

21.1 General introduction

The electrical properties of fibres are of less obvious technical importance than, for example, the mechanical properties. Apart from their intrinsic interest, the first stimulus for their investigation came from the use of fibres as insulating materials, and much important work was done in the Bell Telephone Laboratories. Later, the use of resistance and capacity methods for measuring the moisture condition of textile materials, and of capacity methods for measuring irregularity, increased the interest in electrical properties. With the introduction of synthetic fibres, the troubles due to static charges, both in processing and in use, became more frequent and more severe. The electrical properties are interrelated. The liability of materials to static charges is determined by their electrical resistance. The electrical resistance is, on what seems to be the most likely theory, mainly determined by the permittivity of the material. It is, therefore, most appropriate to consider first the dielectric properties, then the electrical resistance, and finally static.

21.2 Definitions of dielectric properties

The *permittivity*, ϵ , of a material may be defined either in terms of the capacitance, C , of a condenser with the material between parallel plates of area A and separation d , or in terms of the force F between two charges Q_1 and Q_2 at a distance r in the material. Expressed in SI units as $\text{kg}^{-1} \text{m}^{-3} \text{s}^4 \text{A}^2$ ($A = \text{ampere}$) or F/m ($F = \text{farad}$), the relations contain no arbitrary numerical factors and are:

$$C = \frac{\epsilon A}{d} \quad (21.1)$$

$$F = \frac{Q_1 Q_2}{4\pi \epsilon r^2} \quad (21.2)$$

This does, however, mean that *in vacuo* the equations become:

$$C = \frac{\epsilon_0 A}{d} \quad (21.3)$$

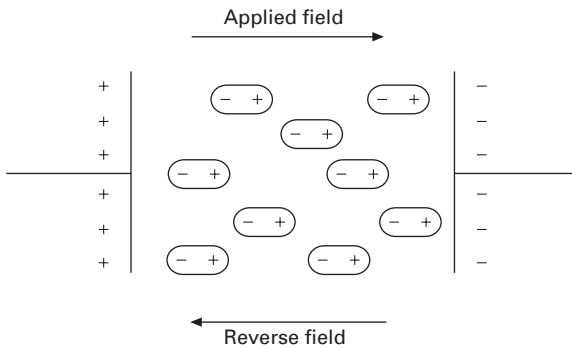
$$F = \frac{Q_1 Q_2}{4\pi \epsilon_0 r^2} \quad (21.4)$$

where ϵ_0 is the permittivity of a vacuum, which is a fundamental physical quantity with the value 8.854×10^{-12} F/m. For many purposes, it is more convenient to use the *relative permittivity*, $\epsilon_r = \epsilon/\epsilon_0$; which is also called the *dielectric constant*.

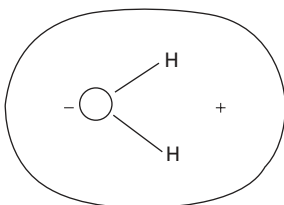
Physically, dielectric effects are due to polarisation in the medium (Fig. 21.1). This gives rise to a reverse field, which reduces the force between two charges and reduces the potential difference between the charged plates of a condenser, which thus increases its capacitance (given by charge/potential difference). The polarisation may be due either to the alignment of permanent dipoles, such as the water molecule (Fig. 21.2), or to the separation of charge, which forms induced dipoles (Fig. 21.3). Because of its influence on capacitance, the relative permittivity is important in alternating current electricity. For a pure capacitance, current is proportional to rate of change of voltage and is therefore, with a sinusoidal applied voltage, 90° out of phase with voltage. By contrast, in a pure resistance, current is in phase with voltage. In actual practice, dielectrics are imperfect, and a real condenser (Fig. 21.4(a)) acts as a combination of capacitance and resistance. The current through the condenser due to an applied voltage of frequency f Hz is made up of a current proportional to $1/R_p$ in phase with the applied voltage and a current proportional to $2\pi f C_p$ at 90° to the applied voltage, where R_p and C_p are the equivalent parallel resistance and capacitance, respectively (Fig. 21.4(b)). The current vector diagram is shown in Fig. 21.4(c).

The relative permittivity is then given by:

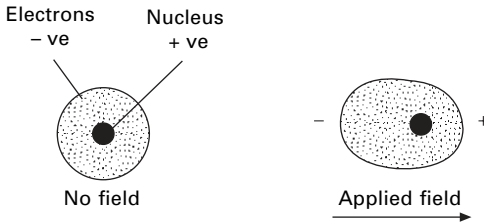
$$\epsilon_r = \frac{C_p}{C_0} \tag{21.5}$$



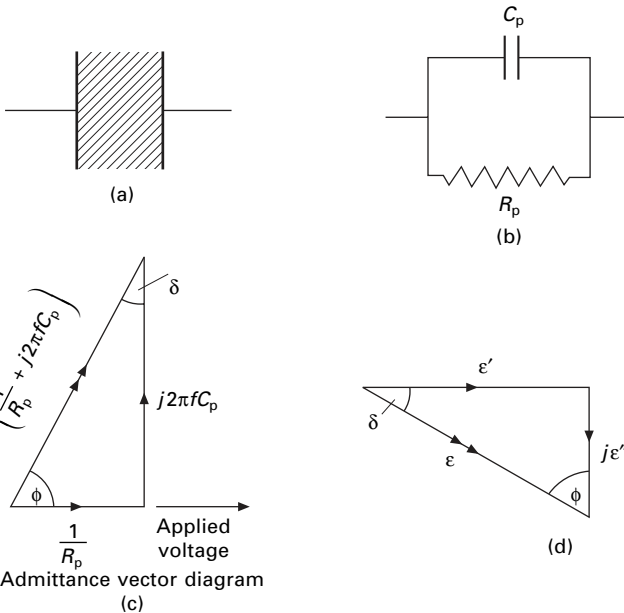
21.1 Polarisation of a medium.



21.2 A permanent dipole – the water molecule.



21.3 An induced dipole-distortion of the distribution of electrons round the nucleus of an atom.



21.4 Representation of a real dielectric: (a) condenser with dielectric; (b) equivalent parallel circuit; (c) current vector diagram for circuit; (d) vector diagram – complex dielectric constant.

where C_0 = capacitance of the condenser with a vacuum (or, in practice, air) as dielectric.

The imperfection of the dielectric may be expressed as:

$$\text{dissipation factor, or loss tangent} = D = \tan \delta = \frac{1}{2\pi f C_p R_p} \quad (21.6)$$

where δ = loss angle, or as power factor = $\cos \phi = [\text{mean power dissipated in condenser} / \text{voltage} \times \text{current (r.m.s. values)}] = D / \sqrt{1 + D^2}$, where $\phi = (\pi/2) - \delta$ = phase angle. Table 21.1 shows the values of these quantities for pure capacitance and resistance; with real materials, the values lie between these limits.

An alternative method of expressing the properties of the material is in terms of a complex permittivity, ϵ , with the vector diagram of Fig. 21.4(d). We have:

Table 21.1 Dielectric properties

	Vector diagram	Power factor	Dissipation factor	Loss angle	Phase angle
Pure capacitance	$\uparrow j \cdot 2\pi f C_p$	0	0	0	$\pi/2$
Pure resistance	$\rightarrow 1/R_p$	1	∞	$\pi/2$	0

$$\epsilon = \epsilon' - j\epsilon'' \quad (21.7)$$

It can be shown that real part of permittivity = $\epsilon' = \epsilon$, as defined above, and imaginary part of permittivity = loss factor = $\epsilon'' = 1/2\pi f C_p R_p$ and dissipation factor = $\tan \delta = \epsilon''/\epsilon'$.

21.3 Measurement

21.3.1 Experimental methods

To measure the dielectric properties, the material must be placed between the plates of a condenser and the impedance measured. For measurements on material in the form of film, a simple parallel plate condenser, with the plates fitting closely to the film, can be used. Fibres are less easy to handle. Balls [1] used parallel plates and carefully packed cotton fibres either perpendicular or parallel to the plates. Hearle [2] used conical electrodes. A layer of yarn, about 2 mm thick, was wound on the inner cone, and the outer cone was then pressed on it. With this arrangement, densities of packing of about 80% by volume were obtained with continuous-filament yarns, and of about 50% with staple-fibre yarns.

The method of measurement of impedance depends on the frequency being used for the test¹. At audio-frequencies (from about 50 Hz to 100 kHz), a bridge method is suitable. Resonance methods can be used up to about 100 MHz. The condenser is connected in series with an inductance L in a resonant circuit, with the current measured by a high-impedance voltmeter across the condenser. At the resonant frequency f_0 , the current has a maximum value. The capacitance $C = L/(2\pi f_0)^{1/2}$ and $\tan \delta = \Delta f/f_0$, where Δf = difference in frequency between the two values for which the current is $1/\sqrt{2}$ times the maximum value. Circuit-magnification meters, or Q-meters, can be used for this method. At very high frequencies (10 GHz), Shaw and Windle [3] used a cavity resonator. If a small dielectric specimen is placed along the axis of the cavity parallel to the electric field, the resonant frequency of the cavity is given by:

$$f = f_e \left[1 - 1.86 (\epsilon_r - 1) \frac{v_s}{v_e} \right] \quad (21.8)$$

where f_e = resonant frequency of empty resonator, v_s = volume of specimen and v_e = volume of cavity.

¹The methods noted here are those used for the data in this chapter. Subsequent advances in electronics have changed the details of the technology, but not the principles.

At optical frequencies, the dielectric properties can be obtained from a study of refraction and absorption in the fibres by using the equations:

$$\epsilon_r = n^2(1 - k^2) \quad (21.9)$$

$$\tan \delta = \frac{2k}{(1 - k^2)} \quad (21.10)$$

where n = refractive index and k = absorption index, defined by: $2\pi k = \lambda/x_0$, where λ = wavelength, and x_0 = distance in which amplitude decreases to $1/\exp(x)$ times its original value.

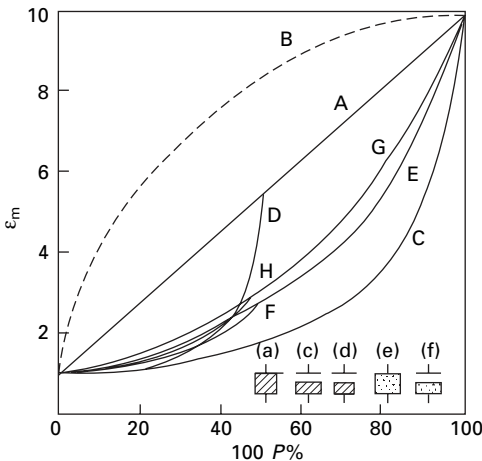
21.3.2 Evaluation of results for an air-fibre mixture

The main difficulty in dealing with fibres is the interpretation of results found with a mixture of air and fibre in order to obtain the properties of the fibrous material itself. Depending on the particular assumptions used, different formulae can be obtained, and it is not easy to see how closely they should fit particular experimental conditions. Some of these relations are described below and shown in Fig. 21.5. We define ϵ_r as the relative permittivity of the fibre material (taken as 10 for the curves in Fig. 21.5), ϵ_m as the effective relative permittivity of the mixture, and P as the volume fraction of fibre between the plates of the condenser.

- If the material is assumed to occupy only a fraction of the total area, but to be continuous between the plates, Fig. 21.5(a), and it is assumed that there is no distortion of the field, we have the parallel mixture law, Fig. 21.5A:

$$\epsilon_m = 1 + (\epsilon_r - 1) P \quad (21.11)$$

Balls [1] used this formula for fibres lined up perpendicular to the plates, but it



21.5 Theoretical curves for the variation of relative permittivity with density of packing.

seems unlikely that, under these conditions, one can neglect the distortion of the electric field. Owing to the high surface/volume ratio in fibres, there will be a large edge effect. The lines of force will concentrate on the region of high relative permittivity and increase the capacity above its expected value. Some curve such as Fig. 21.5B will be obtained.

- If the material is assumed to occupy the whole area, but only a fraction of the distance between the plates, Fig. 21.5(c), we have the series mixture law, Fig. 21.5C:

$$\frac{1}{\epsilon_m} = (1 - P) + \frac{P}{\epsilon_r} \quad (21.12)$$

- A combination of the above two cases, with α as the fraction of area occupied and β as the fraction of the distance between the plates (Fig. 21.5(d)), presents the problems of averaging referred to in Section 20.3.2 in relation to a mixture of mechanical properties. One model gives the following equation:

$$\epsilon_m = \frac{\alpha}{[(1 - \beta) + \beta/\epsilon_r]} + (1 - \alpha) = \frac{\alpha^2}{[(\alpha - p) + P/\epsilon_r]} + (1 - \alpha) \quad (21.13)$$

With $\alpha = 0.5$, this gives Fig. 21.5 D.

- If molar polarisations are additive, the following equation holds [4]:

$$\frac{\epsilon_m - 1}{\epsilon_m + 2} = P \frac{\epsilon_r - 1}{\epsilon_r + 2} \quad (21.14)$$

This system is indicated in Fig. 21.5(e) and gives the curve Fig. 21.5E. It is not valid for large particles owing to the failure of the assumption on which it is based that the Lorentz internal field holds at all places. It has been shown to be a good approximation for small values of P [5]. Various improvements on this formula for particular conditions have been suggested [6–8], and Polder and van Santen [9] have discussed the problem more generally.

If ϵ_r is very nearly equal to 1, so that the difference between $\epsilon_m + 2$ and $\epsilon_r + 2$ is negligible. Equation (21.14) reduces to:

$$\epsilon_m - 1 = P(\epsilon_r - 1) \quad (21.15)$$

which is the same as equation (21.11) leading to Fig. 21.5A.

This is valid for a mixture of gases but would not be expected to be so for fibres, though it was used by Balls [1] for fibres arranged with their axes parallel to the plates.

- A combination of (C) and (E), illustrated in Fig. 21.5(f), would give the curve Fig. 21.5F.
- Licktecker [10] proposed a logarithmic relation, which, for a mixture with one component having unit relative permittivity, reduces to Fig. 21.5G:

$$\log \epsilon_m = P \log E_r \quad (21.16)$$

This has been applied, with experimental support, by Shaw and Windle [3] to the transverse relative permittivity of fibres wound solenoidally.

- A combination of (C) and (G) gives Fig. 21.5H. Hearle [2] obtained curves similar to, but not in quantitative agreement with, this when the density of packing between cones was varied by altering the pressure applied to the outer cone. Different curves, corresponding to different densities in the bulk of the material, can be obtained by using staple-fibre and continuous-filament yarns and by varying the winding tension. An example is given in Fig. 21.6.

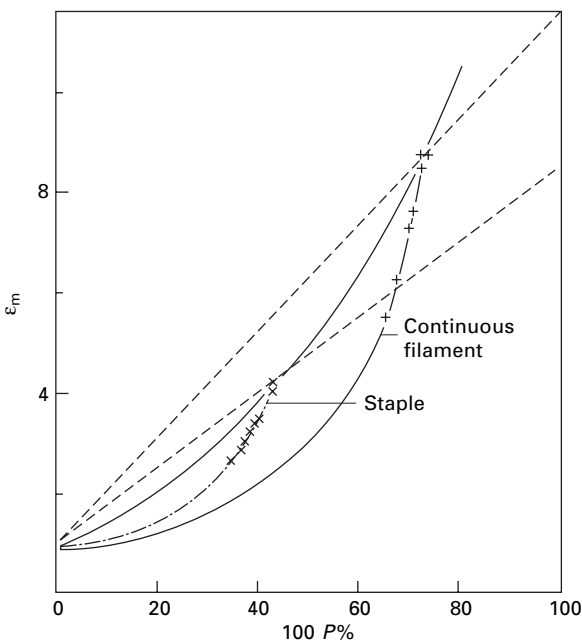
Where the experimental arrangement approximates closely to one of the above models, it may be possible to obtain an accurate extrapolation formula, but, in general, the problem has not been solved.

For dry fibres having a comparatively low permittivity, Errera and Sack [11] overcame the problem by immersing the fibres in a mixture of liquids and adjusting the mixture until the introduction of the fibres made no difference. The permittivities of fibre and liquid were then equal.

21.4 The effect of frequency

21.4.1 General

Frequency has a most important influence on dielectric properties, in a way similar to its influence on dynamic mechanical properties. Owing to their inertia, and to restraints in the structure, the dipoles take a certain time to reverse direction. This is characterised as their relaxation time. At low frequency, the dipoles line up in the



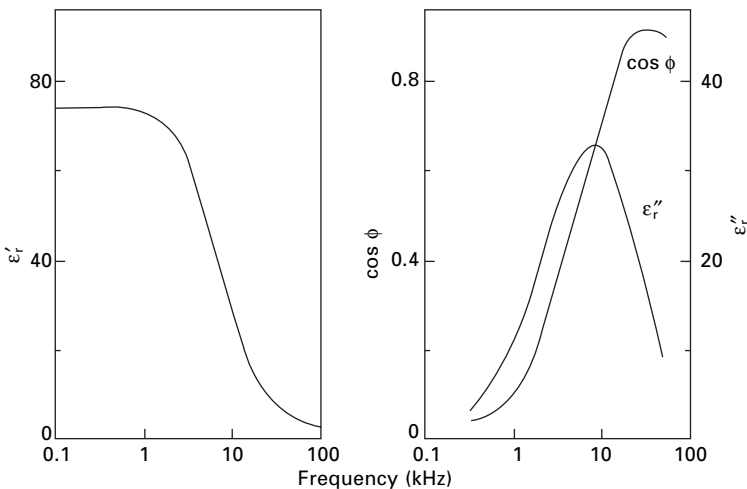
21.6 Practical variation of relative permittivity of viscose rayon with density of packing [2].

field, reverse direction when the field reverses, and so contribute to a high permittivity. At high frequencies, the dipoles will not follow the changes at all, and there will be no contribution to the permittivity. At intermediate, transitional frequencies the reversals of field take place at intervals comparable to the relaxation time, the response of the dipoles is sluggish, which gives a phase difference between voltage and current, and energy is dissipated due to internal friction. Different types of dipole will have different relaxation times, so that, as the frequency is raised, the permittivity drops in steps and the dielectric loss peaks. When the theory is worked out exactly, it is found that the maximum in ϵ'' occurs at the same frequency as the maximum rate of decrease of ϵ' ; the maximum of $\cos \phi$ is displaced to a slightly higher frequency.

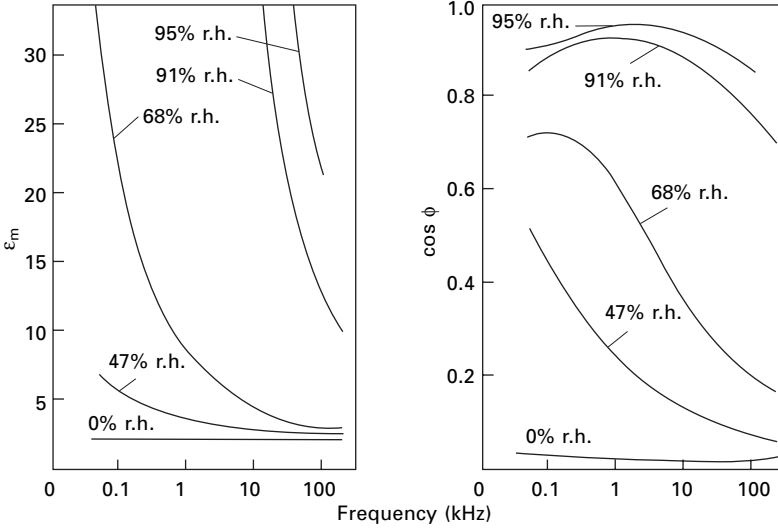
The general behaviour is illustrated by the results for water and ice. At low frequencies, the dipolar water molecules line up in the field, to give a relative permittivity of about 80. At higher frequencies, the permittivity drops in a step, and there is a maximum in the power factor. For ice, (Fig. 21.7), in which the considerable restraints in the structure limit the movement of the dipoles, this occurs at about 10 kHz; but, for liquid water, in which the molecules are less restrained, the permittivity remains constant up to about 1 GHz, and then drops rapidly and passes half its low-frequency value at about 20 GHz. Above these frequencies, there will still be electronic polarisation, but at high enough frequencies this will cease, and there will be a further decrease in permittivity.

21.4.2 Fibres

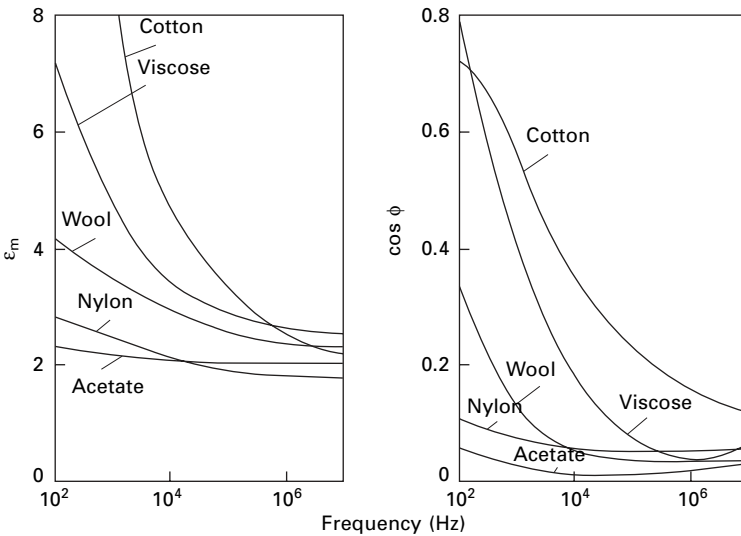
Figures 21.8 and 21.9 show results obtained by Hearle [2, 12] for cotton, viscose rayon, acetate, wool and nylon over the range of frequencies between 50 Hz and 10 MHz. Other values are included in the summary given later in Table 21.4. These results show the great influence of frequency on the dielectric properties, an influence



21.7 Dielectric properties of ice.



21.8 Dielectric properties of cotton yarn in cone condenser [2]. Cotton 44%; air 56%.



21.9 Variation of dielectric properties with frequency for various fibre-air mixtures at 65% r.h. [2, 12].

that becomes more marked the damper the specimen. The changes occur gradually and not in steps, which indicates that a range of relaxation times is involved.

Above 5 kHz, the permittivity decreases in a manner similar to that in ice, but, below 5 kHz, the permittivity curve does not flatten out, as does that of ice, but continues to increase as the frequency decreases. This must correspond to a comparatively large-scale polarisation phenomenon with a long relaxation time. The

maximum in the power factor for damp cotton at 50–100 Hz indicates that there must be a dominant relaxation time of the order of 1/100 second. These effects are probably due to a polarisation of the ion distribution in microscopic or sub-microscopic regions of the fibre structure, or possibly even across the whole fibre. This is the same as the Maxwell–Wagner effect, or interfacial polarisation, which occurs when there are heterogeneities in the conductivity and permittivity of a material between the plates of a condenser.

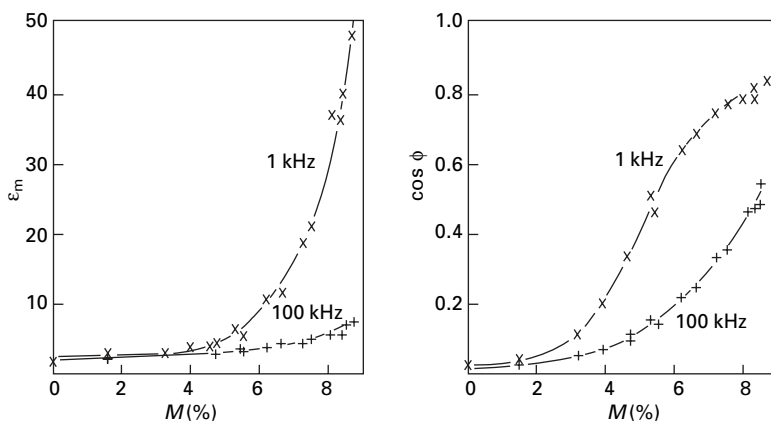
In several types of fibre (viscose rayon, acetate, fairly dry cotton), the power factor begins to increase with an increase in frequency in the region of 1 MHz. These results suggest that, at some frequency greater than 10 MHz, there will be a maximum in the power factor and a corresponding drop in the permittivity. The way in which the curves for viscose rayon and acetate at various humidities come together suggests that this effect is independent of the presence of water. It is probably associated with the lining-up of polar groups within the fibre.

In wool, Windle and Shaw [13, 14] found a decreasing power factor as the frequency increased from 3 to 26 GHz. This indicated the presence of a maximum in the power factor at some frequency below this. This is probably essentially the same effect as that which is suggested for viscose rayon, acetate and cotton by tests at lower frequencies.

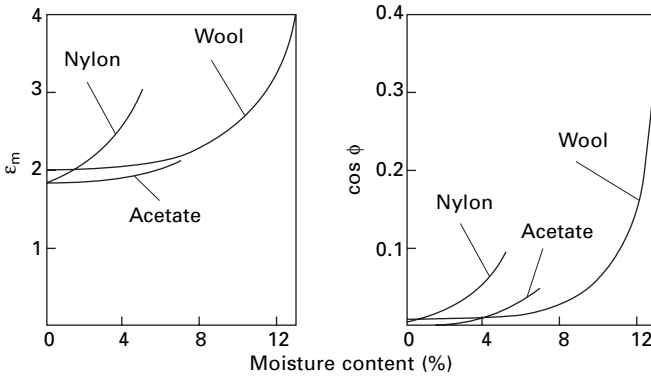
It is interesting to notice that relaxation effects occur in the mechanical behaviour of fibres at similar frequencies to those found in the dielectric properties (see [Section 16.5](#)).

21.5 The effect of moisture

As would be expected, moisture has a marked effect on the dielectric properties; this is illustrated for cotton, acetate, wool and nylon in Figs 21.10 and 21.11. At the higher frequencies, the dielectric properties of the cellulosic fibres are consistent with the assumption that the water molecules are restrained in a manner similar to that in ice. For wool, the permittivity is lower, which indicates that the absorbed water molecules are more tightly held and cannot line up in the field. This behaviour



21.10 Variation with moisture content M of dielectric properties of cotton [2].



21.11 Variation with moisture content of dielectric properties of various fibres at 1 kHz [2].

is particularly marked at low moisture contents and is consistent with Speakman's suggestion (see Section 12.2.1) that the water first absorbed by wool is firmly bound to hydrophilic groups in the side chains of the keratin molecule. At the lower frequencies, in some materials (notably cotton, in which the permittivity reaches very high values), the effect of water becomes greater than it would be even if it were acting with a relative permittivity of 80, which indicates its importance in freeing other units in the structure so that they can polarise.

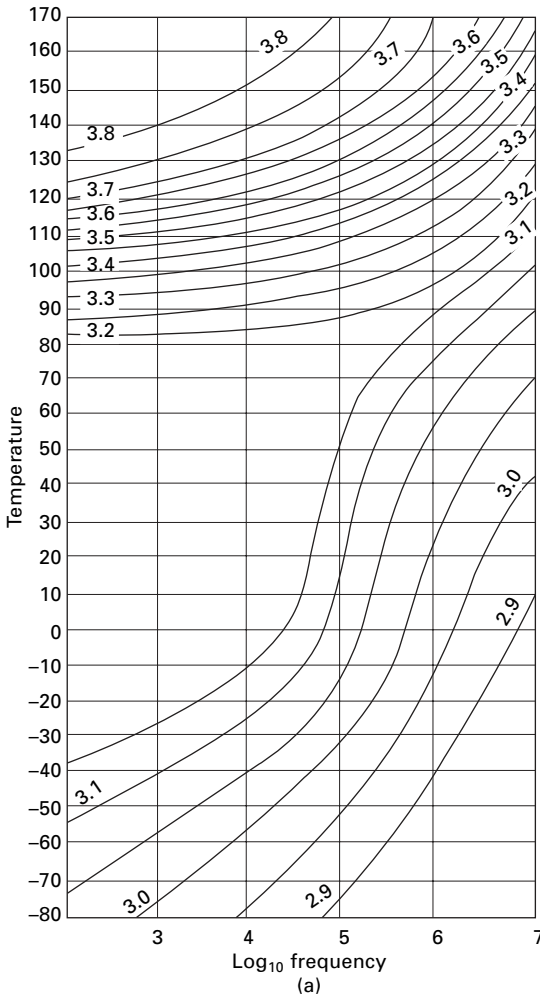
Windle and Shaw [14] have explained their results for wool at very high frequencies in terms of a three-phase theory of moisture absorption. The components of the system were regarded as dry wool, with experimentally determined properties; localised absorbed water, in which the molecules cannot rotate; intermediate absorbed water, in which the molecules are very little restricted; and mobile absorbed water, in which the molecules are as free as in liquid water. Using expressions for the dielectric properties of a mixture of dielectrics, assigning values for the dielectric properties of each component, and dividing up the absorbed water in proportions found theoretically, they obtained a good agreement between experiment and theory.

Of the non-absorbing fibres, polyester (PET) and polyvinylidene chloride (*Saran*) showed no variation in dielectric constant, and only a small change in power factor between 0 and 65% r.h. Polyvinyl chloride (*Vinyon*) and glass (*Fiberglas*) showed a marked change at low frequencies, which was presumably due to surface effects. In general, the effect of additives will have a major effect when the dielectric properties are not dominated by moisture absorption.

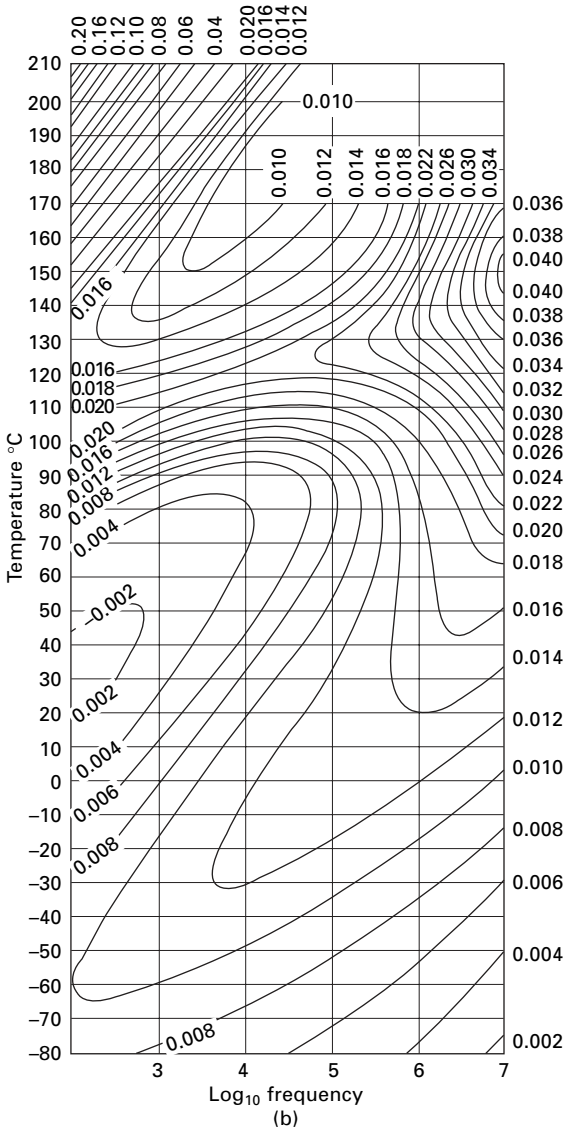
21.6 The effect of temperature

A rise in temperature, reducing the restraints on the dipoles, causes an increase in permittivity in solid materials. (In liquids and gases, where the intermolecular restraints are small, an increase of temperature causes a greater disorganisation, a less regular alignment of the dipoles, and thus a lower permittivity.) As for dynamic mechanical properties, the effects of temperature and frequency are often similar. This is shown

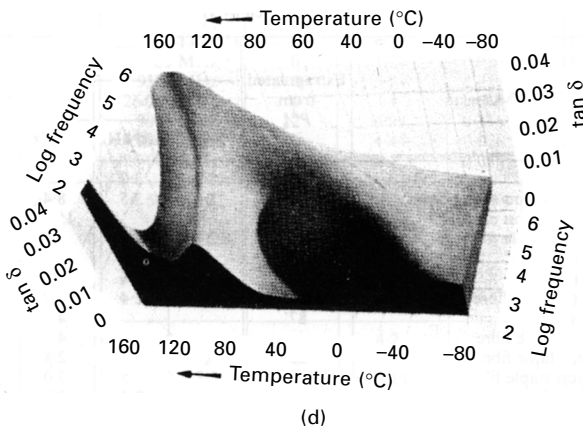
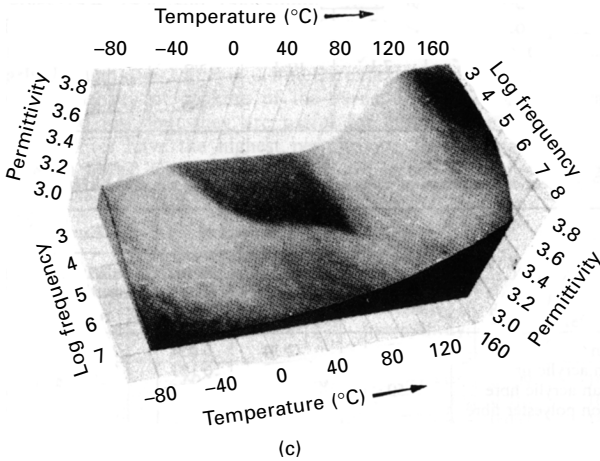
by Reddish's results [15] for polyethylene terephthalate (*Terylene*) film (Fig. 21.12). To include the effect of both variables, contour maps and solid models are used. It will be seen that there is a maximum in $\tan \delta$, occurring at about 1 MHz at room temperature and moving to lower frequencies at lower temperatures; this would correspond to the maximum suggested earlier Section (21.4.2) as being likely in the high-frequency region. At higher temperatures, there is another sharper maximum. These two ridges in $\tan \delta$ in the 3D models correspond to the peaks in mechanical loss shown in Fig. 21.13. Corresponding to the maxima in $\tan \delta$, there are rapid dips in the values of the permittivity. Note that the permittivity plots are the inverse of dynamic modulus plots and would correspond to compliance plots. There is another



21.12 Influence of temperature and frequency on dielectric properties of polyester (*Terylene*) film: (a) relative permittivity contour map; (b) dissipation factor contour map; (c) relative permittivity solid model; (d) dissipation factor solid model. After Reddish [15].



21.12 (Continued)

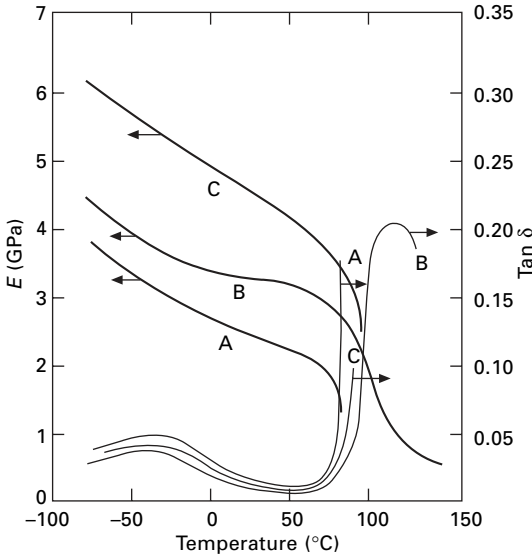


21.12 (Continued)

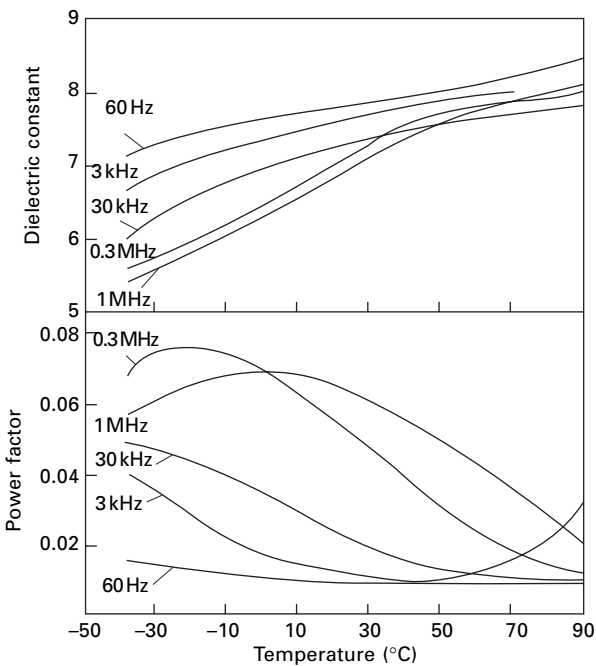
interesting feature: an increase in $\tan \delta$ at low frequency at 160 °C. Although there is no observable maximum, this may indicate another transition at a higher temperature but below the melting point. This may be associated with permanent setting of polyester fibres. Figure 21.14 shows the results obtained by Stoops [17] for dry cellulose film (Cellophane). These also include a low-temperature maximum and, at 60 Hz, indications of a high-temperature maximum. Baker and Yager [18] obtained somewhat similar results with dry nylon 6.10. Table 21.2 shows values of the relative permittivity of nylon and keratin film at 25 and 40 °C at various moisture regains.

21.7 The effect of other factors

The permittivity of an anisotropic material, such as a fibre, would be expected to vary with the direction in which the electric field is applied. The results obtained by Balls [1] for cotton fibres indicate that the axial permittivity is about twice the transverse permittivity, but, as is indicated above Section (21.3.2), the extrapolation on which



21.13 Dynamic mechanical modulus and $\tan \delta$ of poly(ethylene terephthalate) as measured by Kawaguchi [16] at about 100 Hz: A, undrawn, 2% crystallinity; B, undrawn, 50% crystallinity; C, drawn 5 \times , 25% crystallinity.



21.14 Variation of dielectric properties of cellophane. After Stoops [17].

Table 21.2 Effect of temperature on permittivity of nylon and keratin films [19]

Moisture regain (%)	Relative permittivity			
	Nylon film		Keratin film	
	25 °C	40 °C	25 °C	40 °C
0	4.2	4.5	4.7	4.8
1.8	5.0	6.0		
3.6	7.1	10.2	5.0	5.3
7.2			5.7	6.5
10.8			7.0	8.6

Table 21.3 Effect of extraction on dielectric properties at 65% r.h. and 1 kHz [2]

Material	Density of packing (%)	Unextracted		Extracted	
		Relative permittivity	Power factor	Relative permittivity	Power factor
		ϵ_m	$\cos \phi$	ϵ_m	$\cos \phi$
Nylon	50	2.34	0.054	2.43	0.063
Acrylic fibre <i>Orlon</i>	40	2.28	0.123	1.73	0.0044
Acrylic fibre <i>Acrilan</i>	50	2.00	0.076	1.94	0.043
Polyester fibre <i>Dacron</i>	50	39.4	0.773	1.66	0.007

these results are based is of doubtful validity. At 3 GHz, Shaw and Windle [3] found that the relative permittivity of dry wool fibres was 3.88 ± 0.15 with the electric field parallel to the fibre axis and 4.41 ± 0.11 with the electric field perpendicular to the fibre axis.

The presence of impurities would be expected to alter the dielectric properties; in particular, ionic impurities would probably have a considerable effect at low frequencies. Table 21.3 shows the effect of the removal of surface dressings from some synthetic fibres by extraction in methanol and benzene. Only with the polyester fibre was there a large change, which was probably due to the removal of an anti-static finish, in the values obtained.

21.8 Summary of results for various materials

Tables 21.4, 21.5 and 21.6 summarise results for various materials at frequencies ranging from supply frequencies (50 Hz) to optical frequencies (10^{15} Hz). The figures given by Hearle [2] are extrapolated linearly through $\epsilon_r = 1$ at $P = 0$, and the experimental point is found with maximum density of packing of the yarns, $P\%$: this will give values that are too low, but they are useful for comparative purposes. The cellulosic fibres have the highest permittivity, these being followed by the protein fibres, with the synthetic non-hygroscopic fibres having the lowest values. The power factors follow a similar order.

Table 21.4 Permittivities obtained by Hearle [2]

Material	Extrapolated from P%	Relative permittivity			
		0% r.h.		65% r.h.	
		1 kHz	100 kHz	1 kHz	100 kHz
Cotton	44	3.2	3.0	18	6.0
Viscose rayon staple fibre	44	3.6	3.5	8.4	5.3
Viscose rayon c.f.	73			15	7.1
Acetate staple fibre	45	2.6	2.5	3.5	3.3
Acetate c.f.	79			4.0	3.7
Wool	53	2.7	2.6	5.5	4.6
Nylon staple fibre	53	2.5	2.4	3.7	2.9
Nylon c.f.	87			4.0	3.2
Acrylic staple fibre <i>Orlon</i>	42	2.8	2.3	4.2	2.8
Acrylic staple fibre <i>Orlon</i> (extracted)	38			2.8	2.5
PVC staple fibre <i>Vinyon</i>	46	2.7	2.5	3.0	2.6
PCVD <i>Saran</i> c.f.	70	2.9	2.4	2.9	2.4
Polyester staple fibre <i>Dacron</i> (extracted)	48	2.3	2.3	2.3	2.3
Glass <i>fiberglass</i> c.f.	63	3.7	3.4	4.4	3.6

c.f. = Continuous-filament yarn

Table 21.5 Other values of dielectric properties

Material	Frequency	Moisture regain (%)	Relative permittivity	Power factor	Reference
Cellophane film	60 Hz	0	7.7	0.009	15
	10 kHz	0	7.3	0.016	15
	1 MHz	0	6.7	0.062	15
	3000 MHz	0	4.04		3
Wool	8 kHz	0	5.4		11
	60 kHz	0	4.4		11
	120 kHz-13 MHz	0	4.2		11
	3000 MHz	0	3.70	0.030	13
	9300 MHz	0	3.54	0.019	13
	26 000 MHz	0	3.4	0.0.15	14
	3000 MHz	12	4.99	0.146	13
	9300 MHz	12	4.44	0.076	13
26 000 MHz	12	4.1	0.068	14	
Keratin film	500 Hz	0	5		20
	11 kHz	0	4.5		20
	1 MHz	0	4		20
	500 Hz	12	9		20
	11 kHz	12	7.5		20
	1 MHz	12	5.5		20
Nylon	10 kHz	0	4.2		11
	500 kHz	0	3.26		11
	10 MHz	0	3.15		11
	3000 MHz	2	3.13		3
Nylon film	11 kHz	0	4		21
	11 kHz	4	8		21

Table 21.6 Relative permittivity at optical frequencies

Fibre	$\epsilon_r = 2$ with light vibration:	
	Parallel to fibre axis	Perpendicular to fibre axis
Cotton	2.50	2.34
Viscose rayon	2.37	2.31
Acetate	2.19	2.16
Wool	2.40	2.37
Casein	2.37	2.37
Nylon	2.50	2.31
Polyester fibre <i>Terylene</i>	2.96	2.37
Acrylic fibre <i>Orlon</i>	2.25	2.25
Polyethylene	2.43	2.28
Glass	2.40	2.40

* From refractive indices in Table 24.3

21.9 References

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22.1 Introduction

When electricity was first intentionally conducted from one place to another (from an electrified tube to an ivory ball) by Stephen Gray in 1729, the material used as the conductor was hempen pack-thread. Gray eventually covered distances of up to 233 m along the corridors of his house. In order to do this, he had to support the pack-thread and, after an abortive attempt in which fine copper wires were used, he suspended the thread by silk filaments. Thus both the conductor and the insulator were textile fibres. Soon afterwards, Du Fay found that pack-thread was a better conductor when it was wet. Then, in 1734, Gray discovered metallic conductors, and, apart from some use for insulating purposes, interest in the electrical resistance of fibres did not revive for nearly 200 years [1].

22.2 Definitions

The electrical resistance of a specimen, i.e. the voltage across the specimen divided by the current through it, is determined both by the properties of the material and the dimensions of the specimen. For most substances, the property of the material is best given by the specific resistance ρ (in Ω m), which is defined as the resistance between opposite faces of a 1 m cube, but, as with mechanical properties (see [Section 13.3.1](#)), it is more convenient with fibres to base a definition on linear density (mass per unit length) than on area of cross-section. A *mass-specific resistance* R_s is therefore defined as the resistance in ohms between the ends of a specimen 1 m long and of mass 1 kg, giving units of Ω kg/m². The two quantities are related as follows:

$$R_s = \rho d \quad (22.1)$$

where d = density of material in kg/m³.

In practice, it is more convenient to express R_s in Ω g/cm², when the numerical values for most fibres will differ by less than 50% from the values of ρ expressed in Ω cm. With these units, the resistance R of an arbitrary specimen is given by the relation

$$R = R_s \frac{l}{NT} \times 10^5 \quad (22.2)$$

where l = distance between the ends of the specimen in cm, N = number of ends of yarn or fibre and T = linear density of yarn or fibre in tex.

Because of the wide range of resistance values, results are frequently expressed in terms of the logarithm of resistance.

22.3 Methods of measurement

22.3.1 Measurement of resistance

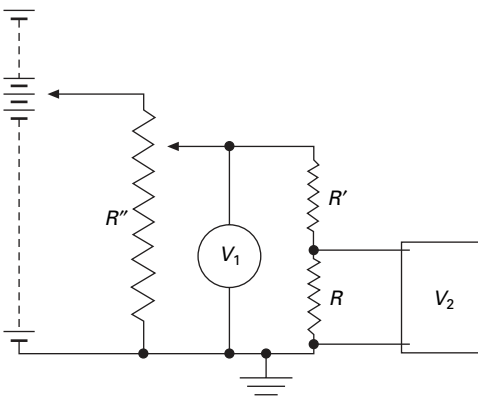
Ideally, the resistance should be measured accurately, instantaneously and at a constant voltage. The difficulties of doing this are increased by the high values of resistance that have to be measured and the wide range that is covered. A variety of methods has been used [1].

The simplest method of measurement is the use of an ammeter in series and a voltmeter across the resistance. This can be done when the resistance of the material is low. With a sensitive galvanometer, the method has been used for resistances up to $10^9 \Omega$, but the time taken for the galvanometer to come to rest may be a disadvantage. Wheatstone bridge methods may also be used for fairly low resistances. The charging or discharging of a capacitor through the resistance is a method of measurement of high resistance. The general relation for the charge Q on a capacity C to which a voltage V_0 has been applied through a resistance R for a time t is:

$$Q = V_0 C (1 - e^{-t/CR}) \quad (22.3)$$

For the capacity discharging, $Q = V_0 C e^{-t/CR}$. Various arrangements may be used to apply these relations, but they all suffer from the defects that the test must last for a measurable time and that the voltage varies during the test.

With high-resistance stable resistors, comparison methods can be used. Fig. 21.1 shows the circuit used by Hearle [2]. The voltage V_1 can be measured by a low-resistance voltmeter. The voltage V_2 must be measured by a voltmeter whose resistance is much greater than that of the unknown resistance R . The resistance to be measured is given in terms of the standard resistance R' by the relation



22.1 Circuit for measurement of high resistances.

$$R = R' \left(\frac{V_2}{V_1 - V_2} \right) \quad (22.4)$$

By this method, high resistances can be measured quickly with a known voltage V_2 adjustable by the potentiometer R'' across the specimen. Hersh and Montgomery [3] used a slightly more complicated circuit in a null method, which does not require such a high-resistance detector.

In measuring high resistances, great care must be taken to avoid the pick-up of stray voltages, which necessarily take a long time to discharge.

22.3.2 Arrangement of specimens

Many different arrangements of the material to be tested have been used [1]. The resistance has been measured along single fibres, along many fibres in parallel, along single ends of yarn, along many ends in parallel, parallel to the weft and parallel to the warp in cloth, across yarn and across cloth, and with special electrodes, such as those of the Shirley Moisture Meter (see [Section 7.3.5](#)).

In most of his experiments, Hearle [2, 4] used yarn wound on a polythene former and then held between bulldog clips, lined with tinfoil, 1 cm apart. Hersh and Montgomery [3] stuck fibres or pieces of yarn onto brass tabs with silver conducting paint.

The specimens must be conditioned by being placed in a suitable atmosphere. A simple conditioning chamber is satisfactory for work at constant temperature. Hearle [2] used a glass jar containing saturated salt solutions to control humidity. Leads were brought out through a tight-fitting stopper. A sample of the fibre was suspended in the jar and removed to measure moisture content. Alternatively, the resistance may be measured immediately after removal of the specimen from the conditioning atmosphere.

Securing constant moisture conditions at different temperatures is more difficult. The most satisfactory method is to enclose the specimen in a space so small that no appreciable evaporation can take place, which thus keeps the moisture content constant. Hearle [5] sealed specimens between sheets of rubber, brought out fine copper leads, and immersed the whole in a bath of paraffin.

22.4 Results of experiments

22.4.1 The influence of moisture

Moisture is the most important factor in determining the resistance of most textile materials and causes a variation over a range of at least 10^{10} times. Even the difference between 10 and 90% r.h. will cause a million-fold difference of resistance, namely, a tenfold decrease in resistance for every 13% increase in relative humidity.

For most hygroscopic textile fibres between 30 and 90% r.h., relations of the following form hold:

$$\log R_s = -n \log M + \log K \quad (22.5)$$

$$R_s \cdot M^n = K \quad (22.6)$$

where M = moisture content (%), and n and K are constants.

When plotted over a wider range of moisture conditions, a sigmoidal relation between $\log R_s$ and $\log M$ is obtained (Fig. 22.2). At low moisture contents (below 3.5% for cotton, 7% for viscose rayon and 4% for wool and silk), the following form fits the results:

$$\log R_s = -n' M + \log K' \quad (22.7)$$

where n' and K' are constants. A relation of this form was also found to fit the results for acetate and some specimens of nylon [6].

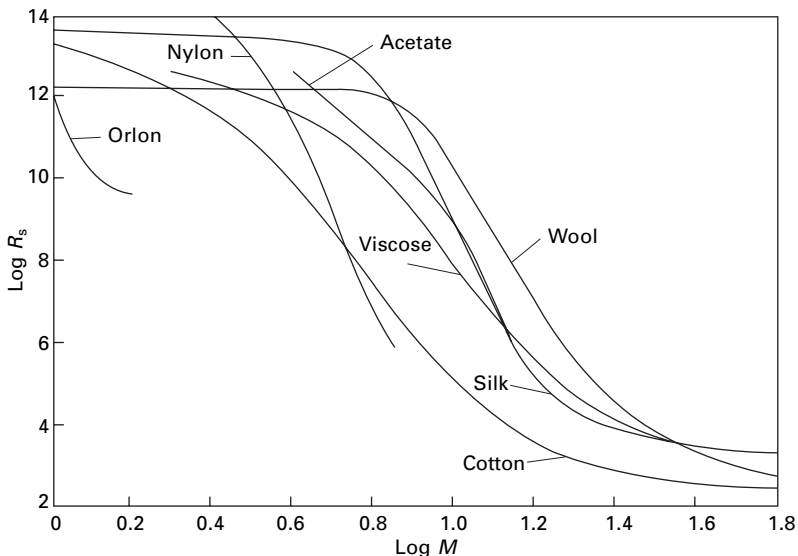
The resistance of a specimen at constant temperature has been found to be a single-valued function of moisture content, no hysteresis being detectable. It follows that there must be hysteresis between resistance and humidity. Nevertheless, for a given part of the hysteresis loop, relations of the following form are found to fit the experimental data fairly well:

$$\log R_s = -aH + b \quad (22.8)$$

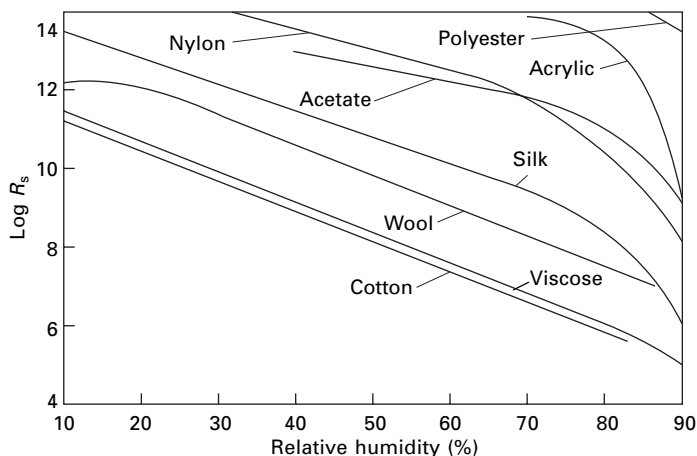
where H = relative humidity, and a and b are constants.

22.4.2 Comparison of different materials

Figure 22.2 shows results for various materials plotted in terms of moisture content; Fig. 22.3 shows them in terms of relative humidity. Table 22.1 gives values of $\log R_s$ at 65% r.h., and of n and $(\log K - n)$. The latter quantity, which is equal to the value of $\log R_s$ at $M = 10\%$, is more useful for comparative purposes than the value of \log



22.2 Variation of resistance of fibres with moisture content [2, 6].



22.3 Variation of resistance of fibres with relative humidity [2, 7].

Table 22.1 Electrical resistance results, along yarn [2, 6, 7]

Material	n	$(\log K - n) = \log R_s$ at $M = 10\%$	$\log R_s$ at 65% r.h.	r.h. % for $R_s = 10^{10} \Omega \text{ g/m}^2$
Cotton	11.4	5.3	6.8	30
Washed cotton	10.7	6.0	7.2	30
Mercurised cotton	10.5	6.8	7.2	30
Flax	10.6	6.8	6.9	30
Viscose rayon	11.6	8.0	7.0	30
Washed viscose rayon	12.0	9.0	7.5	30
Acetate		9.0	11.7	85
Silk	17.6	9.0	9.8	65
Wool	15.8	10.4	8.4	55
Washed wool	14.7	11.9	9.9	60
Nylon			9–12	85
Orlon acrylic fibre (as received)			8.7	85
Purified Orlon acrylic fibre			14	95
Terylene polyester fibre (as received)			8.0	85
Purified Terylene polyester fibre			14	95

K , which has to be obtained by extrapolation and is greatly affected by any error in the value chosen for n . Table 22.2 gives values of n' and $\log K'$ obtained at low moisture contents.

The values of n for the different cellulosic fibres are very nearly the same. Hearle [2] found that they can all be fitted with reasonable accuracy by the relation:

$$\log R_s = -11.2 \log M + \log K \quad (22.9)$$

where the value of $\log K$ can be found by measuring the resistance at one moisture content.

Table 22.2 Electrical resistance results: low moisture contents [8]

Material	n'	$\log K'$	Upper limit of relation, $M\%$	Lower limit of tests, $M\%$
Cotton	1.90	16.0	3.5	1.3
Viscose rayon	0.47	13.6	7	2.2
Wool	0	12.7	4	0
Silk	0.15	13.9	4	1.4
Acetate [6]	0.72	16.5	> 12	4

Within the limits of experimental error, Hearle found no difference between 12 different cottons (two American, five Pakistani, two Egyptian, Brazilian, Tanguis and Uganda). A comparison of the results for cotton and viscose rayon shows that they are in reasonable agreement with the assumption that the conduction is in the non-crystalline region of the fibre, which will have a resistance determined by its own moisture content. Cellulose acetate shows a rather high resistance when considered in terms of either moisture content or relative humidity.

The protein fibres have larger values of n (between 16 and 18 in most cases), and, except at very low moisture contents, they have a much higher resistance than the cellulosic fibres. The change in resistance with moisture content at low moisture contents becomes very small, and in wool it is almost non-existent.

There is a wide variation, depending on their history and the presence of additives, in the resistance of different specimens of nylon. Nylon has a high resistance at a given humidity, but, when plotted against moisture content, the resistance values fall below those of viscose rayon. The curves of $\log R_s$ against $\log M$ show no linear portion. It has been shown by Sharman *et al.* [9] that the resistance of nylon increases as the draw-ratio increases; they consider that the change is greater than would be explained by a change of regain.

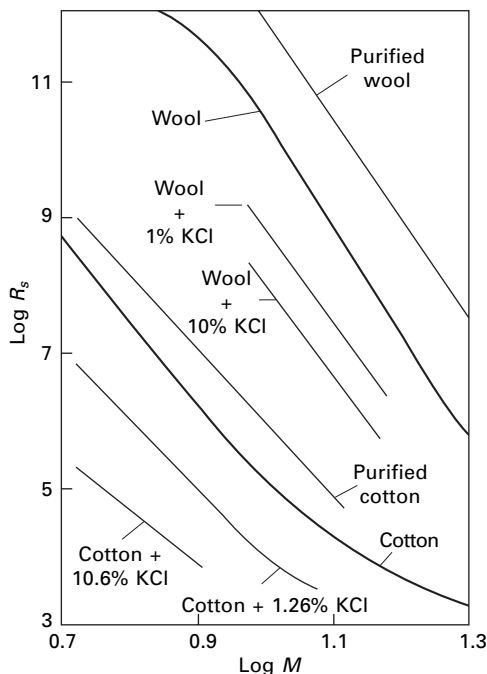
The acrylic fibres show a low resistance at a given moisture content, and at a given relative humidity they may even have a resistance as low as that of wool.

Fibres such as polyester or vinyl fibres, which absorb little water, all have very high resistances. Their resistances decrease at a rate of about ten times for every 10% increase in relative humidity up to about 80% r.h.; above this humidity, the resistance decreases more rapidly. However, for these fibres, anti-static finishes are commonly applied to lower the resistance, as indicated by the million-fold increase in the resistance on removing finish from the polyester fibre in Table 22.1.

The high-modulus, high-tenacity (HM-HT) polymer fibres are inherently good insulators, though there is some effect of moisture in aramid fibres. Glass and ceramic fibres are also good insulators. Surface finishes can, of course, cause a modification of properties. Carbon fibres are fairly good conductors of electricity, with a resistivity of about $15 \Omega \text{ m}$.

22.4.3 Effect of impurities

The resistance of the hygroscopic fibres depends on their electrolyte content, as is illustrated by the results for cotton and wool in Fig. 22.4. The addition of a salt such



22.4 Resistance of wool and cotton as received, purified, and with added electrolyte [2].

as potassium chloride lowers the resistance. At low salt contents, the evidence indicates that conductivity is approximately proportional to electrolyte content, but, at high salt contents (greater than 1%), O'Sullivan [10] found that the resistance of cellulose film at a given moisture content was independent of the nature or amount of salt present.

Washing in distilled water increases the resistance, and a further increase may be obtained by washing in calcium sulphate solution. Walker and Quell's results [11] show the increase in resistance between raw cotton (0.4% of sodium and potassium salts) and washed cotton:

	R_s , $M\Omega$ g/cm ²
raw cotton	0.5
after washing 200 g in 5 litres distilled water	14
after washing 200 g in 40 litres distilled water	12–25
after washing in CaSO ₄ solution followed by distilled water	18–37

The action of the calcium sulphate solution is to replace the monovalent ions left behind after washing in distilled water by less conducting bivalent ions (see [Section 22.5.3](#)). The residual ions are probably associated with ionic groups in the fibre molecule, for example, carboxyl (—COO—) groups present as impurities in cellulose molecules. Church [12] found that, when hydrogen ions were replaced by calcium ions in paper, the resistance increased six times.

Any wet processing, such as bleaching or dyeing, that alters the electrolyte content will alter the electrical resistance. The resistance of the synthetic fibres is much affected by the presence of surface finishes. For example, Hayek and Chromey [13] found a reduction of 10 000 times by a suitable anti-static agent.

Boyd and Bulgin [14] have shown that, when about 30% of carbon black is included in viscose rayon fibres, their specific resistance at 0% r.h. falls from between 10^{14} and $10^{15} \Omega \text{ cm}$ to less than $10^6 \Omega \text{ cm}$. This must be due to the presence of a continuous conducting path of carbon black. With increase of humidity, the resistance increases slightly, presumably owing to a greater dispersion of the carbon black. There is also a change with humidity in the critical concentration of carbon black at which the resistance begins to drop markedly: this rises from 26% carbon black in the dry state to 30% at saturation.

22.4.4 Effect of temperature

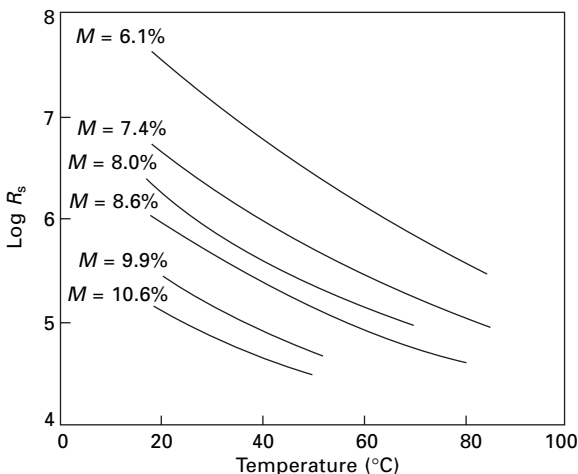
The resistance of fibres decreases as the temperature increases, a rise of 10°C causing a fall of the order of five times. A typical set of results is shown for cotton in Fig. 22.5.

For cotton, viscose rayon and wool, Hearle [5] found that the rate of change of $\log R$ with temperature varied separately with moisture content M and temperature $\theta^\circ \text{C}$.

$$\frac{-d(\log R)}{d\theta} = a - bM - c\theta \quad (22.10)$$

where a , b and c are constants for a given material. Values of a , b and c are given in Table 22.3. The value of a gives the rate of change of $\log R$ with temperature under dry conditions at 0°C , and the values of b and c give the change of $d(\log R)/d\theta$ with moisture content and temperature, respectively.

Clark and Preston [15] have found that the same equation fits the results for



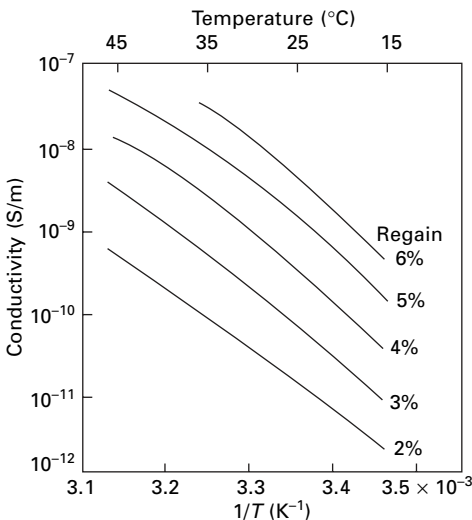
22.5 Variation of resistance of cotton with temperature [5].

Table 22.3 Values of a , b and c [5]

Material	a (per deg C)	b (per deg C per unit moisture content)	c (per deg C per deg C)
Cotton	0.0863	0.005 35	0.000 35
Viscose rayon	0.0707	0.001 86	0.000 37
Wool	0.0960	0.002 12	0.000 57
Acetate*	0.0528	0.000 80	0.000 25
Silk†	0.0934	0.002 87	0.000 82

*Only tested over small range.

†Near 20 °C and 10% moisture content.



22.6 Variation of conductivity of drawn nylon with temperature [9].

viscose rayon at 24.5% regain down to -60°C . For silk, a relation of the above form is not strictly accurate. For nylon at 20°C and 6% moisture content, it was found that $d(\log R)/d\theta = 0.05$ per $^{\circ}\text{C}$. Sharman *et al.* [9] found that curves of \log (conductivity) against the reciprocal of temperature were approximately parallel at different regains, as is shown in Fig. 22.6.

22.4.5 Arrangement of specimen

One would expect the specific resistance of fibres to vary with the direction of measurement, but, owing to the experimental difficulties, no values for the transverse specific resistance of fibres are available. O'Sullivan [10] found that the resistance of cellulose film parallel to the direction of extrusion was 0.8 times that perpendicular to the direction of extrusion. Hearle and Jones [16] found that the ratios of resistances with three different electrode systems varied with the material and the moisture

content, which indicated that the ratios of specific resistances in different directions varied with these factors.

All the results in the literature, except for those in one paper [17], indicate that the experimentally obtained specific resistance of fibres is independent of the dimensions and form of the specimen. In other words, there is no composite specimen effect, and the resistance of a specimen is proportional to its length and inversely proportional to its area of cross-section (or mass per unit length). This relation will break down if the contact resistance between electrode and specimen becomes comparable with the resistance of the specimen.

Hersh and Montgomery [3] tested nylon specimens ranging in linear density from 3 to 340 den (from 0.33 to 38 tex) and showed that they all gave the same specific resistance. Hearle [4] found only a very small change in resistance when cotton and viscose rayon were subjected to tensions up to near their breaking point.

22.4.6 Polarisation and related effects

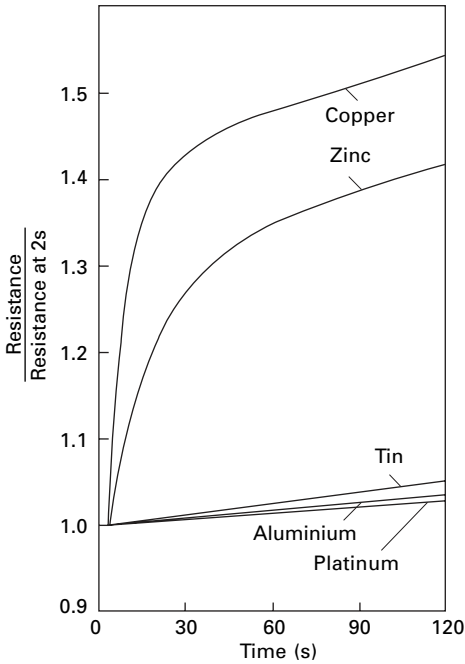
If polarisation, whether electrolytic or electrostatic, causes a back electromotive force (e.m.f.) to occur, it will be detectable in three ways: the resistance will increase with time as the back e.m.f. develops; the resistance will decrease with voltage; and the back e.m.f. will be present, dying away, after the applied voltage has been removed.

Several workers have found that the variation of resistance with time is undetectable or very slight, except at low and high humidities. For raw cotton with tin electrodes, Hearle [4] obtained a significant variation of resistance with time only above 90% r.h. At 17.4% moisture content, the resistance doubled in 30 s. With cotton containing added potassium chloride, the resistance increased with time down to below 50% r.h. With one specimen of wool, the resistance remained constant even at 27% moisture content, but, with another specimen, there was an increase of 7% per minute at 17% moisture content. The nature of the electrodes is an important factor in polarisation effects. The curves in Fig. 22.7 show that, at 9.3% moisture content, the resistance of cotton between copper and zinc electrodes increases rapidly with time, but that, with tin, aluminium, or platinum electrodes, it changes only very slowly. Jones [18] found that a large stainless-steel anode was most effective in eliminating polarisation. On ashing polarised cotton fibres, Williams and Murphy [19] found most of the ash near the electrodes.

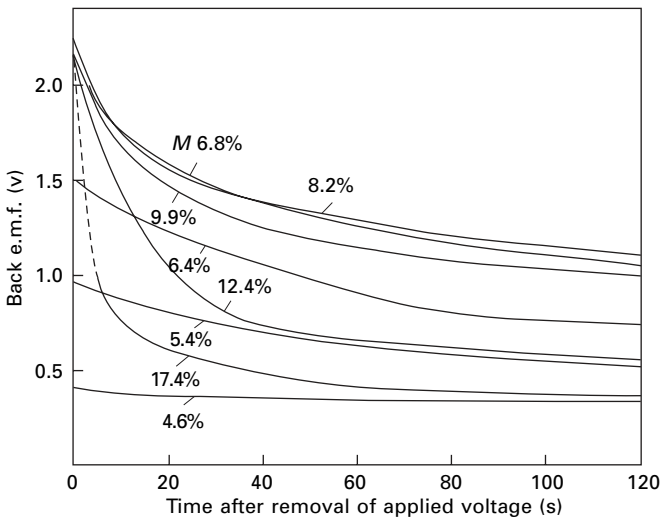
The above effects are typical of polarisation as it occurs in electrolytic solutions, when it is most marked if there is a rapid discharge of ions at the electrodes. It is due to the prevention of the rapid attainment of equilibrium by a slow process at the electrode and is much affected by the nature of the electrodes.

Other effects, such as heating, which will change the temperature and may cause drying, and the transport of water or ions in the specimen, have been suggested as a cause of variation of resistance with time. Although it is likely that these effects may be appreciable in some conditions, they have never been definitely observed.

Back e.m.f. of the order of 2 V has been found by Hearle [4] and others. A set of results for cotton is shown in Fig. 22.8. At low moisture contents, there is only a small back e.m.f. As the moisture content increases, the back e.m.f. also increases



22.7 Variation of resistance of cotton with time for various electrodes [4]. Moisture content = 9.3%.



22.8 Back e.m.f.s in cotton, at various moisture contents, after applying 122 V for 1 min [4].

and reaches a value of about 2 V at 7% moisture content. At higher moisture contents, the back e.m.f. remains the same, but above 9% moisture content it dies away more rapidly after the removal of the applied voltage. The value of the back e.m.f. was found to be different with electrodes of different metals.

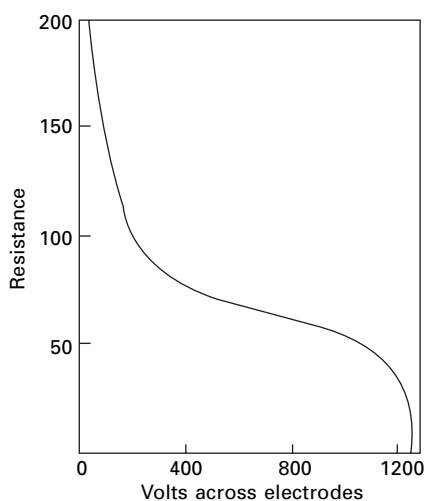
Polarisation effects have also been reported below 25% r.h. for cotton and wool. Murphy [20], working with cotton, found that, under these conditions, the back e.m.f. varied with the applied voltage, and he obtained values of over 100 V. This behaviour indicates electrostatic polarisation.

The variation of resistance with voltage in fibres was observed by Evershed [21] in 1913. Fig. 22.9 shows a typical result for cotton. The decrease of resistance with voltage up to 50 V is adequately explained by the presence of a back e.m.f. of the order of 2 V (Fig. 22.10). Similar effects are observed with other fibres, though with wool the resistance does not vary with voltage below 80% r.h.

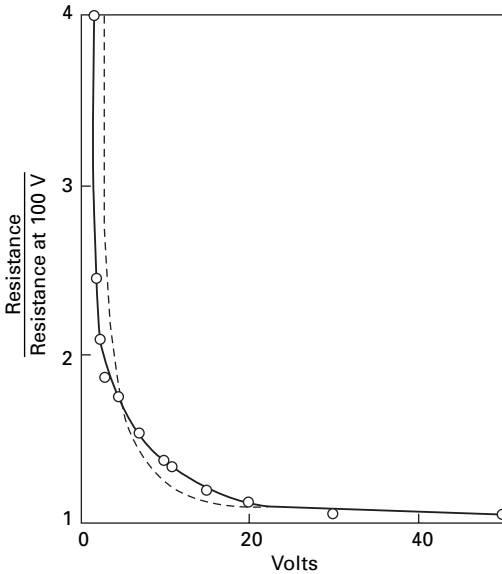
The continuing decrease at higher voltages found by Evershed and others is greater than that due to a small back e.m.f. By testing specimens of various lengths, Hearle [4] showed (Fig. 22.11) that the specific resistance depended on the average field strength (or what comes to the same thing, the current density) rather than on the actual applied voltage.

Hersh and Montgomery [3] have found the resistance of cotton yarns to be ohmic in the range 50–2000 V. However, Cusick and Hearle [22] have suggested that this is because they allowed some time to elapse before measuring the resistance, and consequently an increase of resistance with time fortuitously masked the decrease with voltage. In a later comment, Hersh and Montgomery [23] have suggested that the change in resistance is due to a heating of the specimen. This would be influenced by the air velocity in the neighbourhood of the specimen.

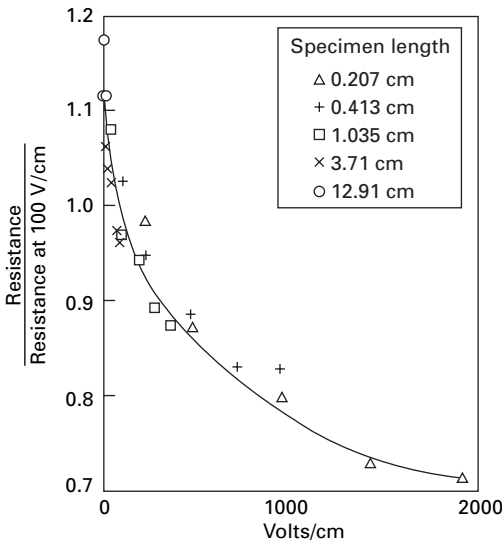
Cusick and Hearle [22] also found that the rate of change of resistance of cotton with time increased as the voltage increased, as shown in Fig. 22.12. When the specimen is left with no voltage applied, the resistance recovers at a similar rate to its previous increase.



22.9 Variation of resistance of cotton with applied voltage. After Evershed [21].



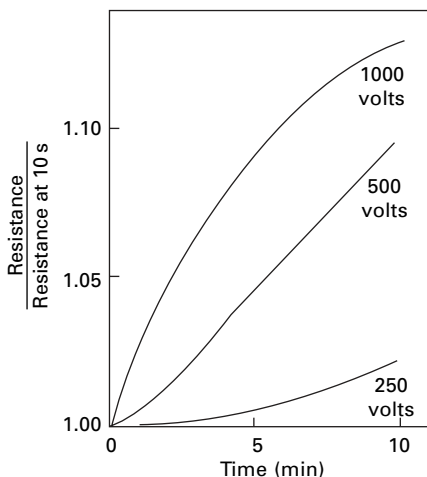
22.10 Variation of resistance of cotton (moisture content = 6.4%) with applied voltage up to 50 V. The dotted line is the theoretical curve for a back e.m.f. of 2 V [4].



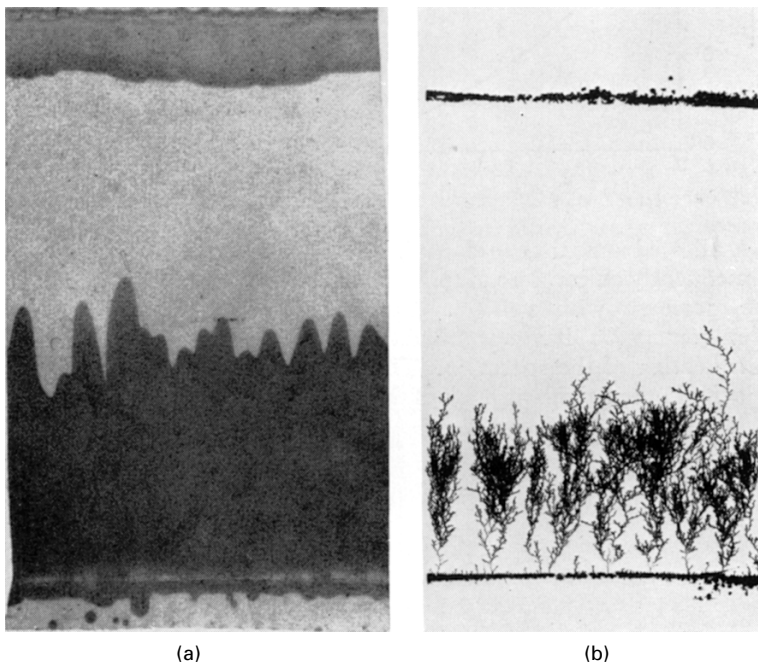
22.11 Variation of resistance with field strength. The points are four specimens of various lengths [4].

22.4.7 Electrolytic effects

During conduction in cellulose film impregnated with salts, O’Sullivan [24] observed phenomena similar to those occurring in the electrolysis of salt solutions. When the film is soaked in sodium chloride, an acid region develops at the anode and an



22.12 Effect of voltage on change of resistance of cotton with time [22].



22.13 Electrolytic effects during conduction in cellulose film. (a) Film impregnated with sodium chloride and an indicator, showing acid and alkaline regions at electrodes. (b) Film impregnated with silver nitrate, showing deposition of silver at cathode and entry of copper at anode.

alkaline region at the cathode. Figure 22.13(a). With silver nitrate in the film, ‘treeing’ occurs (Fig. 22.13(b)) as the silver is deposited at the cathode. The conditions are just those which would cause ‘treeing’ in electroplating (high potential gradient, unstirred bath and low conductivity) and, as in electroplating, it may be avoided by using potassium silver cyanide instead of silver nitrate.

King and Medley [25] measured the amount of hydrogen liberated during conduction in keratin film and found that it was about 90% of that expected from the quantity of electricity passed. There were also small quantities of oxygen and carbon dioxide from the anode reactions.

O'Sullivan [26, 27] measured the bulk mobilities of ions in cellulose film. Typical results are given in Table 22.4.

22.4.8 Resistance noise

Owing to the arrival of current in discrete charges, there is a variable component in direct current. This gives rise to resistance noise, which is one of the factors limiting the amplification of small signals. The magnitude of these random fluctuations has been worked out by Schottky [28] for current carried by electronic charges.

Boyer [29], working with films of various polymers, including cellulose and nylon, has found that the noise level is much higher than that given by Schottky's formula and that the noise has a frequency distribution characteristic of the particular polymer. He concludes that this is due to the arrival of ions at the electrodes in 'avalanches', owing to their being held up at places in the polymer until some movement of the structure allows them to continue to flow.

22.5 Theoretical

22.5.1 Nature of the conduction

In a consideration of the mechanism of conduction of electricity, the first questions to be answered are: 'Where is the current flowing?' and 'What is carrying the current?' Both of these problems have to be solved mainly by circumstantial evidence.

Hersh and Montgomery [3] have shown that for nylon filaments the resistance is inversely proportional to the area of cross-section. This indicates that conduction is predominantly a volume effect, with the current flowing through the bulk of the material. If conduction had been a surface effect, the resistance would have been inversely proportional to the circumference (i.e. the square root of the area or cross-

Table 22.4 Bulk mobility of ions in cellulose film [26, 27]

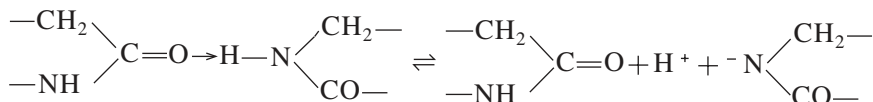
Ion	Mobility in $\text{cm}^2 \text{s}^{-1} \text{V}^{-1}$ at moisture content of:			
	10%	20%	30%	40%
H^+	3×10^{-8}	4×10^{-6}	2.5×10^{-5}	8×10^{-5}
OH^-	1.6×10^{-8}	1.6×10^{-6}	8×10^{-6}	2.5×10^{-5}
K^+	3×10^{-6}	6×10^{-7}	3×10^{-6}	6×10^{-6}
Ag^+	1.6×10^{-7}	4×10^{-6}	1.3×10^{-5}	2.5×10^{-5}
Cl^-	3×10^{-9}	8×10^{-7}	8×10^{-6}	2×10^{-5}
Fe^{2+}		2.5×10^{-7}	1.3×10^{-6}	1×10^{-5}
Cu^{2++}		2.5×10^{-8}	1×10^{-6}	5×10^{-6}
$\text{SO}_4^{2--}, \text{CrO}_4^{2--}$		2×10^{-7}	2.5×10^{-6}	1×10^{-5}
Ca^{2++}				5×10^{-7}

section). Different types of cotton also have the same specific resistance, though here the range of fineness covered is smaller; different qualities of wool differ to an appreciable extent only at low moisture contents, when the influence of impurities is great. Indirect evidence that conduction is a volume effect is provided by the lack of hysteresis between resistance and moisture content (which is a volume, not a surface, quantity), despite the hysteresis between moisture content and relative humidity. Thus, in the hygroscopic fibres, it appears that volume conduction is the dominant effect, surface conduction being negligible in comparison.

Both the close association between resistance and moisture content and the relation between the resistances of cotton and viscose rayon indicate that the current will be flowing in the non-crystalline regions of the fibre. Indeed, the ordered arrangements of cellulose molecules in a crystalline region would be expected to be highly insulating.

In the synthetic fibres, with higher resistance and negligible moisture absorption, surface conduction is likely to be more important and may be the dominant mechanism. Certainly when conducting surface finishes are applied, the current will be almost entirely on the surface.

Current may be carried either by electrons or by ions. Baxter [30], in 1943, put forward a theory that conduction in wool was by electrons, the water molecules acting as impurity centres in an electronic semiconductor, but most workers have assumed that conduction is by ions. Where the products of electrolysis have been directly observed by O'Sullivan [24], using cellulose film, and by King and Medley [25], using keratin film, the current must be ionic. The variation of resistance with electrolyte content and the polarisation effects also support this view. Thus, where there is evidence, it indicates that conduction is ionic, but, where there is no special evidence (for example, at low moisture contents), it cannot be definitely stated that conduction is not electronic. A specialised mechanism that Baker and Yager [31] have suggested for the polyamides is the mobility of hydrogen atoms (protons) from hydrogen bonds. This can, however, be regarded as equivalent to other forms of ionic conduction, since it is essentially an ionisation at the hydrogen bond:



With the possible exceptions noted above, the general picture is of ionic conduction taking place through the bulk of the material. The next step is to consider theories that will explain the enormous variation of resistance with moisture content, the large variation with temperature, and other effects, such as the higher resistance of protein fibres and the low conductivity of bivalent ions. There are two possible causes of variation of resistance: there may be changes in the number of ions available for conduction or there may be changes in the rate at which the ions move through the material under a given applied voltage.

For a specimen having ν ions per unit length available for conduction, with z as the valency of the ions and e as the electronic charge, and on the assumption that the ions move with an average velocity u under a potential difference V between the ends of the specimen, the current I and resistance R are given by:

$$I = vzeu \quad (22.11)$$

$$R = \frac{V}{I} = \frac{V}{vzeu} \quad (22.12)$$

For further study, it is convenient to separate the factors by taking logarithms:

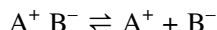
$$\log R = \log V - \log v - \log ze - \log u \quad (22.13)$$

22.5.2 Influence of permittivity on dissociation of ion pairs

There has been no success in attempting to explain the enormous changes of resistance with moisture content on the basis of changes in rate of ion movement. The most likely theory, proposed by O'Sullivan [32] and based on breaks in conducting water paths, was shown by Hearle [33] to be impossible because of the polarisation that would occur. For a successful theory, we must look to changes in the number of available ions.

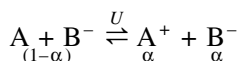
Strong electrolytes are completely ionised, and the ions can be held together in molecules only by electrostatic forces. In solutions in liquids of high permittivity, such as water, these forces are so weak that there is no close association of ions, but even weak inter-ionic forces prevent the ions from acting as completely free particles.

If the permittivity of the solvent is lower, the electrostatic forces will be stronger, and we may consider an equilibrium between ion pairs and free ions

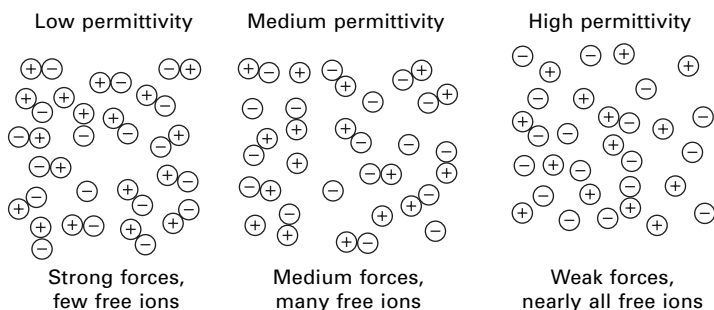


The variation in this equilibrium offers a possible explanation of variations in resistance. A rise in permittivity would cause more dissociation, making more free ions available for conduction and consequently lowering the resistance. This is illustrated diagrammatically in Fig. 22.14.

A simplistic theory, which applies macroscopic ideas to molecular phenomena and does not take account of the interaction of all the ions present, has been put forward by Hearle [33]. Let α be the degree of dissociation of the ion-pairs:



It can be shown that, as a consequence of the Law of Mass Action:



22.14 Effect of permittivity on association of ions.

$$\frac{\alpha^2}{1 - \alpha} = A e^{-U/kT} \quad (22.14)$$

where U = the energy of dissociation, k = Boltzmann's constant, T = absolute temperature and A = a constant, of the order of the ratio of the total volume to the volume occupied by ions.

The energy needed to separate two electrostatic charges in a medium of relative permittivity ϵ_r is given by:

$$U = \frac{U_0}{\epsilon_r} \quad (22.15)$$

where U_0 = the energy needed to separate the ions in a medium of unit relative permittivity and is thus a constant. Hence:

$$\frac{\alpha^2}{1 - \alpha} = A e^{-U_0/\epsilon_r kT} \quad (22.16)$$

If $\alpha \ll 1$, that is when most of the ions are associated in pairs:

$$\frac{\alpha^2}{1 - \alpha} \approx \alpha^2 \quad (22.17)$$

Hence:

$$\alpha = A^{1/2} e^{-U_0/2\epsilon_r kT} \quad (22.18)$$

But, if v_0 is the total number of electrolyte molecules per unit length of specimen, then the number of ions available for conduction is given by:

$$v = 2 \alpha v_0 \quad (22.19)$$

and, substituting in equation (22.13), we get:

$$\begin{aligned} \log R &= \log \frac{V}{uz e} - \log \alpha - 2 \log v_0 \\ &= \log \frac{V}{2 A^{1/2} uz e v_0} + \frac{U_0 \log e}{2 k T} \frac{1}{\epsilon_r} \end{aligned} \quad (22.20)$$

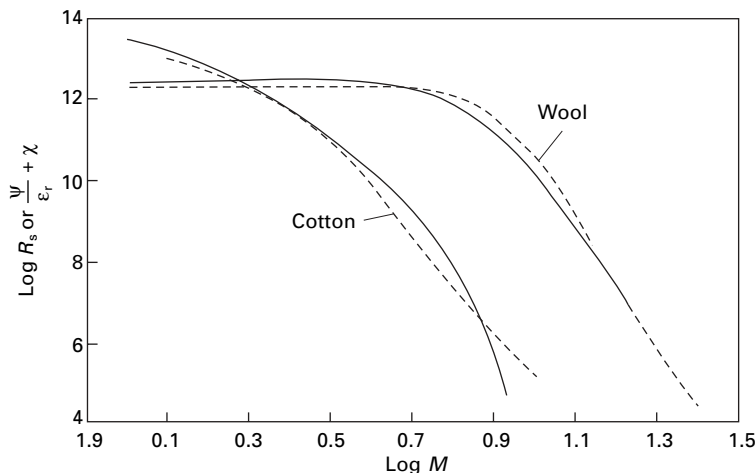
This may be written:

$$\log R = \frac{\Psi}{\epsilon_r + \chi} \quad (22.21)$$

where $\Psi = (U_0 \log e)/(2 k T)$ and $\chi = \log (V/2 A^{1/2} u z e v_0)$.

After suitable values for Ψ and χ have been chosen, equation (22.21) can be tested with experimental results. Figure 22.15 shows a comparison of Hearle's values of resistance with theoretical predictions in which Balls's values [34] of the permittivity of cotton and King's values [35] of the permittivity of keratin film have been used. For cotton, there is a good fit with $\Psi = 76.8$ and $\chi = 1.1$ and for wool with $\Psi = 42.2$ and $\chi = 3.6$. The coincidence of the bending-over of the curve for wool is particularly striking.

From the value chosen for Ψ , the values of U_0 can be calculated. With $\Psi = 76.8$



22.15 comparison of experimental (full lines) and theoretical (dotted lines) curves for variation of resistance of cotton and wool with moisture content [33]. The theoretical expressions are:

$$\text{Cotton: } \quad \text{Log } R_s = \frac{76.8}{\epsilon_r} + 1.1$$

$$\text{Wool: } \quad \text{Log } R_s = \frac{42.2}{\epsilon_r} + 3.6$$

and at room temperature, $T \approx 300 \text{ K}$, this gives $U_0 \approx 1.5 \times 10^{-18} \text{ J}$. This may be compared with the energy required to separate two electronic charges, initially at a distance apart equal to the ionic diameter, i.e. of the order of $5 \times 10^{-10} \text{ m}$, which gives $U_0 \approx 5 \times 10^{-18} \text{ J}$. Thus the chosen value of Ψ proves to be of the right order of magnitude.

This theory will explain the high resistance of multivalent ions. If the ions have valencies z_1 and z_2 , then, considering isolated charges separated by a distance X , we have

$$U = \frac{z_1 z_2 U_0}{\epsilon_r} \approx \frac{z_1 z_2 e^2}{\epsilon_r X} \quad (22.22)$$

where U_0 is assumed to be the value for monovalent ions.

Equation (22.21) therefore becomes:

$$\log R = \frac{z_1 z_2 \Psi}{\epsilon_r + \chi} \quad (22.23)$$

The value of $\log R$ is thus increased by an amount $(z_1 z_2 - 1) \Psi / \epsilon_r$ compared with the value with the same number of monovalent ions present. Some values of this quantity are given in Table 22.5. These figures, being differences in $\log R$, give the number of powers of 10 by which the resistance with multivalent ions would be greater than the resistance with monovalent ions. It will be seen that, in almost all cases, conduction by multivalent ions would be negligible.

Although the constants Ψ and χ would not be expected to be exactly the same for different materials, Hearle [36, 37] has shown that, when values of $\log R_s$ are plotted

Table 22.5 Values of $(z_1 z_2 - 1) \Psi / r$ [33]

ϵ_r	$\Psi = 76.8$		$\Psi = 42.2$	
	$z_1 z_2 = 2$	$z_1 z_2 = 4$	$z_1 z_2 = 2$	$z_1 z_2 = 4$
1	76.8	229	42.9	126
5	15.4	46	8.4	25
10	7.7	23	4.2	13
15	5.1	15	2.8	8
20	3.8	11	1.1	3

against values of $1/\epsilon_r$ (all determined under the same conditions), the straight lines do group closely together. In particular, the differences in their permittivities explain the differences in resistance between cellulosic and protein fibres under similar moisture conditions.

22.5.3 Conduction at high moisture contents

At high moisture contents, when the permittivity becomes high, the condition $\alpha \ll 1$ will break down, and dissociation will become almost complete. Equation (22.21) will then cease to apply, and the effect of the permittivity will be small. Theoretical estimates, based on the value of A , and experimental results for the dissociation of electrolytes in liquids both indicate that α becomes near to unity for permittivities greater than 20. Under these conditions, an alternative mechanism will be limiting the conduction. The theory of breaks in conduction paths would also break down at high moisture contents, when breaks become negligible.

At high moisture contents, the ions will be moving along water paths and their speed will be limited by viscous hindrance to their flow. If the paths are narrow and the water is moving with the ions, Poiseuille's equation for the flow of liquids along tubes should apply to the velocity u of the ions, to give:

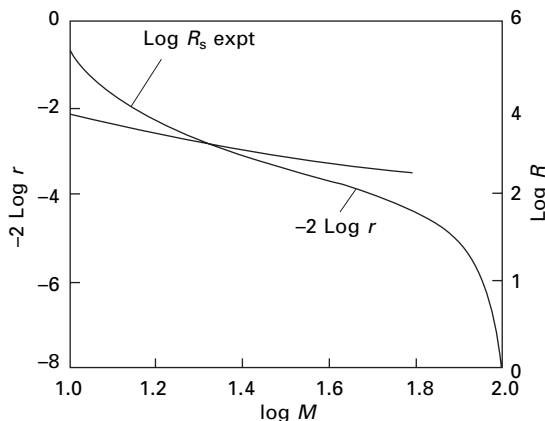
$$u \propto (\text{radius of tube})^4 \propto (\text{volume of water})^2 \propto (\text{regain})^2$$

Note that it is regain r (mass of water per mass of fibre), which tends to infinity as a maximum, and not moisture content M (mass of water per mass of water + fibre), which tends to 1, that is the relevant quantity.

Thus, from equation (22.13):

$$\log R = \log(\text{constant}) - 2 \log r = \log(\text{constant}) - 2 \log M + \log(1 - M) \quad (22.24)$$

As shown in Fig. 22.16, an equation of this form does have approximately the right slope for a plot of $\log R$ against $\log M$ over a range of about 15–30% moisture content for cotton, when the experimental plot starts to level off. Equation (22.24) then has a rapid fall as $\log(1 - M)$ tends to minus infinity. However, at high moisture contents, the tubes become much wider, the ions would effectively be moving through an infinite medium, and the velocity would tend to a constant value, determined by Stokes' equation and giving a constant resistance.



22.16 Comparison of variation of $\log R_s$ and $(-2 \log r)$ with moisture content [33].

22.5.4 An alternative theory

Baxter's [30] theory for wool was that conductance C was due to electrons jumping between absorbed water molecules, so that the decrease in resistance as moisture regain r increased was due to the reduction in distance between absorbed water molecules. His result given below can be transformed into an expression for resistance R :

$$C = A \exp\left(\frac{-B}{r^{1/3}}\right) \quad (22.25)$$

$$\log R = \frac{b}{r^{1/3} - a} \quad (22.26)$$

where r = regain and A , B , a and b are constants.

Christie and coworkers [38, 39] argue that conduction is by mobile protons. Since Baxter's model is independent of the charge carrier, they adapt his equation. For cellulose fibres [38], they find that it is necessary to offset the regain by an amount r_0 , for which they offer possible explanations. The equations become:

$$C = A \exp\left[\frac{-B}{(r - r_0)^{1/3}}\right] \quad (22.27)$$

$$\log R = \frac{b}{(r - r_0)^{1/3} - a} \quad (22.28)$$

This equation gives good agreement with the experimental results for cotton over the measured range to 20% regain. For viscose rayon there is agreement up to 40% regain, but then the conductance levels off.

In order to fit data for wool and silk [39], it was necessary to introduce extra terms to allow for conductivity at zero regain C_0 and for strongly and weakly bonded water:

$$C = C_0 + A_s \exp[-B_s/(r_s)^{1/3}] + A_w \exp[-B_w/(r_w)^{1/3}] \quad (22.29)$$

This accords with two-phase theories of moisture absorption (see [Chapter 12](#)). Although the model could be interpreted as defining the rate at which protons move through the material, it can also be related to the numbers available to jump in a given time, which fits the dissociation model. Introduction of the dependence of dielectric constant on regain might show that there was less difference between the theories than is first apparent.

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