sometimes referred to in terms of the temperature at which they occur, namely \( T_\alpha \), \( T_\beta \) and \( T_\gamma \), \((T_\alpha > T_\beta > T_\gamma)\) and are affected by crystallinity and orientation, moisture, pressure, stereoregularity, etc.

Some polymers show three, clearly resolved relaxation processes, as exemplified by linear and branched PE which displays an \( \alpha \)-relaxation at 60–80°C, \( \beta \) at −20 to −30°C and \( \gamma \) at −120 to −130°C [210]. The \( \alpha \)-transition occurs close to the \( T_g \) and is attributable to motion of the chains associated with the crystalline phase, whilst the \( \beta \)-transition involves amorphous regions which are influenced by the crystalline regions and the \( \gamma \)-relaxation stems from mobility of either branches or chain end groups in the amorphous regions [429]. Other polymers show only two transitions, as represented by PAN containing vinyl acetate or methyl acrylate comonomers, that display two transitions, at −80–110°C and −140°C [368], the former being considered to correspond to molecular motions within the paracrystalline region whilst the latter relates to dipole–dipole interactions between the cyano groups (−CN) in the amorphous regions [430], although the precise nature of the two transitions remain unresolved.

Interpretation of the various secondary transitions is especially difficult in the case of semi-crystalline polymers owing to the presence of both crystalline and non-crystalline phases. For example, PES displays relaxation behaviour that is sensitive to crystallinity (e.g. [404, 431, 432]) namely an \( \alpha \)-transition at ~80°C, associated with segmental motions within the amorphous regions, which becomes broader and is shifted to higher temperatures with increasing crystallinity, and a \( \beta \)-relaxation at approximately −40°C that is insensitive to the degree of crystallinity. However, oriented, semi-crystalline PES has been shown to display three relaxation peaks at around 100°C (\( \alpha \)), −70°C (\( \beta \)) and −230°C (\( \gamma \)) [433]. The three major relaxations in PA 6 (see [434]) occur at approximately +80°C (\( \alpha \)), −40°C (\( \beta \)) and −120°C (\( \gamma \)) [435]: the \( \alpha \)-relaxation, which corresponds to the \( T_g \) of dry PA 6, reflects motion in long chain segments in amorphous regions; the \( \beta \) relaxation arises from motion of non-H-bonded amide groups and in the presence of water, polymer–water units [436], whilst the \( \gamma \) relaxation reflects motion of short polymethylene segments with some involvement of adjacent amide groups.

As discussed briefly above and in detail in Chapter 3, moisture markedly affects the temperature of the \( \alpha \) relaxation (i.e. \( T_\alpha \)) of many amorphous and semi-crystalline polymers, which is perhaps most dramatically illustrated in the case of PA materials such as PA 46, for which the \( T_g \) of the dry material is reduced from +80 to −40°C when the substrate contains 12.4% water [437]. Water also affects both the magnitude and temperature-range of some secondary relaxation processes in polymers. For example, in the case of dry PA 4, whilst an \( \alpha \)-transition located at 81°C and a \( \beta \)-relaxation at −111°C were observed, no \( \beta \) transition was detected. However, the addition of water resulted in the appearance of a \( \beta \)-relaxation at −60°C and the temperature of all three transitions decreased with increasing water content [438].

### 1.4.3 Optical Properties

Textile fibres are dyed for various reasons, most notably to enhance their appearance. This section concerns some of the characteristics of both undyed and dyed fibres. The large and multifaceted area of colour physics is not discussed and readers are directed elsewhere (e.g. [439–443]).

As textile fibres are anisotropic, their optical properties (as with others of their physical properties) vary with fibre direction. Accordingly, textile fibres are birefringent (optically anisotropic) in that their refractive index depends on polarisation by light and varies with the direction of propagation of the light.

#### 1.4.3.1 Polarisation (e.g. [209, 306])

Confusingly, the term polarisation (aka polarization) refers to several scientific phenomena,68 of which perhaps the most commonly known involves the selective orientation of the electric oscillations of electromagnetic waves (visible light), as exemplified by polaroid sunglasses which employ dichroism to reduce glare. Electromagnetic waves comprise both electric and magnetic fields (vectors) that oscillate (vibrate), in phase, at right angles to each other, the two oscillations also being perpendicular to the direction of propagation of the wave. Polarisation refers to the orientation of the wave’s electric field (which may be oriented in a single direction or may rotate as the wave travels), all directions of vibration being equally probable. In essence, non-polarised light can be converted into polarised light using an optical filter (polariser or polarizer) that allows the passage of light of a specific polarisation but which prevents passage of waves of other polarisations. For example, the filter restricts the electric vibrations to a single plane thereby producing plane polarised (aka linearly polarised) light in which the electric vectors are plane parallel (or plane-polarised) with respect to the direction of propagation.69

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68 for example, dielectric polarization (charge separation), wave polarization (electric flux), spin polarization (elementary particles).
69 Polaroid sunglasses function by allowing the passage of only vertically polarised light, thereby preventing passage of horizontally polarised light that is reflected from surfaces and which gives rise to ‘glare’.
In the context of the optical properties of fibres, the term *polarisation* refers to the tendency of an electron cloud within an atom or molecule to be (temporarily) distorted by an externally applied electric field such as that produced by a nearby ion or dipole or, of relevance here, light (i.e. electromagnetic radiation). As implied by the foregoing, there are several mechanisms of polarisation, such as *ionic polarisation* (displacements between positive and negative ions in ionic crystals, e.g. NaCl), *molecular polarisation* (polar molecules in an electric field can experience torque which causes them to align with the applied field) and, of relevance to the optical properties of textile fibres, *electronic polarisation* (aka *electric polarisation*). Electronic mechanisms only occur during the interaction between light and fibres because only electrons are sufficiently light enough to respond to the very high frequency of the light waves involved.

As light passes through a (transparent or translucent) fibre, the applied electric field polarises the electron cloud of the fibre’s constituent atoms/bonds/molecules. As discussed in Chapter 5, the ease with which the electron cloud arrangement in a non-polar species can be distorted by the presence of the electric fields of neighbouring molecules is a measure of the *polarisability* of the atom or molecule. The distortion of the electron cloud induces a dipole moment in the originally non-polar atom or molecule, the induced dipole moment being related to the polarisability of the molecule or atom and the strength of the electric field. Polarisability is commonly expressed as *polarisability volume*, values for which often are of similar magnitude to molecular volumes. Accordingly, the larger the volume occupied by electrons, the greater the polarisability of those electrons; polarisability also increases with increasing number of electrons per unit volume. Polarisability decreases with increasing electronegativity because the electron cloud (or electron density) is more tightly held. This particular characteristic is a feature of the concept of soft and hard compounds, the former having diffuse electron clouds and are polarisable whereas the latter are poorly polarisable owing to their tightly held electron clouds.\(^70\)

The polarisability of a given bond is influenced by neighbouring atoms and, therefore, polarisability is differentiated into three aspects namely one longitudinal aspect (i.e. along a molecular or bond axis) and two transverse aspects (perpendicular to the molecular or bond axis). In the case of textile fibres, although the constituent molecular chains assume a parallel or near parallel arrangement along the fibre axis, owing to the axial symmetry of the fibre, the two transverse aspects are identical.

### 1.4.3.2 Refractive Index

Refractive index (aka *index of refraction*, \(n\)), is a dimensionless quantity that describes the nature of the propagation of light through a medium. A consequence of the polarisation of a transparent or translucent material by light is that the velocity of light within a medium varies for different media, for which Eq. 1.18 applies where \(\nu\) is the velocity of light.

\[
n = \frac{\nu_{\text{vacuum}}}{\nu_{\text{medium}}} \quad (1.18)
\]

An alternative derivation of refractive index describes the fact that when light passes from one medium to another it is refracted (bent), Eq. 1.19, where \(i\) is the angle of incidence and \(r\) that of refraction.

\[
n = \frac{\sin i}{\sin r} \quad (1.19)
\]

Refractive index varies with density, since electron density also increases with density and, therefore, so does electronic polarisability; values of \(n\) for polymers are available [444].

As a consequence of the anisotropy of fibres, refractive index varies as a function of direction of passage of light through the substrate, and, therefore, fibres have two principal refractive indexes (parallel and perpendicular), as discussed below.

### 1.4.3.3 Birefringence

Whilst the refractive index of an isotropic material is identical for all directions of measurement, the refractive index of an anisotropic material, such as a crystal or textile fibre, varies with direction of measurement. A fibre is generally characterised by two refractive indices, one measured along the fibre axis, \(n_p\), and one perpendicular to the fibre axis, \(n_L\). The difference between the two refractive indices \((\Delta n = n_p - n_L)\) is the *birefringence*, which reflects the different polarisability of the fibre to light oscillating along and normal to the fibre axis. Birefringence is observed in materials as

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\(^70\) the concept of Hard and Soft compounds is related to that of Lewis acids and bases, the former being synonymous with a nucleophile and the latter an electrophile.
the result of mechanical orientation in either the solid or liquid states (i.e. stretch and flow birefringence, respectively); thus, polymers melt under forced flow or under tension display birefringence, as also do solid polymers after orientation [440].

The birefringence of the majority of fibres is positive, ranging from 0.010 (wool) to 0.662 (Kevlar 49) [307] (Table 1.5), since \( n > n_\perp \), indicating that the atoms/bonds along the chain are less polarisable than are those disposed laterally. However, PAN, CTA and PVC fibres are negatively birefringent, although only weakly so [307, 445]. Birefringence can be used to determine the degree of molecular orientation in fibres, irrespective of the size and nature of the crystalline and amorphous regions [307].

1.4.3.3.1 Dichroism

As a corollary of the anisotropy of textile fibres, dyed fibres often are dichroic insofar as the depth of shade or colour of the dyeing may vary according to the angle of viewing (i.e. direction of the incident light) owing to orientation of the dye molecules together with that of the polymer molecules in the fibre. For this effect to occur, several aspects must be satisfied [209, 446, 447] namely:

- the dye molecule must itself be dichroic, as observed for asymmetrical dyes in which light absorption occurs along one axis, as exemplified by the essentially linear oscillator axis in the case of planar azo direct dyes or vat dyes;
- the dye molecule must be adsorbed in the fibre in such a manner that the axis corresponding to light absorption is aligned either essentially parallel to or perpendicular to the polymer chain molecules in the fibres;
- the polymer chain molecules in the fibre must be preferentially oriented.

Several workers have used the first two aspects to quantify the orientation of the polymer chains in a fibre by equating the extent of dichroism of the adsorbed dye molecules to the orientation of the fibre molecules [446–449]. The dichroism of dyed cotton has been used as a means of describing the mechanism of dyeing [450] in which context Sumner et al. [451] employed dichroism to determine the effects of soaping treatments on vat dyed cellulosic materials.

In the case of a dichroic dyed fibre, the respective amounts of polarised light parallel and perpendicular to the fibre axis absorbed by the fibre, \( A_\parallel \) and \( A_\perp \), respectively, can be used to determine the dichroic ratio, \( p \), via Eq. 1.20 where \( k_\parallel \) and \( k_\perp \) are the absorption constants and \( c \) the dye concentration [446].

\[
\frac{A_\parallel}{A_\perp} = \frac{k_\parallel c}{k_\perp c} = p
\] (1.20)

1.4.3.4 Lustre

Most textiles are examples of a gonioapparent materials\(^{71}\) and lustre is one of several key attributes of the appearance of textile materials, others include, for instance, colour and texture. Lustre is a particular gonio metric property which can be defined as the display of different intensities of light, reflected both specularly and diffusely, from different parts of a (fibre, yarn and fabric) surface exposed to the same incident light [11]. Lustre is a complex sensation that depends on both the characteristics of the textile material being viewed (e.g. fibre and yarn type, woven/knitted/non-woven construction) and the viewing conditions employed. Despite much research attention over many decades, which continues till recent times (e.g. [209, 452–457]), no objective quantitative parameter has yet been developed to describe fibre lustre and, consequently, subjective (visual) assessment of this important fibre property is routinely employed [453, 458] with adjectives such as shiny, lustrous, matt and dull being common. Nonetheless, several equations have

\(^{71}\) one whose appearance changes with change in illumination or viewing angle.
been developed to describe fibre lustre employing data obtained using goniophotometers; recently, fuzzy logic and image processing have been applied to lustre determination in textiles [456, 457].

In simple terms, a surface is perceived as being lustrous if its brightness differs under different angles of observation or illumination. Lustre can be considered as textile fibre gloss which is a function of several fibre characteristics, such as the refractive index, cross-sectional shape and smoothness of a fibre, fibre surface regularity (e.g. hairiness), fibre fineness, the structure and arrangement of yarn in a fabric, filament/yarn crimp and twist, and, in the case of synthetic fibres, the presence of delustrant (see Section 1.4.3.4.1). As such, fibres that are uniform will display high lustre, as observed in the cases of silk filaments which have a characteristic smooth surface, as well as man-made and synthetic fibres. In contrast, natural fibres (with the exception of silk) tend to be irregular in terms of uniformity. Indeed, Adderley [459] proffered that the characteristic dullness of cotton was attributable to the fibre’s irregular shape and that the marked improvement in lustre imparted by mercerisation (Chapter 3) could be attributed to the fibres assuming a more regular, round cross-sectional shape.

1.4.3.4.1 Delustrants
Extruded man-made and synthetic fibres are typically transparent and highly lustrous. The addition of a delustrant reduces lustre and also increases opacity (and covering power), the most common delustrant being powdered TiO₂ (particle size range: 0.3–0.4 μm in the case of PES fibres [213]), although other compounds such as ZnS, Al₂O₃ and synthetic resins [321] can be used. Only a small amount of TiO₂ (e.g. 0.2% in the case of PA fibres [213]) is required to reduce transparency whilst additional levels are employed to secure fibres of differing lustre, these being referred to as clear (aka bright) in the case of fibres that do not contain delustrant, semi-matt (aka semi-dull) and matt (aka dull), the latter two variants being produced using additions of 0.5% and up to 2% TiO₂, respectively, in the case of PA fibres [213]. The presence of delustrant within the fibre will reduce lustre because the small particles of typically TiO₂ scatter the transmitted light thereby increasing the extent of diffuse reflection.

References