple mixture law would give the relation:

$$\text{mixture specific heat} = C' = \frac{C_0 + 4.2r}{1 + r} \quad (6.1)$$

where  $C_0$  = specific heat when dry and  $r$  = fractional regain.

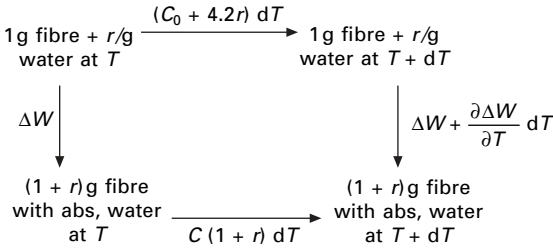
Changes at constant relative humidity will, as discussed in [Chapter 8](#), have a very much larger effective specific heat because of the contribution from the heat of sorption associated with the regain changes.

Even at constant regain, however, equation (6.1) will not predict actual specific heats, for two reasons. Firstly, the absorbed water may not be behaving like liquid water: it may be more like ice with a specific heat of about 2 J/(g K). Secondly, the absorption of water, which loosens up the fibre structure, may change the effective specific heat of the polymer molecules. A correction term,  $\Delta C$ , will therefore be added to  $C'$  to give the actual specific heat,  $C$ . The term  $\Delta C$  can be related to changes in the heat of wetting with temperature. If  $\Delta W$  is the difference between the heat of wetting from zero regain and the heat of wetting from regain  $r$ , it follows from the First Law of Thermodynamics that the changes in heat along either of the two alternative routes shown in [Fig. 6.4](#) must be the same. Hence:

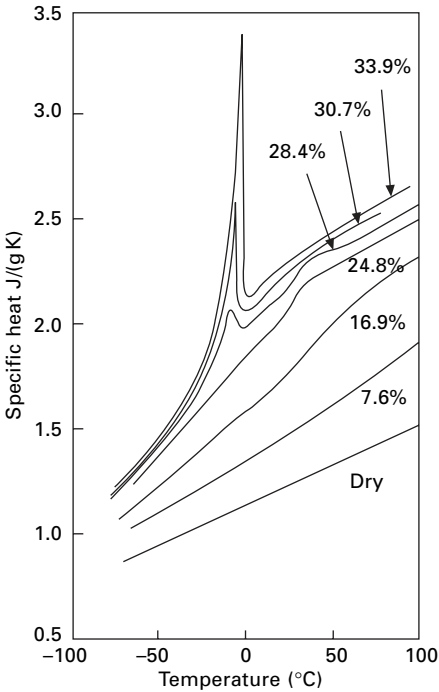


6.3 Specific heat of PTFE (Teflon) near room temperature [8].





6.4 Alternative routes for moisture absorption and temperature change.



6.5 Variation of specific heat of wool with regain. From Haly and Snaith [11].

$$\Delta W + C(1 + r) dT = (C_0 + 4.2r) dT + \Delta W + (\partial \Delta W / \partial T) dT \tag{6.2}$$

from which:

$$C = \frac{C_0 + 4.2r}{1 + r} + \frac{\partial \Delta W / \partial T}{1 + r} \tag{6.3}$$

Hearmon and Burcham [10] found agreement, within the limits of experimental error, between values of  $\Delta C$  and  $(\partial \Delta W / \partial T) / (1 + r)$  for wood cellulose. The values of the  $\Delta C$  term ranged from about 0.1 J/(g K) at medium regains and room temperature to 0.4 J/(g K) at high regains and 60 °C, so that the correction is small but appreciable.

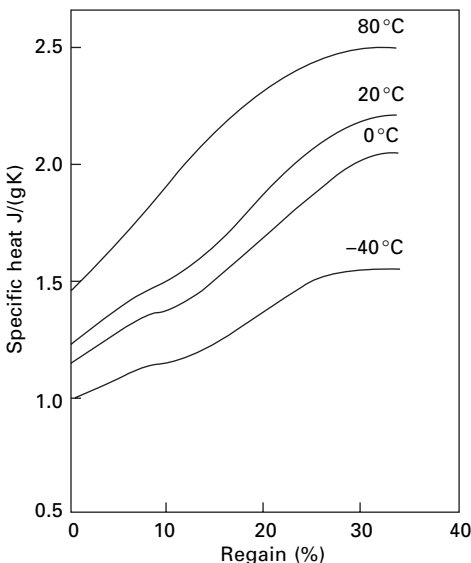
Figure 6.5 shows how the specific heat of wool varied with moisture regain in some studies by Haly and Snaith [11], using an adiabatic calorimeter. Examples of

particular plots of variation of specific heat with temperature are shown in Fig. 6.6. Very careful experimental work is needed, and various corrections have to be applied: for example, in addition to the usual need to minimise energy losses, a correction is required for the influence of evaporation into the small void space in the sample container. On the first heating, a small dip in the curve was often found at about 50 °C: this is probably due to the release of elastic energy set in the fibres during its compression into the container.

The specific heats generally show a linear variation with temperature, with a higher slope at higher regains. However, in the samples at all regains above zero, there is a definite upturn at about 50 °C: it becomes more pronounced at higher regains and may be a latent heat from a small, diffuse, first-order transition.

A much more distinct peak appears at low temperatures at regains greater than 25%. At a regain of 34%, this effect is large and sharp and has its peak just below 0 °C: it is obviously associated with a change in loosely held water from an ice-like to a liquid-like form. The latent heat of fusion of this transition is 200 J/g of water at 34% regain. At lower regains, the peak is less marked, and its maximum occurs at lower temperatures. In all cases, the rise to the peak starts at -30 °C, which indicates that this is the temperature at which the first absorbed water to be involved in the effect goes through the transition: the further absorbed water will have an effect at successively higher temperatures.

These results for wool are of interest not only in themselves, but also as being indicative of effects that may occur in other fibres.



6.6 Individual plots of variation of specific heat of wool samples with regain at various temperatures. From Haly and Snaith [11].

## 6.2.2 Thermal conductivity

Until the 1980s, there are no records of direct measurement of the thermal conductivity of fibres. However, an estimate of relative values can be obtained by comparing the results of measurements of thermal conductivity of pads of different fibres packed to the same density [12, 13]. Some values are given in Table 6.2. The protein fibres have a lower conductivity than the cellulosic fibres. Experiments can also be made with materials in the solid form. Figure 6.7 shows the variation of thermal conductivity of horn, which is a similar material to wool, with regain, and Table 6.3 gives values for the thermal conductivity of some solid polymers.

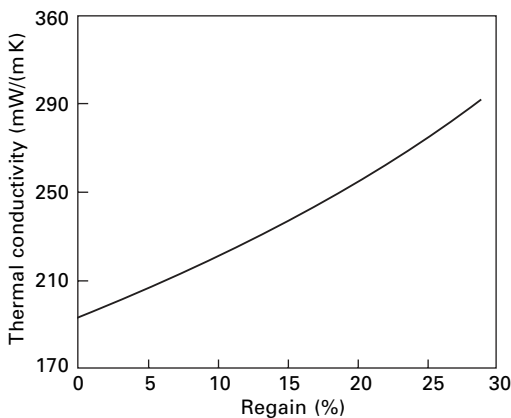
*Table 6.2* Thermal conductivity of pads of fibres with a bulk density of  $0.5 \text{ g/cm}^3$  [12, 13]

Fibre	Thermal conductivity (mW/(m K))
Cotton	71
Wool	54
Silk	50

*Note:* Still air has a thermal conductivity of  $25 \text{ mW/(m K)}$

*Table 6.3* Thermal conductivity of polymers [1, 12]

	Thermal conductivity (mW/(m K))
Cellulose acetate	230
Nylon	250
Polyester (PET)	140
Polyethylene	340
Polypropylene	120
Polyvinyl chloride (PVC)	160



*6.7* Variation of thermal conductivity of horn with moisture regain [12].

Kawabata [14, 15] has measured the longitudinal conductivity of fibres, using the apparatus shown in Fig. 6.8(a). About 10 000 fibres are clamped at 20 mm width with 3 mm between the clamps. Since the heat flow is very small, about 20 mW, great care has to be taken to avoid errors. The conductivity  $K_L$  is given by:

$$K_L = \frac{qL}{A\Delta T} \tag{6.4}$$

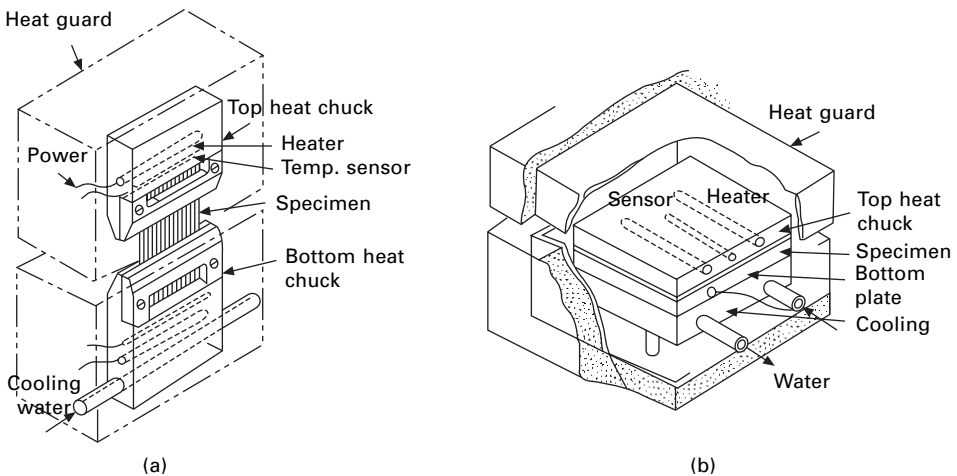
where  $q$  = heat flow rate,  $L$  = specimen length,  $A$  = total area of fibre cross-sections and  $\Delta T$  = temperature difference between ends.

In order to determine the anisotropy of thermal conductivity, Kawabata used a composite film of aligned fibres with an epoxy matrix at a fibre volume fraction of about 80%. An area of film,  $50 \times 50 \text{ mm}^2$  and between 0.5 and 1 mm in thickness, was clamped between plates as shown in Fig. 6.8(b). The transverse conductivity  $K_T$  was calculated from a series mixture law, though this is not strictly valid for an assembly of cylinders in matrix. Owing to the high volume content, the error may be small.

$$K_T = \frac{qV_F}{[A\Delta T/L] - \left[ \frac{q(1 - V_R)}{K_R} \right]} \tag{6.5}$$

where  $V_F$  = fibre volume fraction and  $K_R$  = thermal conductivity of resin.

Table 6.4 shows the measured thermal conductivities. The high values for carbon fibres reflect the continuous ring structure and for aramids the close sequence of benzene rings. The values for the different aramid and carbon fibres shows the importance of molecular arrangement and orientation, which would also account for the differences between filament and staple. The conductivities of these fibres increase by about 25% between 20 and 200 °C. There is a high degree of anisotropy, though



6.8 Thermal conductivity measurement units: (a) axial; (b) transverse. From Kawabata [14].

Table 6.4 Thermal conductivities of fibres. From Kawabata [14, 15]

Fibre	Thermal conductivity (W/(m K))		Anisotropy $K_L/K_T$
	Longitudinal $K_L$	Transverse $K_T$	
Aramid			
<i>Kevlar 29</i>	3.05	0.192	15.9
<i>Kevlar 49</i>	3.34	0.212	15.8
<i>Kevlar 149</i>	4.74	0.230	20.6
Carbon			
<i>Torayca T-300</i>	6.69	0.530	12.6
<i>Torayca M-308</i>	18.33	0.667	27.5
<i>Torayca M-408</i>	58.81	1.215	48.4
E-glass	2.250	0.509	4.42
Nylon	1.43	0.171	8.38
Polyester filament	1.26	0.157	8.01
Polyester staple	1.18	0.127	9.25
Polypropylene	1.241	0.111	11.18
Acrylic	1.028	0.172	5.93
Rayon filament	1.89	–	–
Rayon staple	1.41	0.237	5.97
Cotton	2.88	0.243	11.85
Flax	2.851	0.344	8.23
Wool	0.48	0.165	2.91
Silk	1.49	0.118	12.64

the results for glass fibre, which is expected to be isotropic, suggest that the composite mixture equation underestimates the transverse fibre conductivity. The increasing anisotropy in the aramid and carbon fibres correlates with the increasing anisotropy of their moduli.

Lavin [16] confirms the correlations of thermal and electrical conductivities with moduli of carbon fibres. In PAN-based fibres there was an almost exponential increase in thermal conductivity from 5 to 100 W/(m K) with an increase in moduli from 250 to 600 GPa. In pitch-based fibres, the thermal conductivity reached almost 900 W/(m K) at 950 GPa.

### 6.2.3 Thermal expansion and contraction

Only a limited amount of work on the reversible thermal expansion of fibres has been done. Some values of the coefficients of expansion are given in Table 6.5. It will be noticed that the coefficient for nylon and polyester fibres is negative. This anomalous contraction may also occur with other fibres. The thermodynamic arguments discussed in Section 20.8.1 may be applied to thermal expansion and contraction. Equation (20.62) is:

$$\left(\frac{\partial S}{\partial l}\right)_T = -\left(\frac{\partial F}{\partial T}\right)_l \quad (6.6)$$

where  $S$  = entropy,  $l$  = length of fibre,  $F$  = tension of fibre and  $T$  = temperature.

Table 6.5 Coefficient of linear expansion of fibres (axial)

Fibre	Coefficient of expansion per degree C
Cotton [17]	$4 \times 10^{-4}$
Cellulose acetate [18]	$0.8\text{--}1.6 \times 10^{-4}$
Nylon fibre [17]	$-3 \times 10^{-4}$
Polyester (PET) [17]	$-10 \times 10^{-4}$ above $80^\circ\text{C}$
Polyethylene [18]	$2 \times 10^{-4}$
Polyacrylonitrile (PAN) [19]	$10 \times 10^{-4}$

Since

$$\left(\frac{\partial F}{\partial T}\right)_l = -\left(\frac{\partial F}{\partial l}\right)_T \left(\frac{\partial l}{\partial T}\right)_F \quad (6.7)$$

the coefficient of linear expansion =  $\left(\frac{1}{l}\right)\left(\frac{\partial l}{\partial T}\right)_F$

$$= \left(\frac{1}{l}\right) \frac{(\partial S/\partial l)_T}{(\partial F/\partial l)_T} = \left(\frac{1}{l}\right) \left(\frac{\partial S}{\partial F}\right)_T \quad (6.8)$$

This means that the expansion is positive when stretching the fibre causes an increase of entropy, i.e. a greater degree of disorder due to increasing thermal vibrations. It is negative when the entropy decreases on stretching, i.e. the material becomes more highly ordered, as it does in a rubber when the molecules are straightened (see Section 20.1.2). This is more commonly observed as an increase in tension, indicating that the fibre wants to contract, on heating. Superimposed on the above effect there is the usual volume expansion due to the fact that the molecules take up more space at higher temperatures when they are vibrating more strongly. In rubber, this leads to the thermoelastic inversion: at zero tension, a rubber expands on heating because of the volume change, but a rubber specimen held at constant tension will contract axially if its extension is greater than about 10%. As shown in Section 20.3.2, the tie-molecules, which link the crystallites in nylon and polyester fibres, are in an extended rubbery state. Consequently, the coefficients of expansion can be negative as shown in Table 6.5.

A useful property of carbon fibres is their low coefficient of thermal expansion.

## 6.3 References

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