CHAPTER 1

An introduction to textiles, dyes and dyeing

The manufacture of textiles is a major global industry. It provides vast quantities of materials for clothing and furnishings, and for a variety of other end-uses. This book deals specifically with textile coloration. It begins by introducing this subject along with some technical terms and concepts related to dyes, fibres and dyeing. At this stage, mastery of all the new ideas is not necessary. They will be encountered again throughout the book.

Several examples of the molecular structures of dyes will be presented in this chapter so that the reader gains some familiarity with the variations in molecular size, shape and ionic character. Do not be intimidated by these. In due course, the relationship between the key features of the molecular structure of a dye and its dyeing properties will be more evident.

1.1 HISTORICAL BACKGROUND

1.1.1 Natural dyes and fibres

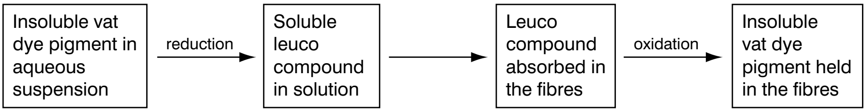
The production of fabrics and their coloration precedes recorded history. Several cultures had established dyeing technologies before 3000 BC. These ancient artisans transformed the available natural fibres – linen, cotton, wool and silk – into fabrics, at first by hand, and later using simple mechanical devices. Short fibres were first carded or combed, to lay them parallel to one another. Drawing out of a band of combed fibres by pulling, with gradual twisting, produced yarn. Finally, yarns were interlaced to form a woven fabric. The techniques used hardly changed until the Industrial Revolution, when they became fully mechanised.

Although finely ground, coloured minerals, dispersed in water, were used in paints over 30 000 years ago, they easily washed off any material coloured with them. Natural dyes were extracted from plant and animal sources with water, sometimes under conditions involving fermentation. Fabric was dyed by soaking it in the aqueous extract and drying. These dyes had only a limited range of dull colours and the dyeings invariably had poor fastness to washing and sunlight. The fastness of a dyeing is a measure of its resistance to fading, or colour change, on exposure to a given agency or treatment. Most natural dyes also lacked substantivity for fibres such as wool and cotton. Substantivity implies some attraction of the dye for the fibre, so that the dye in the solution gradually becomes depleted as it is absorbed by the fibres.

The poor substantivity and fastness properties of natural dyes often improved if the fabric was first treated with a solution containing a salt of, for example, iron, copper or tin. The conditions used favoured combination of the metal ions with the particular fibre, or their precipitation inside it. These metal salts were called mordants. When the pre-mordanted fabric was soaked in a bath of a suitable natural dye, the dye penetrated into the fibres and reacted with the metal ions present. This reaction decreased the water solubility of the dye so the colour was less likely to bleed out on washing. The word ‘mordant’ originated from the French verb *mordre* meaning ‘to bite’. In Chapter 13, we shall see that the idea of the dye biting the mordant, to form a stable dye–metal complex, is a useful description. In modern dyeing procedures, the dye reacts with the mordant in the fibre in a separate process after dyeing, or the metal is incorporated into the dyestuff during its manufacture.

A few natural dyes gave better quality dyeings of cotton or wool, but involved long and difficult processes. For example, the colorant extracted from madder root, from the plant *Rubia tinctorium*, dyed cotton pre-mordanted with aluminium and calcium salts to give the famous Turkey Red. Using an iron mordant, the same colorant gave a purplish-black.

Indigo, extracted from leaves of the plant *Indigofera tinctoria,* and Tyrian Purple from Mediterranean sea snails of the genera *Murex* and *Purpura*, are water-insoluble pigments called vat dyes. These do not require mordants. During the time of the Roman Empire, wool cloth dyed with Tyrian Purple was so highly prized that only the ruling class wore garments made with it. For dyeing with Indigo, a water-soluble, reduced form of the dye was first obtained by extraction and fermentation. The process became known as vatting, from the name of the vessels used – hence the term ‘vat dye’. The soluble, reduced form of the dye is called a leuco derivative. Leuco Indigo has substantivity for wool and cotton fibres. After dyeing, air oxidation of the pale yellow leuco dye, absorbed in the fibres, regenerates the dark blue, insoluble pigment trapped inside them. Because of this, the fastness to washing is very good in comparison to most natural dyes. Scheme 1.1 outlines the essential steps in vat dyeing.



Scheme 1.1

1.1.2 The development of synthetic dyes and fibres

In 1856, William H Perkin reacted aniline with acidic potassium dichromate solution in an attempt to prepare the anti-malarial drug quinine. From the dark, tarry reaction mixture, he isolated a purple, water-soluble compound that dyed both wool and silk directly when immersed in its solution. No mordant was required. Perkin established a factory for the large-scale production of aniline and for the manufacture of this dye, later called Mauveine. He not only discovered the first major synthetic dye, but founded the modern chemical industry.

Mauveine (proposed structure **1**, Figure 1.1) is a cationic dye since each of its molecules has a positive ionic charge. The methyl groups in the structure of Mauveine arose from the use of aniline contaminated with toluidenes (aminotoluenes). Such cationic dyes are often called basic dyes since many, like Mauveine, have free amino groups capable of salt formation with acids.

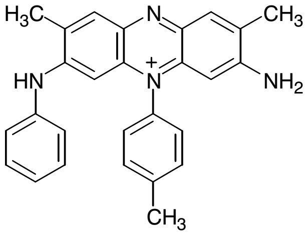


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Figure 1.1 Proposed structure of Mauveine

Mauveine has some substantivity for wool and silk. Such protein fibres contain both amino and carboxylic acid groups. In a neutral dyebath, the amino groups (NH_2) in the wool are neutral but the carboxylic acid groups (CO_2H) dissociate giving negatively charged carboxylate anions (CO_2^-), associated with positively charged sodium cations (Na^+). Under these conditions, dyeing with a cationic dye

(Dye^+) involves a process of cation exchange in which the more substantive dye cation replaces the sodium ion associated with the carboxylate group in the wool or silk (Scheme 1.2).

$$H_2N{-}Wool{-}CO_2^-\,Na^+ + Dye^+(aq) \longrightarrow H_2N{-}Wool{-}CO_2^-\,Dye^+ + Na^+(aq)$$

Scheme 1.2

Perkin even developed a method for dyeing cotton with Mauveine using tannic acid as a mordant. This polycarboxylic acid was precipitated inside the cotton fibres as a tin salt. The mordanted cotton, immersed in a solution of Mauveine, absorbed the cationic dye (positively charged), which combined with the anionic carboxylate groups of the tannic acid (negatively charged) inside the fibres. Perkin's achievements are all the more impressive when we consider the limited scientific information available in 1856. This was a period of heated debate over Dalton's atomic theory; the formation of organic compounds was still believed to require a living organism, and Kekulé had not yet proposed the hexagonal structure of benzene (1865).

Two years after the isolation of Mauveine, Peter Greiss discovered the diazotisation reaction of primary aromatic amines, which produces diazonium ions, and later, in 1864, their coupling reaction with phenols or aromatic amines to give azo compounds. Primary aromatic amines such as aniline ($C_6H_5NH_2$) are often diazotised by treatment with sodium nitrite ($NaNO_2$) in acidic aqueous solution at temperatures around 0–5 °C (Scheme 1.3). The diazonium cation produced ($C_6H_5N_2^+$) will couple with a phenol in alkaline solution (in a similar way to the reaction shown in Figure 1.2), or with an aromatic amine in weakly acidic solution, to form an azo compound. This coupling reaction is an electrophilic aromatic substitution, like nitration or chlorination, with the diazonium ion as the electrophile. Today, over half of all commercial dyes contain the azo group (–N=N–) and many thousands of azo compounds are known. Diazotisation and coupling are therefore two very significant reactions.

$$C_6H_5{-}NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5{-}N_2^+Cl^- + NaCl + 2H_2O$$

Scheme 1.3

Each molecule of the azo dye Orange II (Figure 1.2) has an anionic sulphonate group and will dye wool in the presence of an acid. It is therefore classified as an acid dye. In acidic solution, both the amino and carboxylate groups in wool bond with protons, becoming cationic (NH_3^+) and neutral (CO_2H), respectively. Under these conditions, the wool absorbs anionic dyes (Dye^-), such as Orange II, by a process of anion exchange (Scheme 1.4).

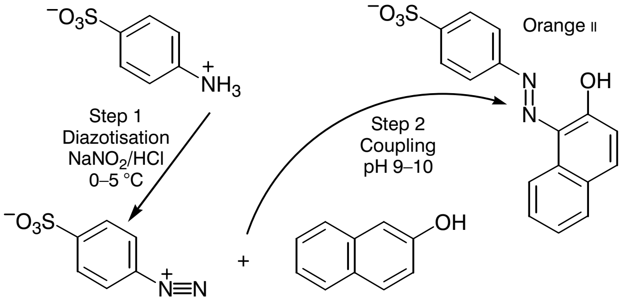

Figure 1.2 Formation of the azo dye Orange II by diazotisation and coupling

$$Na^{+\,-}O_2C{-}Wool{-}NH_2 + 2HCl \longrightarrow HO_2C{-}Wool{-}NH_3^{+}Cl^{-} + NaCl$$

$$HO_2C{-}Wool{-}NH_3^{+}Cl^{-} + Dye^{-}\,(aq) \longrightarrow HO_2C{-}Wool{-}NH_3^{+}Dye^{-} + Cl^{-}\,(aq)$$

Scheme 1.4

Many of the first synthetic dyes were cationic dyes like Mauveine (**1**). These had brilliant colours, but poor fastness to washing, and particularly to light. Their use on cotton still required pre-mordanting with tannic acid. Congo Red (**2**, Figure 1.3), first prepared in 1884, was one of the first synthetic dyes that would dye cotton directly, without a mordant. This is also an anionic azo dye, but, unlike Orange II, its more extended molecular structure imparts substantivity for cotton. Dyeings on cotton with Congo Red only had poor fastness to washing, but the so-called direct cotton dyes that followed were better in this respect.

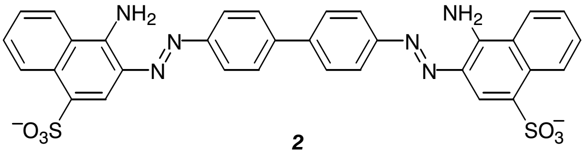

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Figure 1.3 Congo Red

Synthetic Indigo was first prepared in 1880 and produced commercially in 1897. Indigo is a vat dye applied to both wool and cotton according to Scheme 1.1. The water-insoluble, blue pigment gives a pale yellow, water-soluble leuco form on reduction (Figure 1.4). Indigo, one of the oldest colorants, is widely used for dyeing cotton yarn for blue jeans. It was not until the discovery of Indanthrone in 1901, however, that other synthetic vat dyes of outstanding fastness to washing and light became available. Precipitation of a water-insoluble pigment inside a fibre is still one of the important ways of producing a dyeing with good fastness to washing.

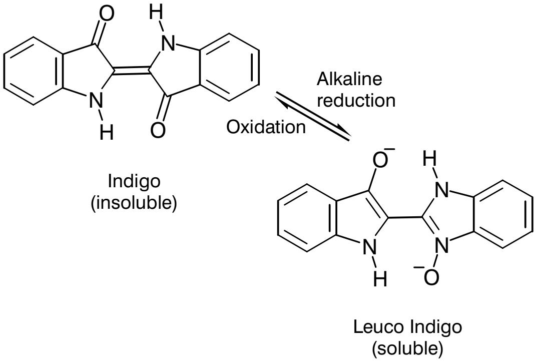
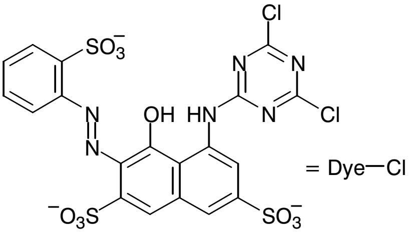


Figure 1.4 Reversible reduction and oxidation for Indigo

The first fibre-reactive dyes did not appear until 1956. Under alkaline conditions, these dyes react with the ionised hydroxyl groups in cotton cellulose forming a covalent bond with the fibre (Figure 1.5). Cellulose is the name of the chemical constituting cotton. It is a polymer of glucose and therefore a



$$\text{Cell—OH} + \text{HO}^- \longrightarrow \text{Cell—O}^- + H_2O$$

$$\text{Cell—O}^- + \text{Dye—Cl} \longrightarrow \text{Cell—O—Dye} + \text{Cl}^-$$

Figure 1.5 The molecular structure of a simple reactive dye (Dye–Cl) and its reaction with the hydroxyl group in cotton (Cell–OH) polyalcohol. It is conveniently represented by the short formula Cell–OH. The strong bond between the reactive dye and the cellulose ensures good fastness to washing and the simple chemical structures of the dyes often result in bright colours. Dyes with simple molecular structures can often be prepared with a minimum of contaminating isomers and by-products that tend to dull the colour. Inducing a chemical reaction between a fibre and an absorbed dye molecule is another significant way of producing dyeings of good washing fastness. Reactive dyes have become one of the most important types of dye for dyeing cotton and some types are valuable for wool dyeing.

Synthetic dyes, obtained from coal tar and petroleum chemicals, have totally replaced natural dyes. It would be quite impossible to meet even a small fraction of today's market requirements for colour using only naturally occurring dyes, although a few are still used to colour foods and cosmetics. Since the earliest days of the synthetic dyestuff industry, there has been a constant demand for dyes with brighter colours, and with better fastness properties, for an increasing range of fibre types. Of the many thousands of known synthetic dyes, only a few thousand are manufactured today. They represent the market-driven selection of those with the required performance.

Before the twentieth century, textiles were made exclusively from natural fibres such as cotton or wool. The first artificially made fibre of regenerated cellulose was Chardonnet's artificial silk, first produced in 1884. This was manufactured from cellulose nitrate (Cell–O–NO_2), obtained by esterification of cellulose with nitric acid (Scheme 1.5). Forcing an ethanol-diethyl ether solution of cellulose nitrate through tiny holes in a metal plate, and then rapidly evaporating the volatile solvents in warm air, produced very fine, solid filaments of this material. This is the extrusion process. It is a key step in the production of all artificially made fibres. Because cellulose nitrate is highly flammable, the filaments were then treated to hydrolyse it back into cellulose. Later, better processes were found for the preparation of cellulose solutions, their extrusion, and the solidification of the cellulose. Modern fibres of regenerated cellulose are called viscoses. They have some properties similar to those of cotton and can be dyed with the same types of dye.

As for most alcohols, the hydroxyl groups of cellulose can also be esterified with

$$\text{Cell—OH} \quad + \quad \text{HONO}_2 \longrightarrow \text{Cell—O—NO}_2 \quad + \quad \text{H}_2\text{O}$$

Scheme 1.5

acetic anhydride to produce cellulose acetates (Scheme 1.6). In 1921, a cellulose acetate fibre was produced with about 80% of the cellulose hydroxyl groups acetylated. This cellulose acetate gave silky, lustrous filaments on extrusion of its acetone solution followed by immediate evaporation of the solvent. These filaments were quite different from cotton or viscose. In particular, they were relatively hydrophobic (water-repelling), whereas cotton and viscose are hydrophilic (water-attracting). Initially, cellulose acetate proved difficult to dye satisfactorily with existing ionic dyes. Effective dyeing occurred, however, using a fine aqueous dispersion of non-ionic, relatively insoluble, hydrophobic dyes. This type of dye is called a disperse dye, of which (**3**) is an example (Figure 1.6). We now know that such dyes are soluble in the hydrophobic cellulose acetate and dyeing occurs by the fibres continually extracting the small amount of dye dissolved in the water. Dye dissolving from the surface of the fine particles in suspension constantly replenishes the dye in solution. As we shall see later, disperse dyes are suitable for dyeing almost all types of artificially made fibre by the same mechanism (Figure 1.7).

$$\text{Cell—OH} + (CH_3CO)_2O \longrightarrow \text{Cell—O—COCH}_3 + CH_3CO_2H$$

Scheme 1.6

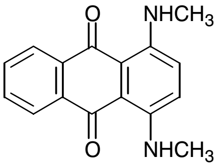


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Figure 1.6 Disperse Blue 14

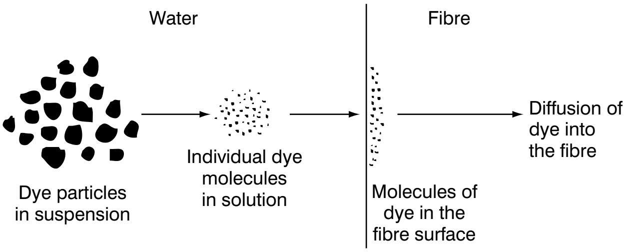

Figure 1.7 The mechanism of dyeing a synthetic fibre with a disperse dye

We often forget that the development of fibres of regenerated or modified cellulose, and much of dyeing technology, occurred with little understanding of the molecular nature of fibres. The idea of a polymer molecule was not accepted before 1925. The work of Staudinger, Mark, Carothers and others, eventually confirmed that fibres consist of bundles of long, linear molecules of very high molecular weight. Without this scientific advance, the production of the fully artificially made fibres such as nylon (1938) and polyester (1945) might have been impeded. Today, thanks to advances in polymer chemistry and engineering, there are a variety of artificially made fibre types to meet the demand of a growing world population. They account for almost half of total fibre consumption.

During most of the twentieth century, almost all the major developments in the dyestuff and coloration industries originated in Western Europe, predominantly in Germany, Switzerland and Britain. Then, over the last two decades of the twentieth century, a massive global reorganisation took place and the European suppliers of dyestuffs and of dyed or printed materials were seriously threatened as manufacturers in developing countries became much more competitive. A number of factors contributed to this continuing trend:

(1) the rapid industrial development of many developing countries and the global availability of technology and machinery for textile manufacture and coloration; countries such as Japan, India, China and Korea have become major players on the textile stage.

(2) much more restrictive legislation in Europe and North America for dyestuff manufacture and use with minimum impact on health and the environment; this has become a key issue in the future of the colorant and textile industries in the developed nations of the Western block.

(3) the majority of chemicals and processes presently in use were introduced prior to 1975 and their originators have no further patent protection; the perceived low probability of developing new types of textile fibres and dyes has considerably limited fundamental research in these areas.

One effect of these influences has been a drastic rationalisation of the dyestuff industry in Western Europe. Some dyestuff divisions separated from their parent company (Zeneca from ICI in Britain, and Clariant from Sandoz in Switzerland). In other cases, dyestuff producers have merged: Ciba merged with Geigy in Switzerland and may yet absorb Clariant; Hoechst and Bayer joined forces as DyStar in Germany; and BASF bought Zeneca. More recently, Yorkshire Chemicals has bought Crompton and Knowles, the major American dye manufacturer, and the merger of DyStar and BASF is imminent. The more recent history of the dyestuff industry is described in a series of four articles by Park and Shore [1].

1.2 MODERN TEXTILES

1.2.1 The classification of fibres

There are seven major fibre types. Table 1.1 shows these in bold face along with their estimated global consumption for the year 2000. The four main groups of textile fibres are:

(1) animal or protein fibres;
(2) vegetable or cellulosic fibres;
(3) regenerated fibres based on cellulose or its derivatives;
(4) fully synthetic fibres.

There are, of course, other natural and artificially made fibres besides those listed in Table 1.1, but these are of lesser importance. All these fibres are dyed in a wide range of colours, with various fastness properties, for a multitude of different textile products. Each type of fibre requires specific types of dyes and dyeing methods. Fortunately, the dyeing of many minor fibres is often very similar to that of a chemically related major fibre. For example, the dyeing of mohair is very similar to wool dyeing. The 5×10^{10} kg of fibres consumed annually require about

Table 1.1 Classification of the major textile fibres and their estimated global consumption in 2000 (kg)

Natural fibres			Artificial fibres	
Protein	Cellulose	Mineral	Regenerated	Synthetic
Wool 3.1×10^9	**Cotton** 23.7×10^9	Glass	**Viscose** 2.7×10^9	**Nylons** 4.5×10^9
Silk	Linen	Metal	**Cellulose acetates** 0.3×10^9	**Polyesters** 12.5×10^9
Mohair	Ramie			**Acrylics** 3.5×10^9
Cashmere				Polyolefins

8×10^8 kg of a few thousand different dyes and pigments. The textile coloration industry is not only large but also extremely diverse.

1.2.2 Textile manufacture

Textile consumption is closely related to growing world population and consumer affluence. To satisfy market demand for fabric, fully automated, high-speed production, with a minimum of defects, is essential. The following outline of textile manufacture identifies the major processes, the division of operations, and situates coloration in the overall scheme. Chapter 2 provides more details on fibres and textile manufacturing.

Cotton and wool are only available as short staple fibres of pre-determined length, but artificially made fibres are available either as continuous filaments or short fibres cut to any required length. Textile manufacturing using natural fibres starts with the opening, separation and mixing of short fibres. The carding process draws them out into a band of parallel fibres (sliver), and drawing out and twisting of this yields spun yarn. Opening, carding or drawing may also serve to blend two or more staple fibres; for example, cotton and staple polyester. Continuous filaments do not require such preliminary operations.

The major methods of fabric assembly from yarns of staple fibres, or from continuous filaments, are weaving and knitting, both of which, being fully automated, have significant production rates.

The production of a textile material from fibres involves a defined sequence of operations to produce yarns and assemble them into fabric. Each process is a necessary prerequisite for the next. The situation of dyeing in the production scheme, however, is not necessarily rigidly defined. Dyeing may occur at any stage during textile manufacture: on loose fibre, or on the intermediate forms such as sliver or yarn, or on fabric, towards the end of the manufacturing cycle. Even garments and finished articles can be dyed. This means that a variety of dyeing machines is required for the different types of textiles. Dyeing usually involves contact between an aqueous solution or dispersion of the dyes and the textile material, under conditions that promote substantivity and produce uniform coloration throughout. Printing, on the other hand, is the localised application of different dyes to different specific areas on one face of a fabric, according to some predetermined colour design. This book primarily discusses textile dyeing but Chapter 23 deals with printing.

Before textile fibres are dyed, they are washed or scoured to remove natural impurities, lubricating oils (added to aid carding, spinning or knitting) and size (used to reinforce the warp yarns in weaving). Bleaching eliminates any coloured impurities and is often necessary for white goods containing natural fibres, and before dyeing pale, bright shades. This stage of production is called preparation. Its objective is to clean the material before dyeing and finishing so that it wets easily and uniformly absorbs solutions of chemicals and dyes. Poor quality preparation, particularly when it is uneven, is a major cause of faulty dyeings.

The final stage in the manufacture of a textile is finishing. This involves treatments to improve the appearance or performance of the material. It might consist of a simple mechanical process such as calendering (to give the fabric a flat, compact surface) or napping (to break fibres and raise the ends forming a pile). Modification of the functional characteristics of a fabric often involves chemical finishing. The processes range from the simple application of a softening agent to improve the material's handle and reduce static electricity, to those that render cotton fabric flame resistant or crease resistant. Most chemical finishing is for fabrics of natural fibres, particularly for those containing cotton. This satisfies consumer demand for cotton materials having the easy-care characteristics associated with fabrics made from synthetic fibres. Many finishing processes, particularly those involving chemicals, can modify both the colour and the fastness properties of a dyed fabric, and these effects must therefore be known in advance.

Table 1.2 illustrates the sequence of some of the processes used for production of a knitted cotton fabric that will be dyed before assembly into the final article. Piece dyeing usually refers to dyeing of fabric as distinct from dyeing of a completed article such as a garment. Textile manufacture is highly specialised.

Table 1.2 Outline of the production of a dyed knitted fabric of cotton

Type of process	Specific process	Industrial unit
Yarn Production	(1) Opening (2) Carding (3) Spinning	Spinning mill
Fabric construction	(4) Knitting	Knitting mill
Preparation	(5) Scouring (6) Bleaching	
Coloration	(7) Dyeing	Dyehouse or finishing mill
Finishing	(8) Mechanical or chemical finishing	

Consequently, yarn production, fabric construction, and dyeing and finishing often take place in different locations with clear divisions between mechanical manufacturing operations and the wet processing associated with preparation, dyeing or printing, and finishing.

The seven major fibre types have quite different properties. The materials produced from these have a wide variety of end-uses, and each fabric has its particular aesthetic, colour fastness and technical requirements. There are therefore different types of dyes and processing methods for dyeing and printing. The manufacture of any fabric will always involve a compromise between the desired quality and performance, and the overall production cost. Today, fully automated and environmentally friendly processes are the norm: automation is essential to remain competitive, and national and local governments now demand lower levels of air and water pollution. The environmental impact of textile production and coloration is the most significant challenge facing the industry in Europe and North America today. Eventually, more environmentally sound methods of production and disposal will also be forced upon producers in the developing world as they expand further.

1.3 COLOUR, DYES AND DYEING

1.3.1 Light and colour

Colour sensation is a characteristic of human experience. Nature provides a particularly vivid display of colour. We use colours in many varied ways; for example, for clothes, paints, foods, lighting, cosmetics, paper, furnishings, and for identification and security. Despite our familiarity with it, there is no simple answer to the question ‘What *is* colour, and how do we see it?’: we understand so very little of the complex processes involved in colour vision. There are three main stages in the perception of colour, but each one consists of numerous complicated processes:

(1) absorption of coloured light entering the eye by the sensitive cells in the retina lining the back of the eyeball;
(2) transmission of nerve impulses from the retina to the brain via the optic nerve;
(3) interpretation of these signals when they reach the visual cortex in the brain.

To understand colour, some knowledge of the nature of light is essential. Light is a form of energy usually considered as being propagated at high speed in the form of electromagnetic waves. All types of electromagnetic radiation are characterised by their wavelength (λ) (the distance between the wave crests), or by the frequency (ν) (the number of waves that pass a point in a given time). Figure 1.8 illustrates the variations of the electric and magnetic fields associated with an electromagnetic wave.

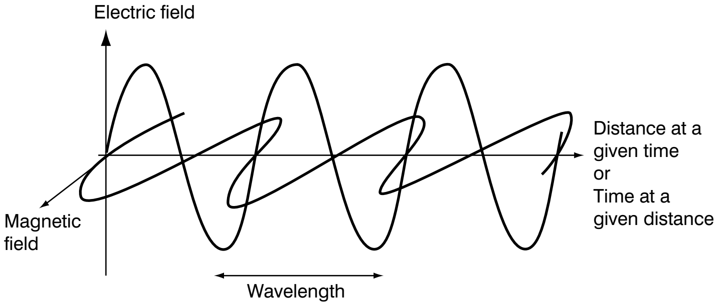

Figure 1.8 Variations of the electric and magnetic fields associated with an electromagnetic wave

The wavelength multiplied by the frequency ($\lambda \times \nu$) gives the speed of wave propagation. This is always constant in a given medium (speed of light in a vacuum, $c = 3.0 \times 10^8$ m s^{-1}). The human eye can detect electromagnetic waves with wavelengths in a narrow range between about 400 and 700 nm (1 nm = 1×10^{-9} m), comprising what we call visible light. We are also familiar with X-rays (λ = 0.3 nm), ultraviolet light (λ = 300 nm), infrared rays (λ = 3000 nm) and micro- and radio waves ($\lambda > 3 \times 10^6$ nm = 3 mm), whose wavelengths vary by many orders of magnitude. Spectral analysis of daylight, or white light – using a prism, for example – separates it into various coloured lights, as seen in the rainbow. The red, orange, yellow, green, blue and violet spectral colours of the rainbow correspond to lights with wavelengths of about 650, 600, 575, 525, 460 and 420 nm, respectively.

An object viewed in white light, which consists of all wavelengths in the visible region (400–700 nm) in about equal proportions, will appear coloured if there is selective absorption of some wavelengths and reflection or transmission of the others. Objects with high reflectance of all wavelengths of white light will appear white, whereas strong absorption of all wavelengths produces black. Table 1.3 lists the colours that an observer sees when the colorant in a material absorbs a single

Table 1.3 Colours of typical spectral bands, and colours perceived after their absorption by a material viewed in white light

Light absorbed by the material		
Wavelength band (nm)	Colour of the light absorbed	Perceived colour of the reflected light
400–440	Violet	Greenish-yellow
440–480	Blue	Yellow
480–510	Blue-green	Orange
510–540	Green	Red
540–570	Yellowish-green	Magenta
570–580	Yellow	Blue
580–610	Orange	Greenish-blue (cyan)
610–700	Red	Blue-green

range of wavelengths from white light. One important point should be noted in this table. Absorption of a single group of wavelengths cannot produce the colour green from the combined, non-absorbed wavelengths. For this, it is necessary to have two absorption bands, one in the red range above 600 nm, and the other in the blue–violet range around 450 nm. Dyes with two such absorption bands are much more difficult to prepare, and consequently there are fewer green dyes than there are of other colours. Because of this, the colour green is often produced by mixing yellow (blue-absorbing) and blue (red-absorbing) dyes.

1.3.2 Colorants, dyes and pigments

A colorant is a substance capable of imparting its colour to a given substrate, such as paint, paper or cotton, in which it is present. Not all colorants are dyes. A dye must be soluble in the application medium, usually water, at some point during the coloration process. It will also usually exhibit some substantivity for the material being dyed and be absorbed from the aqueous solution. On the other hand, pigments are colorants composed of particles that are insoluble in the application medium. They have no substantivity for the material. Since the particles are too large to penetrate into the substrate, they are usually present on the substrate surface. The pigment is therefore easily removed unless fixed with an adhesive.

Most textile dyeing processes initially involve transfer of the coloured chemical, or its precursor, from the aqueous solution onto the fibre surface; a process called adsorption. From there, the dye may slowly diffuse into the fibre. This occurs down pores, or between fibre polymer molecules, depending on the internal structure of the fibre. The overall process of adsorption and penetration of the dye into the fibre is called absorption. Absorption is a reversible process. The dye can therefore return to the aqueous medium from the dyed material during washing, a process called desorption. Besides direct absorption, coloration of a fibre may also involve precipitation of a dye inside the fibre, or its chemical reaction with the fibre. We have already seen that these two types of process result in better fastness to washing, because they are essentially irreversible processes.

For diffusion into a fibre, dyes must be present in the water in the form of individual molecules. These are often coloured anions; for example, sodium salts of sulphonic acids such as Congo Red (**2**, Figure 1.3). They may also be cations such as Mauveine (**1**, Figure 1.1), or neutral molecules with slight solubility in water, such as disperse dyes (**3**, Figure 1.6). The dye must have some attraction for the fibre under the dyeing conditions so that the solution gradually becomes depleted. In dyeing terminology, we say that the dye has substantivity for the fibre and the dyebath becomes exhausted.

The four major characteristics of dyes are:

(1) intense colour;
(2) solubility in water at some point during the dyeing cycle;
(3) some substantivity for the fibre being dyed;
(4) reasonable fastness properties of the dyeing produced.

1.3.3 Dye classification and nomenclature

The Colour Index was first published in 1924 by the Society of Dyers and Colourists (SDC) and is the major catalogue of dyes and pigments. The third revised edition is published jointly by the SDC and the American Association of Textile Chemists and Colorists (AATCC). In it, dyes are classified according to chemical constitution (30 subgroups) and usage (19 subgroups) [2]. Table 1.4 gives partial classifications of dyes as presented in the Colour Index.

The first three volumes of the third edition of the Colour Index (CI) give extensive information on the 19 subgroups of dyes classified according to usage. In each subgroup, dyes have a Colour Index Generic Name based on the particular application and hue. For example, CI Acid Red 1 is a red acid dye, with similar dyeing properties to Orange II in Figure 1.2 (CI Acid Orange 7). CI Reactive Blue 4 is a blue reactive dye. Dyes in any one application subgroup will be used for specific fibres using similar dyeing methods. For each dye listed, useful data on

Table 1.4 Classification of dyes according to chemical constitution and usage

Classification according to chemical constitution	Classification according to textile usage
Azo dyes	Acid dyes
Anthraquinone dyes	Azoic dyes
Heterocyclic dyes*	Basic dyes
Indigoid dyes	Direct dyes
Nitro dyes	Disperse dyes
Phthalocyanine dyes	Mordant dyes
Polymethine dyes	Pigments
Stilbene dyes	Reactive dyes
Sulphur dyes	Sulphur dyes
Triphenylmethane dyes	Vat dyes

* Includes a number of different subgroups containing heterocyclic systems (only the most important subgroups in each classification are given)

dyeing methods and fastness properties are tabulated where the information is available. Dyes of known molecular structure are given a CI Constitution Number (5 digits). The direct dye Congo Red (**2**) is CI Direct Red 28 and has CI Constitution Number 22120. Information for other dyes illustrated in this chapter is given below:

(1) Figure 1.4, Indigo, CI Vat Blue 1, Constitution 73000;
(2) Figure 1.5, CI Reactive Red 1, Constitution 18158;
(3) Figure 1.6 (**3**), CI Disperse Blue 14, Constitution 61500.

Volume 4 of the Colour Index gives the chemical constitutions, along with tables of intermediates used in dye manufacture. Volume 5 is particularly useful because of the documentation on the commercial names used by the dye manufacturers. In addition, later volumes and supplements of the Colour Index provide regular updates of the information in the first five volumes. The Colour Index is also available in digitised form on a compact disc (CD-ROM). The 4th edition of the Colour Index, which appeared in 2000, is available on-line with particularly favourable registration fees for multiple users.

The variety of commercial names of dyes from different suppliers is a problem for the uninitiated. Most dyes with the same manufacturer's brand name belong to the same dyeing class. They are usually applied to a particular type of fibre by the same or similar dyeing methods. For example, the Remazol dyes, marketed by

DyStar, are all reactive dyes with vinyl sulphone reactive groups, used mainly for dyeing cotton.

A reference to the colour of the dye usually follows the brand name. The name may also include other descriptive references to particular characteristics of the dye, such as particularly good fastness properties, ability to form metal complexes, or its physical form. The commercial name usually ends with an alphanumeric code. These codes range from quite simple to quite obscure. They may relate to the particular hue of the dye, the relative amount of actual colorant in the formulation, or the application properties.

For example, Indanthren Golden Yellow RK is a vat dye manufactured by BASF (Badische Anilin und Soda Fabrik). 'Indanthren' is the brand name used for their range of vat dyes. 'Golden Yellow' indicates the colour and the code 'RK' shows that this dye is a reddish yellow and applied using a cold-dyeing method. The letter 'R' stands for the German word *rot* = red (the dye is listed as CI Vat Orange 1) and the 'K' comes from the German *kalt* = cold. On the other hand, BASF manufacture Procion Red H-E3B. 'Procion' is their brand name for reactive dyes for cotton. All the Procion dyes with 'H-E' in the code are dyes with two identical reactive groups. Reaction of the dye with the cotton occurs under hot ('H') conditions. The '3B' in the code shows that this is a bluish red (B = blue); bluer than similar red dyes with a code B, but redder in hue than dyes with a 6B in the code. In other cases, the alphanumeric code following the name of the dye may be of little or no value to the dye user. An old paper on dyestuff nomenclature by C L Bird [3] is still useful reading on this subject.

One major problem with the Colour Index classification is that dyes from different suppliers, which have the same registered CI Generic Name and Constitution Number, may have quite different dyeing properties. The Colour Index information is simply an indication that dyes of the same Generic Name contain the same base colorant. The different commercial products will usually contain different amounts of the predominant dye, of other minor dye components, and of auxiliary chemicals. They may, therefore, have different dyeing properties. Some manufacturers erroneously use the Colour Index nomenclature without official registration and their products may not be equivalent, or even close, to those with registered names.

Figure 1.9 illustrates the approximate relative annual consumption of the major types of fibres and dyes estimated for the year 2000. The inner pie chart gives the data for fibres and the lengths of the outer arrows indicate the relative proportions of the various kinds of dyes used. There is a close relationship between the relative

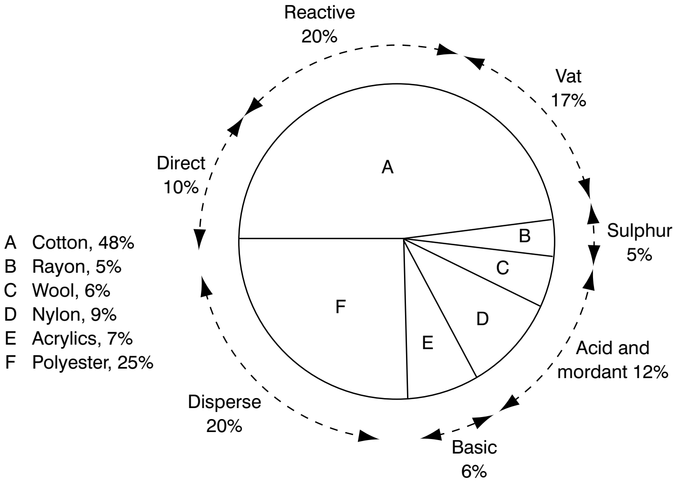

Figure 1.9 Relative annual global consumption of fibres and dyes estimated for the year 2000 (fibre production 5 × 10^{10} kg/year, dye consumption 8 × 10^{8} kg/year)

amounts of fibres produced and the quantities of dyes used to colour each type. The arrows showing dye consumption are situated around the types of fibres that they are used for. Thus, direct, reactive, vat and sulphur dyes are used to colour the cellulosic fibres cotton and viscose, whereas acid and mordant dyes are used for wool and nylon.

This chapter has introduced some simple concepts related to fibres, textile production, dyes, colour and dyeing processes. Before discussing the use of specific kinds of dyes in textile dyeing, and the basic principles involved, the following chapters first deal with the materials to be dyed: the textile fibres, their polymeric nature, manufacture and properties.

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2. A Abel, *Surface Coatings Int.*, **81** (2) (1998) 77.
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CHAPTER 2

Fibres and textiles: properties and processing

This chapter on textile production complements the brief introduction in Section 1.2.2. It reviews some properties of fibres, their conversion into yarns and fabrics, and the objectives of wet processing in manufacturing textiles. The emphasis is on the relationship between dyeing and textile properties and processes. Table 1.1 in the previous chapter identified the seven major fibre types: cotton, wool, viscose, cellulose acetates, nylons, polyesters and acrylics. Later chapters will consider the production, characteristics and dyeing of all these fibres.

2.1 PROPERTIES OF FIBRES

A fibre is characterised by its high ratio of length to thickness, and by its strength and flexibility. Fibres may be of natural origin, or artificially made from natural or synthetic polymers. They are available in a variety of forms. Staple fibres are short, with length-to-thickness ratios around 10^3 to 10^4, whereas this ratio for continuous filaments is at least several millions. The form and properties of a natural fibre such as cotton are fixed, but for artificially made fibres a wide choice of properties is available by design. The many variations include staple fibres of any length, single continuous filaments (monofilaments), or yarns constituted of many filaments (multi-filaments). The fibres or filaments may be lustrous, dull or semi-dull, coarse, fine or ultra-fine, circular or of any other cross-section, straight or crimped, regular or chemically modified, or solid or hollow. The lustre and handle depend on the shape of the cross-section and on the degree of crimping developed in a process called texturising (Section 3.4).

Natural fibres have a number of inherent disadvantages. They exhibit large variations in staple length, fineness, shape, crimp, and other physical properties, depending upon the location and conditions of growth. Animal and vegetable fibres also contain considerable and variable amounts of impurities whose removal before dyeing is essential, and entails much processing. Artificially made fibres are much more uniform in their physical characteristics. Their only contaminants are small amounts of slightly soluble low molecular weight polymer (oligomers) and some surface lubricants and other chemicals added to facilitate processing. These are relatively easy to remove compared to the difficulty of purifying natural fibres.

Water absorption is one of the key properties of a textile fibre. Protein or cellulosic fibres are hydrophilic and absorb large amounts of water, which causes radial swelling. Hydrophobic synthetic fibres, such as polyester, however, absorb almost no water and do not swell. The hydrophilic or hydrophobic character of a fibre influences the types of dyes that it will absorb. Dyeing in a wide range of hues and depths is a key requirement for almost all textile materials.

The regain of a fibre is the weight of water absorbed per unit weight of completely dry fibre, when it is in equilibrium with the surrounding air at a given temperature and relative humidity. Table 2.1 shows some typical values. The regain increases with increase in the relative humidity but diminishes with increase in the air temperature. Le Châtelier's principle states that a system at equilibrium will respond so as to counteract the effects of any applied constraint. Water absorption by a fibre liberates heat (exothermic) and will therefore be less favourable at higher temperatures (more heat). The heat released is often a consequence of the formation of hydrogen bonds (Section 3.3) between water molecules and appropriate groups in the fibre. When the final regain is approached by drying wet swollen fibres, rather than by water absorption by dry fibres, the

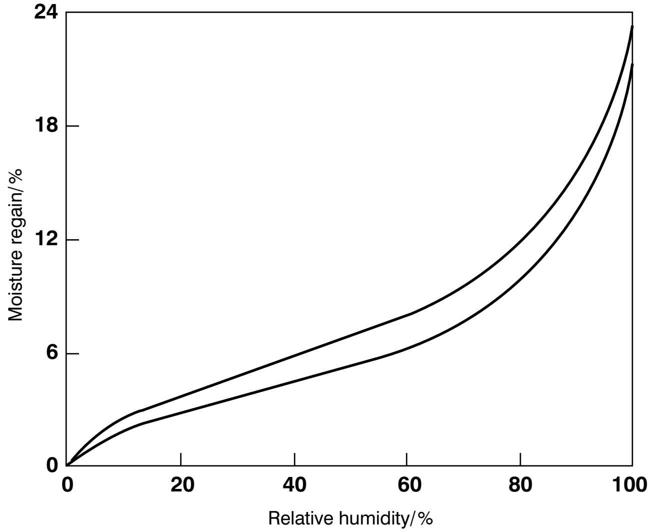


Figure 2.1 Equilibrium regain of cotton fibres by absorption (lower curve) and desorption (upper curve) at 25 °C [1]

Table 2.1 Regain values of fibres obtained by water absorption at 65% relative humidity and 20 °C

Fibre	Regain
Wool	13.0–15.0
Viscose	13.0
Cotton	7.0–8.0
Cellulose diacetate	6.0–6.5
Nylons	4.0–4.5
Cellulose triacetate	2.5–3.0
Acrylics	1.0–2.5
Polyester	0.4

regain is higher. The swollen wet fibres are more accessible to water so they retain more of it at equilibrium (Figure 2.1).

For hydrophilic fibres such as wool, cotton and viscose, the relatively high regain values significantly influence the gross weight of a given amount of fibre. This has consequences in buying and selling, and is also significant in dyeing. Amounts of dyes used are usually expressed as a percentage of the weight of material to be coloured. Thus, a 1.00% dyeing corresponds to 1.00 g of dye for every 100 g of fibre, usually weighed under ambient conditions. For hydrophilic fibres, the variation of fibre weight with varying atmospheric conditions is therefore an important factor influencing colour reproducibility in repeat dyeings. For example, the weight of 100 g of dry cotton varies from about 103 g to 108 g as the relative humidity of the air changes from 20% to 80% at room temperature.

The mechanical properties of fibres, such as tensile strength, flexibility and elasticity, are important in determining the behaviour of a fabric. Some fibres have quite remarkable physical and chemical properties, such as high heat or chemical resistance, or high elasticity with good recovery. Although a detailed discussion of these is beyond the scope of this book, the important physical and chemical properties of the major fibres are discussed in subsequent chapters, particularly in relation to dyeing [2,3].

2.2 PRODUCTION AND PROPERTIES OF YARNS

Natural staple fibres arrive at the spinning mill in large bales. A number of preliminary, mechanical operations open up the compressed fibrous mass, eliminate non-fibrous debris, and blend the fibres in preparation for carding. All natural fibres have inherent variations in their properties because of growth differences, and blending of the fibres is vital to ensure constant quality of the yarns produced. Good opening and separation of clumps of fibres is essential for level dyeing of loose fibre in a dyeing machine with circulating liquor.

The objective of carding is to make a continuous band of parallel fibres called card sliver. This process also removes any residual debris and those fibres that are too short for spinning. During carding, the wide band of fibres passes around a large, rotating roller, with metal pins projecting from its surface. Other small rotating rollers on its periphery have similar pins, and comb and align the fibres held on the pins of the larger roller. The natural wax in raw cotton provides sufficient lubrication for carding. In the case of scoured or degreased raw or recycled wool, additional lubricating oil is necessary to avoid excessive fibre breakage and to control the development of static electricity during carding. Scouring removes this oil before dyeing.

Combing is a process similar to carding. It removes more short fibres from card sliver, leaving the longer staple fibres even more parallel to each other. Longer staple length allows greater drawing out of the combed fibres and thus the production of finer yarn. Spinning of carded wool gives the coarse, low-twist yarns for woollen articles, whereas drawing and spinning of combed wool produces the much finer and stronger high-twist yarns for worsted materials.

After carding, the sliver passes to the drawing or drafting process. Several bands of sliver are combined and gradually drawn out by passing them between pairs of friction rollers of increasing speed. The fibres slide over each other increasing their alignment. This produces a finer band of fibres. It is quite weak and a slight twist helps to hold it together. Further drawing and twisting produce a coarse yarn called roving.

Spinning involves drawing out the band of fibres even more, gradually reducing its thickness, but simultaneously twisting the fibres around each other. Twisting increases the number of contact points between fibres so that their natural adhesion provides sufficient strength to avoid breaking the yarn. The yarn will be stronger the longer the staple length of the fibres, the greater the degree of twist inserted, and the higher the fibre adhesion. The latter is greater if the fibres have a natural or artificially-made crimp.

The various spinning technologies give yarns with quite different characteristics. Classical ring spinning requires a pre-formed roving, which is drawn even more and twisted. This produces quite fine yarns. The open-end and friction spinning techniques give much faster rates of production since the yarn is produced directly from card sliver without intermediate drawing. The bobbins of yarn can also be much larger since the twist is not inserted by rotation of the take-up bobbin, as in ring spinning. Open-end and friction spun yarns are courser and cannot be mixed with ring-spun yarns because of their different structures and twist characteristics.

The final step in yarn production is winding. The yarn is wound into hanks, or bobbins of various types, whose size depends on its subsequent use. Winding also allows an opportunity to detect overly thick or thin sections of the yarn and to eliminate them, and ensures that all the yarn on the bobbin has the same tension. Ply yarns are produced at this stage by twisting two or more yarns together, in the opposite sense to their own twist.

During dyeing, it is imperative that all the yarn in hanks or bobbins has equal access to the circulating dye liquor. Yarn uniformly wound onto perforated supports gives packages with either parallel sides (cheeses) or slanting sides (cones). Their permeability must be uniform throughout. Permeability depends on the type and twist of the yarn, the type and density of winding, and the degree of swelling that occurs when the yarns are wet. If packages are too dense, the pressure required to force dye liquor through them is excessive. Obviously, the package must not deform during dyeing, and the yarn must be easy to unwind. Low density or poorly wound packages may become unstable during liquor circulation, or when the direction of circulation changes, and yarn becomes detached from the body. For these reasons, the preparation of yarn hanks and bobbins for dyeing merits particular attention.

The two major characteristics of a yarn are its degree of twist and its thickness or count. The thickness of a yarn, or of continuous filaments, is expressed as the length of a given weight of yarn, or vice versa. For example, the denier of a continuous filament is the weight in grams of 9000 m. A considerable number of older measures gave the yarn count as the number of hanks, containing a defined length of yarn, obtained from a given weight of fibre. Different standard lengths were used for different fibres. For example, a cotton count of 40 corresponds to 40 hanks, each containing 840 yd of yarn produced from 1 lb of cotton fibre. The standard lengths for wool vary from 100 to 560 yd hank^{-1} depending on the region and the spinning system used. This type of count increases as the yarn becomes finer. Since 1960, the tex system has become increasingly popular. In this, the count of a yarn or filament is the weight in grams of 1 km of yarn. The tex number increases as the yarn thickness increases. Since the tex is a metric unit, decimal multiples and fractions are used for coarser and finer yarns. The kilotex (1 ktex = 1000 tex = 1000 g km^{-1}) is used for sliver, and the decitex (1 dtex = 0.1 tex = 0.1 g km^{-1}) for fine yarns and filaments. Note that 1.0 dtex (0.1 g km^{-1}) is equal to 0.9 denier (0.9 g $(9\ km)^{-1}$).

Much of the technology used today for yarn production originally developed from wool and cotton processing. Modern yarn production from natural staple fibres involves considerable resources because of the large number of operations involved. Continuous filament yarns have the advantage of being ready for direct assembly into fabrics. They are also much cleaner than yarns from natural fibres.

2.3 FABRIC MANUFACTURE

The are four major types of textile fabric:

(1) woven fabrics have yarns interlaced at right angles in a repeated pattern (A, in Figure 2.2);

(2) knitted materials consist of interlocking loops of yarn with a regular pattern (B, in Figure 2.2);

(3) non-woven or felt materials have fibres compressed together in random orientations, held by their natural cohesiveness, or by adhesives;

(4) laces are open materials in which yarns are twisted, looped and knotted together.

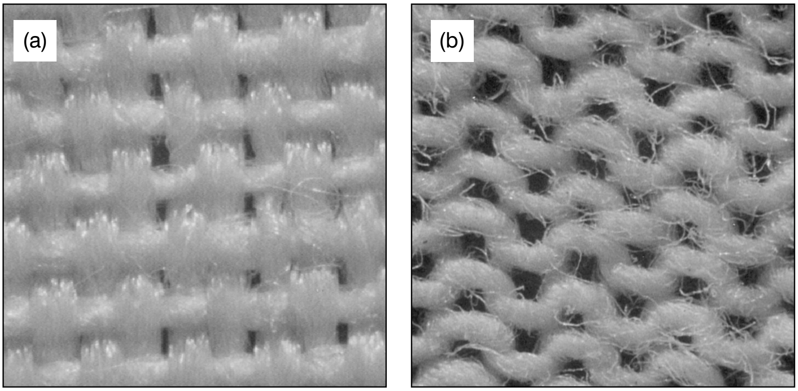


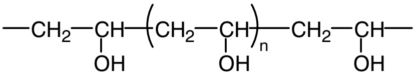
Figure 2.2 Photographs of woven fabric (a) and knitted fabric (b)

The characteristics of a woven fabric depend on the type of fibres present, the fineness and twist of the yarns, the number of yarns per centimetre, and the pattern or weave of the interlaced yarns. The warp yarns, wound side by side on a beam, are threaded through the loom under tension. They run along the length of the fabric. During weaving, raising some warp yarns and lowering others creates a gap for inserting the weft or filling yarn from the side. The positions of the warp yarns then change ready for the next insertion of filling yarn. The two types of yarn are thus woven according to a specific pattern. Winding the warp yarns onto the beam and weft insertion, in the correct colour sequences, is vital when weaving coloured patterns with dyed yarns.

The newer weaving technologies use small projectiles, rapiers, or water or air jets to insert the filling between the warp yarns rather than the older, classical shuttles. They generate much less noise and vibration and increase production speeds.

A woven fabric exhibits maximum resistance to extension in the warp and weft directions. The selvages, running along the edges of the fabric, usually have a more robust and compact woven structure. They stabilise the shape, prevent unravelling and form an area where the fabric can be gripped during manufacturing operations.

During weaving, there is considerable abrasion of the warp yarns from their guided movement through the loom, and from the repeated rapid lifting and lowering required to separate them for insertion of the filling. To avoid excessive abrasion and yarn breakage, the warp yarns usually have a greater twist and a smooth film of size coating their entire length to reinforce them. Sizing chemicals of various types are used depending upon the kinds of fibres present. Good size adhesion on cotton, which has a polar hydrophilic surface, requires use of a polar hydrophilic polymer such as starch. For the hydrophobic surfaces of synthetic fibres, less polar synthetic polymer sizes are preferred. Sizing mixtures include one or more film-forming polymers such as starch, carboxymethyl cellulose (cellulose with some of its hydroxyl groups converted into Cell–O–CH_2–CO_2Na) or polyvinyl alcohol (**1**, in Figure 2.3), as well as wax lubricants, anti-static agents, preservatives, emulsifying agents, and anti-foaming agents. The yarns are usually



$$-CH_2-\underset{OH}{\underset{|}{CH}}-\left(CH_2-\underset{OH}{\underset{|}{CH}}\right)_n-CH_2-\underset{OH}{\underset{|}{CH}}-$$

1

Figure 2.3 Polyvinyl alcohol, used as a film-forming agent in size mixtures treated with an aqueous solution or emulsion of the size, and dried. The amounts of size applied vary from 10–15% solids for cotton (based on the weight of yarn), to 3–5% for synthetic fibres. Optimised recipes give minimum yarn rupture during weaving and are often closely guarded secrets. The size must be removed during preparation for dyeing (Section 2.4), since it interferes with wetting and penetration of dyes and chemicals into the yarns [4].

The perpendicular warp and weft yarns characterise a woven fabric. Knitted materials, however, are constructed of interlocking loops of a single yarn, or a series of parallel yarns. In simple knitted styles such as jersey, each loop, in a series of loops from a single yarn, passes through a loop of the preceding row. Each loop is produced by the action of its own needle carrying the yarn. To minimise friction with the needles and guides, the yarns used in knitting contain a considerable amount of lubricating oil that must be removed before dyeing. The fabric is constructed row after row across the width of the material, or around in a circle, to form what is called a weft knit. When laid flat, circular knitted fabrics have two layers. The higher the number of loops (wales) and rows (courses) per unit distance, the greater the weight and rigidity of the material, the better its recovery after stretching, and the less it is likely to shrink.

Knitting produces fabric much faster than weaving. Knitted materials are flexible, elastic and relatively crease resistant so that clothing made from them fits well. Simple weft-knitted fabrics, however, deform easily in all directions and their dimensional stability is often poor since the yarn is inserted under considerable tension. The shrinkage observed after wetting can be significant. They often have a pronounced tendency to curl at the edges. A yarn breakage can cause the disappearance of a whole series of loops and the formation of a ‘run’. Their handling during wet processing therefore requires more care than for a woven fabric.

In warp knitting, a series of parallel yarns is fed into the machine from a beam, similar to a warp beam in weaving. Each yarn passes through its own needle. Warp knits have vertical columns of loops, but each yarn loops into columns to the left and right in a zigzag pattern. This gives greater resistance to deformation than for a simple knit and a material that is more snag resistant. Interlock knits have a construction intermediate between weft and warp knits.

Besides simple woven and knitted fabrics, there are a large number of other types that have a pile of surface loops or cut loops. These are manufactured by knitting or weaving, or by techniques that combine the features of these two methods. Other types have complex woven or knitted patterns, or may have more than one warp or filling.

The vast majority of carpets are made by simultaneously needle-punching a row of thousands of nylon multi-filaments into a polypropylene backing material in a process called tufting. The backing then advances slightly and another row of tufts is inserted. Application of a latex adhesive to the rear of the backing anchors the tufts in place. Carpet manufacture also consumes lesser amounts of polyester, wool, polypropylene and acrylic fibres. Like fabrics, carpets can be assembled from coloured yarns, dyed using both continuous and batch processes, or even printed.

Non-woven fabrics are formed of a mass of disoriented fibres pressed together and held by their natural adhesion, by tangling them using a needle-punch, with the help of an adhesive, or by heat welding of synthetic fibres, which soften when hot. They often have poor strength but are equally resistant in all directions. Their major applications are for industrial and engineering textiles, and for disposable materials such as sanitary products. Non-woven fabrics are less likely to be dyed than woven or knitted materials but manufacture from pre-dyed fibres is simple if colour is required.

A multitude of different textile fabrics are manufactured, each type with its own characteristic structure and uses. The machinery used for handling these materials, particularly during wet processing, is dictated by the strength and weight of the fabric and its ease of deformation. In addition to weight and strength, the other major attributes of a fabric are flexibility, elasticity, handle, water absorbency, resistance to the conditions met during use, and good dyeability. Many fabrics have a different appearance on the two sides, which becomes even more evident on dyeing. The face of the fabric is usually the one presented during use. Carpets and pile fabrics are extreme examples of this.

Fabrics come in a wide range of widths, superficial weights (g m^{-2}), and air permeabilities, the latter two properties depending on the thread or loop spacing and the degree of twist of the yarns. Heavier fabrics provide better draping characteristics. The properties of a fabric depend on its construction and upon those of the component fibres. For example, fabrics made from viscose filaments are often weak and very absorbent whereas those made from polyester filament are strong and do not absorb water. Fabric properties can thus be modified by using combinations of fibres. Fibres are blended for aesthetic and special effects, for economy and to give fabrics of superior performance in use. For the production of yarns containing different fibres, blending takes place during the opening, carding or drafting operations. Alternatively, yarns of different fibres can be combined during fabric production. Of all fibre blends, those of cotton and polyester staple in particular have become the most important in the modern market. The polyester component gives tensile strength, abrasion resistance and dimensional stability to the fabric, while the cotton provides water absorbency, comfort and reduced pilling (Section 4.3.2).

2.4 PREPARATION FOR DYEING

Newly constructed textile materials are called grey or greige goods. At this stage, the overall manufacturing sequence is far from complete. Natural or synthetic chemicals in fabrics can interfere with wetting and dyeing. Preparation is the series of processes used to remove them in readiness for dyeing and finishing. The objective of preparation is to remove as much of the unwanted impurities as possible from the fibres to produce a fabric that will uniformly absorb solutions of dyes and chemicals. Uniform water absorbency is more critical than complete removal of contaminants. Penetration of solutions into very compact fabrics, made from fine, high-twist yarns packed tightly together, is not necessarily rapid and is even more difficult for poorly prepared goods. Good preparation is vital for successful dyeing and printing since non-uniform absorption of dyes is immediately visible.

The unwanted chemicals are of a very diverse nature. They are often processing aids such as lubricants or warp size. Fabrics containing wool and cotton, however, may contain substantial amounts of natural impurities that impede uniform wetting. These include hydrophobic waxes that are difficult to emulsify. The preparation of wool or cotton fabrics can involve much of a textile finishing mill's resources. Some of the processes that are used in the preparation of materials made from natural fibres are discussed below.

Raw wool fibres may contain 30–50% of impurities including wool wax (often called grease), and inorganic salts (suint), as well as varying amounts of dirt, straw, excrement, and burrs. Before textile manufacturing begins, gentle scouring at 40–50 °C with a weakly alkaline detergent solution removes the bulk of these (Section 7.2.3). Mild alkaline scouring of wool fabric before dyeing eliminates lubricating oil that was added to facilitate carding and spinning. Residues of vegetable material are often apparent in grey wool fabrics. This cellulosic material does not absorb the dyes used for colouring the wool and shows up as pale patches after dyeing. Impregnating the wool with sulphuric acid solution and drying has no effect on the wool but causes hydrolysis of all cellulosic materials. Beating the dried fabric pulverises and removes the brittle cellulose hydrolysis products. The process is called carbonising (Section 7.3.3). The acid remaining in the wool serves for subsequent dyeing operations.

Table 1.2 shows a typical production sequence for manufacture of a cotton jersey. A typical preparation sequence for a woven cotton fabric might include singeing, desizing, kier boiling (alkali-boiling), bleaching and possibly mercerisation (Section 5.4.6). All these processes remove unwanted material from the cotton and improve its quality. In singeing, the fabric rapidly passes through a gas flame. This burns off any short fibres projecting from the fabric surface that abrasion has lifted from the yarns during weaving. The result is a much smoother fabric surface. The next step for most woven fabrics is desizing. Various types of starch are used for sizing cotton warps to reinforce them. Washing alone does not effectively dissolve starch sizes but digestion with appropriate enzymes will eliminate them.

The sizing washed out of a woven fabric is often discarded, so it must be cheap and have minimal environmental impact. Washing liquors from desizing contain substantial quantities of organic chemicals that cause an important pollution problem. They are mostly biodegradable, but this consumes considerable amounts of dissolved oxygen from the water, which adversely affects the local ecosystem. Increasing government requirements for effluent treatment, to prevent high values of this ‘biological oxygen demand’ (Section 8.5.1), have spurred developments in water treatment, and in the use of sizes that can be recovered from the washing liquors and re-used. For cotton/polyester warps, it is now common to use polyvinyl alcohol (**1**) for sizing. This is a water-soluble polymer removed by simple washing in hot water and then possibly recovered by hyperfiltration membrane techniques [5]. Newer no- or low-wetting processes include solvent desizing, sizing with molten, water-soluble polymers, and the application of size in foams.

In kier boiling (alkali-boiling) of cotton materials, the cotton is heated with dilute NaOH solution under pressure for several hours, in the absence of oxygen (Section 5.4.3). Small quantities of detergents and solvents are frequently added. The objective is to eliminate the waxy cotton cuticle, the natural oils, waxes and proteins, as well as various salts and soluble cellulose and carbohydrate derivatives. It also helps to remove any size residues. The removal of the hydrophobic constituents of the cotton fibres renders them much more absorbent. In many modern plants, much faster, continuous processes of this type use higher concentrations of NaOH. They are, however, less efficient than the classical kier process because of the short treatment times.

The aim of bleaching is to remove any unwanted colour from the fibres. This may be the grey or yellow tinge of a natural fibre, or it may be a consequence of discoloration from the manufacturing processes. Bleaching is essential if high quality white goods are being produced, or if the goods will be dyed with pale bright colours. The bleaching process also eliminates any traces of other impurities remaining from the previous preparation steps and improves the absorbency of the material for dyeing and printing. Bleaching agents are usually oxidising agents. Today, the most common bleaching agent is a stabilised alkaline solution of hydrogen peroxide (H_2O_2). This is a powerful oxidising agent that destroys the natural colouring matters present in cotton without undue oxidative damage to the fibres. Any residue of starch in the cotton is rapidly oxidised by the hydrogen peroxide used in bleaching so that the peroxide is less effective in destroying undesirable coloured impurities. In addition, residual starch can also reduce some dyes during dyeing, particularly under alkaline conditions, resulting in decreased colour depth.

Hydrogen peroxide has largely replaced solutions of sodium hypochlorite ($NaOCl$) as a bleaching agent, since the latter chemical requires careful pH and temperature control during bleaching to avoid oxidising the cotton. Hydrogen peroxide also offers other advantages: alkali-boiling and bleaching can be combined into one process; continuous operation is relatively easy; and thorough washing of the bleached fabric is less critical since traces of residual peroxide are less damaging than those of chlorine from sodium hypochlorite. Again, both alkali-boiling and bleaching remove unwanted contaminants from cotton material, which results in waste liquors and large volumes of washing water producing a dilute effluent with an appreciable biological oxygen demand.

Bleaching, in the sense described above, must be distinguished from the destruction of the colour of a dyed fabric, which may be necessary if it must be re-dyed. Such colour stripping usually involves solutions of reducing agents such as sodium hydrosulphite ($Na_2S_2O_4$).

Materials manufactured from artificially made fibres are much easier to prepare than those from natural fibres. Artificially made fibres are relatively clean and any spin-finish or other chemicals such as size are, by design, removable by simple washing with a detergent solution. Bleaching of artificially made fibres is not usually necessary. It is most common when a fabric made of synthetic fibres has a yellow cast from over-heating, or has picked up dirt during manufacture. The process is much milder than for natural fibres.

Since many fabrics requiring bleaching tend to be somewhat yellow, they have a stronger absorption of blue and violet light in the 400–500 nm wavelength range (Table 1.3). Certain colourless compounds absorb non-visible, near ultraviolet light at wavelengths between 300 and 400 nm and transform some of the absorbed energy into a visible blue-violet fluorescence in the 400–500 nm region. This emission of light offsets the absorption of the fibres in this wavelength region, even producing an effect where the reflected light plus the fluorescence causes more visible light to leave the fabric surface than is apparently incident upon it. This gives the impression of a brilliant white. Such compounds are called fluorescent whitening agents or optical brighteners (Section 5.4.5). They are widely used for textiles, paper and in domestic detergents.

Cellulosic and protein fibres are particularly vulnerable to growth by micro-organisms under warm humid conditions. Even though the synthetic fibres are fairly resistant to bacterial degradation, a variety of residual chemicals on the fibre surfaces can serve as nutrients for air-born micro-organisms. Rapid growth of colonies of bacteria produces coloured spots and often a distinct odour. The odour of mildew is from the growth of fungi. Once formed, the coloured pigments from bacterial metabolism are often resistant to vigorous bleaching. This problem can be minimised by ensuring that stored fabric is completely dry and relatively clean. Use of an anti-bacterial agent such as a chlorophenol or a quaternary ammonium compound will prevent this problem.

Effective preparation before dyeing is essential, no matter what the physical form of the textile material, but particularly for fabrics. Uneven preparation invariably results in unlevel dyeing. For loose dyed fibre, and to a lesser extent for dyed yarn, uneven colour is blended by the mixing that occurs in subsequent manufacturing processes. This is impossible for dyed fabric and unlevel colour usually leads to rejection of the goods. In later chapters, we will discuss the preparation of various different types of fibres and see more of the impact of preparation on dyeing processes.

2.5 DYEING AND FINISHING

Textile finishing consists of a variety of mechanical, thermal and chemical processes that improve the appearance, texture or performance of a textile material. Dyeing is usually the first finishing process. Textile materials come in a wide variety of forms and coloration occurs at almost any stage from loose fibres right through to fully formed fabrics, or even made-up articles. Coloration involves dyeing or printing in either batch or continuous processes, depending upon the quantity of material to be processed. The objective of dyeing is to colour the entire material so that the dye has completely penetrated into the fibres and the visible surface has a completely uniform colour. Good penetration of the dyes ensures optimum fastness properties. The diversity of fibres and materials necessitates different types of dyeing machine (Chapter 12).

Mechanical finishing produces a variety of different effects (Section 25.2). In calendering, compressing the fabric between rollers under pressure produces a flat, smooth fabric surface. Raising or napping involves abrading the fabric surface using sharp steel points to break and lift fibre ends, giving a surface pile. Compressive shrinking of cotton fabrics avoids shrinkage when a fabric is wetted. Heat setting of materials made from thermoplastic synthetic fibres stabilises their shape and dimensions (Section 3.4).

The majority of chemical finishing processes are for fabrics containing cellulosic fibres (Section 25.4). The chemicals used often form polymers on heating and are also capable of reacting with the cellulose to generate crosslinks between the polymer molecules. The result of this is a fabric with improved dimensional stability to washing, and crease resistance. In addition, there are a large number of chemical treatments for fabrics that impart specific properties such as water repellence, softness of handle, flame resistance, easy soil release or resistance to bacteria.

The effects of the actual finishing processes on the colour characteristics of the material must be carefully evaluated in advance since finishing can change the shade of a dyed fabric and modify the fastness properties.

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CHAPTER 3

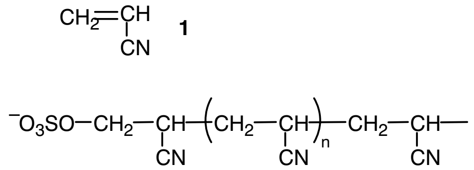
Fibrous polymers

This chapter introduces some principles of polymer chemistry and discusses the structural characteristics of the major fibrous polymers and their important properties, particularly those related to dyeing. Later chapters will provide more details on specific fibres.

3.1 POLYMER STRUCTURE

Polymers consist of molecules with very high molecular weights. The word ‘polymer’ comes from the Greek words *poly* meaning ‘many’, and *meros* meaning ‘part’. It therefore refers to the many simple structural units, linked in a continuous chain, that constitute a polymer molecule. These units are often identical. This repetitive structural pattern in polymers was not clearly recognised before about 1925, after the development of much of the technology for dyeing natural and regenerated fibres.

A monomer is a simple chemical species whose molecules link to produce a polymer. The structures of the monomer acrylonitrile (cyanoethene, **1**) and the polymer that it forms (polyacrylonitrile, **2**) are shown in Figure 3.1. Because the same structural motif often occurs repeatedly in a polymer molecule, the empirical formula can be deceptively simple, despite the very high molecular weight. For example, the empirical formula for polyacrylonitrile is C_3H_3N, the same as for the monomer. The molecular weight of the polymer depends upon the number of repeated monomer units, or degree of polymerisation (DP). To a good approximation, the polymer molecular weight equals the DP times the molecular



$$CH_2{=}\underset{CN}{\underset{|}{C}H} \quad \mathbf{1}$$

$$^{-}O_3SO{-}CH_2{-}\underset{CN}{\underset{|}{C}H}{-}\left(CH_2{-}\underset{CN}{\underset{|}{C}H}\right)_n{-}CH_2{-}\underset{CN}{\underset{|}{C}H}{-}$$

2

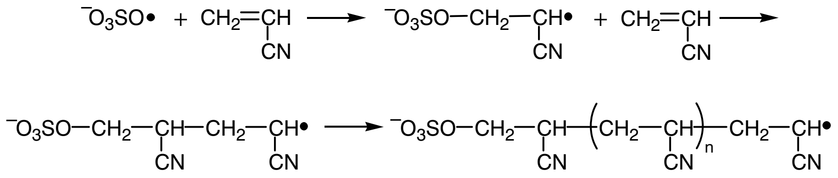
Figure 3.1 Structures of the monomer cyanoethene (**1**) and the polymer that it forms, polyacrylonitrile (**2**) weight of the repeating unit. This is because the number and mass of the groups at the ends of the long polymer molecules (–OSO_3^- in the case of **2**) are negligible in comparison with the total number and mass of the repeating units. The end groups in a polymer come from the monomer itself, or from the initiators used in the polymerisation process. Polyacrylonitrile often has sulphate (–OSO_3^-) and sulphonate (–SO_3^-) end groups derived from the sodium persulphate ($Na_2S_2O_8$) and bisulphite ($NaHSO_3$) that initiate the polymerisation of acrylonitrile. Ionic end groups in a polymer have an important role in ion exchange dyeing processes (Section 1.1.2).

The repeating units and end groups define the molecular structure of a polymer. The next structural level involves the distribution of the values of the molecular weight or DP. Unlike most chemicals, in which all the molecules are identical, the molecules in a polymer have varying numbers of repeating units resulting in a distribution of molecular weights. At an even more refined level, the arrangement of the polymer molecules in three dimensions, and the possibility that their alignment and interaction can lead to the formation of ordered crystalline regions, becomes relevant.

Because polymers consist of molecules with high molecular weights, they are involatile and often insoluble in common solvents. They have poorly defined melting points, or decompose before melting. Not all polymers form fibres. Those polymers that do, have a high molecular weight and long, unbranched, linear molecules with regular structures. Alignment of the long polymer molecules along the fibre axis results in intermolecular attractive forces and the formation of crystalline regions. This promotes fibre strength. Although intermolecular bonding is weak, these attractive forces, between aligned neighbouring molecules along a significant portion of their length, provide resistance to deformation and chain slippage.

Fibrous polymers, with a minimum of chain branching, are made from bifunctional monomers. Vinyl compounds, such as acrylonitrile, are bifunctional since two new bonds form to each monomer unit during polymerisation. The polymerisation of vinyl compounds can be initiated by free radicals, cations or anions. A free radical is a reactive chemical species possessing an unpaired electron. Radical polymerisation is a chain reaction. The initially generated free radical rapidly adds a monomer molecule but each addition regenerates the free radical reactive site at the end of the growing polymer molecule. Termination of the growing chain occurs when two radicals couple together or react by transfer of a hydrogen atom. Cationic and anionic vinyl polymerisation are similar, except the reactive sites are now ionic and the polymerisation is terminated by addition of appropriate chemicals.

Such chain reactions are usually very fast and the product isolated from an interrupted process consists of only residual monomer and fully formed polymer of high DP. Figure 3.2 illustrates the radical polymerisation of acrylonitrile. Polymers made by polyaddition invariably have a skeletal chain composed only of carbon atoms and the repeating unit in the polymer has the same types and numbers of atoms as the monomer.



$$^{-}O_3SO\bullet + CH_2{=}\underset{CN}{CH} \longrightarrow {}^{-}O_3SO{-}CH_2{-}\underset{CN}{CH}\bullet + CH_2{=}\underset{CN}{CH} \longrightarrow$$

$$^{-}O_3SO{-}CH_2{-}\underset{CN}{CH}{-}CH_2{-}\underset{CN}{CH}\bullet \longrightarrow {}^{-}O_3SO{-}CH_2{-}\underset{CN}{CH}{-}\left(CH_2{-}\underset{CN}{CH}\right)_n{-}CH_2{-}\underset{CN}{CH}\bullet$$

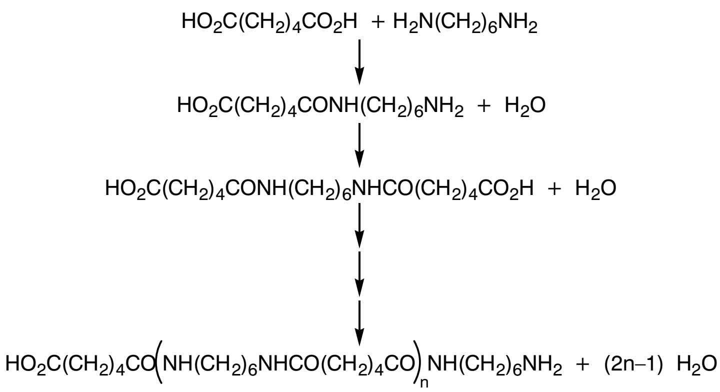
Figure 3.2 Radical polymerisation of acrylonitrile

The formation of esters and amides from carboxylic acids and their derivatives involves the elimination of a simple product of low molecular weight, such as water. These are called condensation reactions (Scheme 3.1). Nylon and polyesters are made by polycondensation. These polymers have long chains containing atoms other than carbon derived from the functional groups of the monomers. Unlike the polyaddition chain reaction, polycondensation involves the stepwise formation of species of gradually increasing molecular weight. Figure 3.3 shows the formation of a nylon polyamide by such a process starting from adipic acid (1,6-hexanedioic acid) and hexamethylenediamine (1,6-hexanediamine). Because the monomers are both bifunctional, the polymer chain has no lateral groups.

$$RCO_2H + C_2H_5OH \longrightarrow RCO_2C_2H_5 + H_2O$$

$$RCO_2H + CH_3NH_2 \longrightarrow RCONHCH_3 + H_2O$$

Scheme 3.1



$$\begin{array}{c} HO_2C(CH_2)_4CO_2H + H_2N(CH_2)_6NH_2 \\ \downarrow \\ HO_2C(CH_2)_4CONH(CH_2)_6NH_2 + H_2O \\ \downarrow \\ HO_2C(CH_2)_4CONH(CH_2)_6NHCO(CH_2)_4CO_2H + H_2O \\ \downarrow \\ \downarrow \\ \downarrow \\ HO_2C(CH_2)_4CO\left(NH(CH_2)_6NHCO(CH_2)_4CO\right)_n NH(CH_2)_6NH_2 + (2n-1)\ H_2O \end{array}$$

Figure 3.3 Formation of a nylon by stepwise polycondensation

The number of reactive functional groups of the monomer or monomers determines the degree of branching along the molecular chain of the polymer they produce. For example, a polyester forms on heating a mixture of a dicarboxylic acid such as terephthalic acid (1,4-benzenedicarboxylic acid) and a diol such as ethylene glycol (1,2-ethanediol). These monomers are both bifunctional and an unbranched linear polymer molecule results, suitable for fibre formation (Figure 3.4). This polymer is thermoplastic. This means that the solid polymer will soften and deform easily when heated to a temperature below its melting point, but it will re-harden on cooling.

If an anhydride, such as phthalic anhydride (cyclic anhydride from 1,2-benzenedicarboxylic acid), is reacted with a triol, such as glycerol (1,2,3-propanetriol), the trifunctional alcohol allows extensive chain branching during the polymerisation reaction. By using a 3-to-2 anhydride-to-triol mole ratio, which gives the same initial numbers of hydroxyl and carbonyl groups, the product is a highly branched network polymer (Figure 3.4). When a partially formed polymer of this type is heated, it will initially soften, like a thermoplastic polymer, but the chain-linking process then continues as uncombined hydroxyl and carboxyl groups react. The polymer becomes even more crosslinked and more rigid. Such materials are called thermohardening or thermosetting. Ultimately, the entire sample of solid polymer may consist of a single giant molecule. Thermosetting polymers are very useful for heat moulding of hard plastic articles. Although such polymers are not crystalline, the molecules are so effectively linked that a mechanically strong material results. They are not used as fibres.

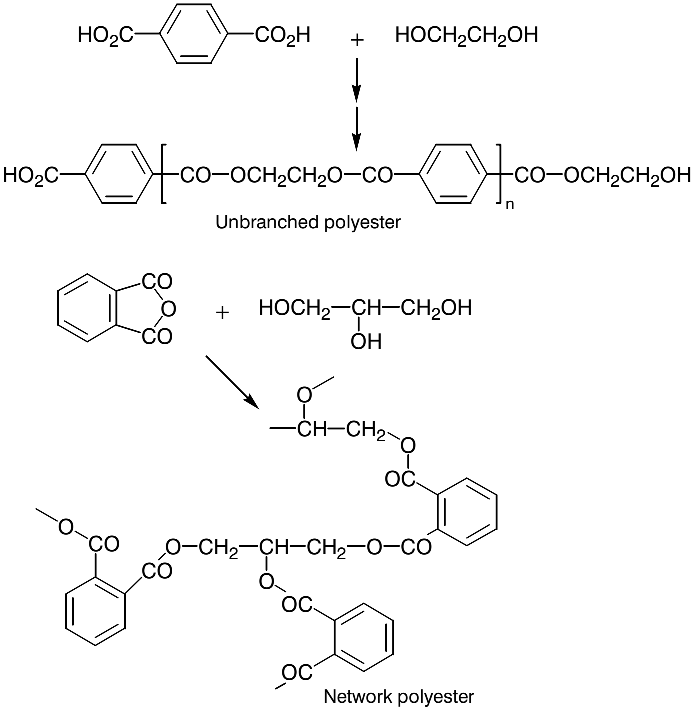
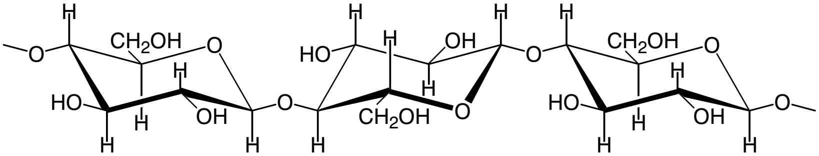


Figure 3.4 Formation of unbranched and network polyesters

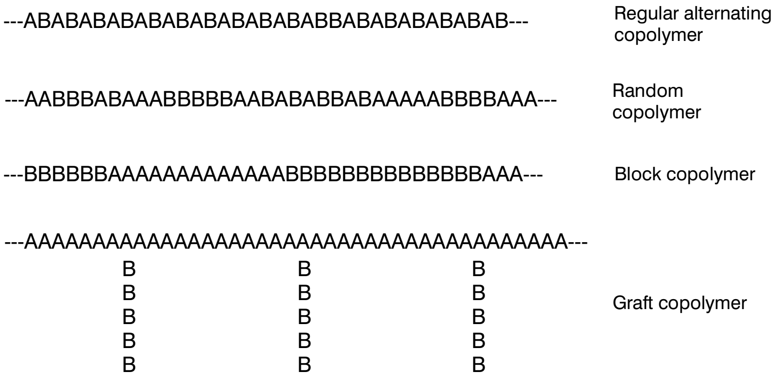
Some fibrous polymers have a single type of repeating unit and are called homopolymers. Cellulose (**3**, in Figure 3.5), for which the repeating unit consists of two linked glucose units (cellobiose), is an example. Others, obtained from a mixture of two or more monomers, are called copolymers. The properties of a copolymer depend upon the relative amounts and the sequence of the different monomer units present in the polymer chains. In many synthetic copolymers, two monomers are present. These may have a regular alternating or random sequence along the polymer chain. In other types, the monomer units may be present in



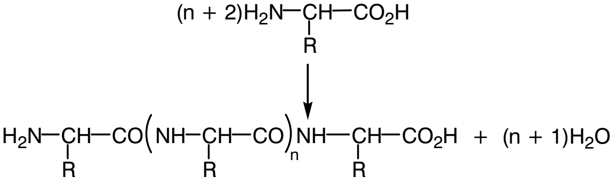
3

Figure 3.5 Cellulose

alternating long sections either along the main chain (block copolymer), or as branches of one type grafted to the main chain of another (graft copolymer) (Scheme 3.2). The three latter types all have textile applications. Proteins are complex copolymers formed by polycondensation of mixtures of α-amino acids. These are carboxylic acids with an amino group attached to the carbon atom next to the carboxyl group. Each protein has a specific sequence of different amino acid units in the polymer chain (Scheme 3.3). There will usually be one amino and one carboxylate end group derived from the appropriate terminal amino acids.



Scheme 3.2



$$(n+2)H_2N{-}\underset{R}{CH}{-}CO_2H \longrightarrow H_2N{-}\underset{R}{CH}{-}CO\left(NH{-}\underset{R}{CH}{-}CO\right)_n NH{-}\underset{R}{CH}{-}CO_2H + (n+1)H_2O$$

Scheme 3.3

Whatever the chemical structure of a fibrous polymer, the nature of the groups along the molecular chain and the end groups determine its chemical and dyeing behaviour. As outlined above, an apparently homogeneous sample of a polymer consists of a variety of molecules of varying length and mass. The molecular weight is not a constant, as for most compounds, but varies depending upon the distribution of polymer molecule sizes. This is known as polymolecularity.

The molecular weight of a polymer may be defined in various ways. The usual molecular weight is the number average molecular weight (Eqn 1). This is the mass of an Avogadro's number of molecules (6.023 × 10^{23}). Molecular weight determinations based on end group analysis or the colligative properties of polymers give this type of molecular weight, from which the average value of the DP is obtained. Polymer molecular weights may also be defined by a weight average (Eqn 2). This type of molecular weight is obtained from measurements of light scattering. The definitions of these two types are

$$\text{Number average MW} = \frac{\sum (m_\mathrm{i} \times n_\mathrm{i})}{\sum (n_\mathrm{i})} \qquad (1)$$

$$\text{Weight average MW} = \frac{\sum (m_\mathrm{i} \times w_\mathrm{i})}{\sum (w_\mathrm{i})} \qquad (2)$$

where n_i and w_i are, respectively, the number of moles and weight of each type of polymer molecule of molecular weight m_i. Of the two, the weight average molecular weight is usually higher.

3.2 MOLECULAR ORGANISATION IN FIBRES

Many properties of fibrous polymers reveal that the molecular chains run along the main fibre axis with a considerable degree of alignment. When the polymer molecules are parallel and closely spaced, intermolecular attractive forces operate and the regular ordering of the chains leads to crystalline behaviour. A crystal is a solid in which there is a regular repetition of the atomic arrangements in three dimensions. When a beam of X-rays is directed at a crystal, and the diffracted beams detected on a photographic film, a pattern of dots is found, characteristic of the crystalline substance. The regular repetition of atomic positions produces sharp diffraction patterns. Less crystalline and non-crystalline materials give diffuse diffraction patterns, or no pattern at all. Analysis of the positions of the dots allows calculation of the distances between repeated planes of atoms in the crystal. The intensities of the diffracted beams producing the dots provides information about the relative electron densities around atoms in the crystal. X-ray diffraction thus identifies the atoms and their relative positions. It is a powerful method for determining the structures of molecules.

Diffraction of an X-ray beam impinging on an extended fibre at right angles to its axis often gives a pattern of dots characteristic of a crystal, but accompanied by the more diffuse pattern characteristic of amorphous materials. Many fibres are partly crystalline in regions where chain orientation is high and the closely spaced chains interact. Fibres also have zones where the arrangement of the molecular chains is completely random. There will be varying degrees of order between these two extremes. The overall conclusion is that the polymer chains may pass through several different crystalline regions and also through zones with increasing degrees of disorder. In the crystalline regions, the polymer chains are aligned in close contact with either neighbouring chains, or with another part of the same chain that is folded back on itself. Some models are shown in Figure 3.6.

Fibre crystallinity has a considerable influence on its mechanical and chemical properties. Usually, the more crystalline the fibre, the harder it is to extend (higher elastic modulus) and to break (higher tensile strength). It is difficult for chemicals to penetrate into the crystalline regions of a fibre since this would require breaking the intermolecular bonds responsible for crystallite formation. Even the small molecules of water may be excluded from the crystalline regions. It is the more amorphous regions of the polymer structure that are readily accessible to

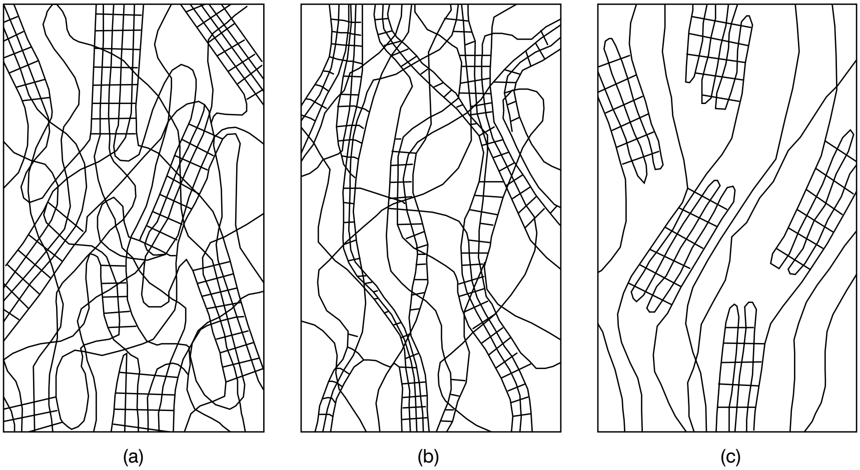

(a) (b) (c)

Figure 3.6 Some models of molecular organisation in fibres: (a) fringed micelles; (b) fringed fibrils; (c) folded chains chemicals and it is here that dye molecules can penetrate. The amorphous regions are those zones where the fibre is weaker but that provide flexibility and accessibility to chemicals. The most crystalline fibres will be those with regularly repeating structural units along the chains, aligned in proximity so that intermolecular bonds stabilise the three-dimensional structure. Copolymers will generally be more amorphous than homopolymers, and polymers with large irregular branching groups will have difficulty crystallising. Fibrous polymers are often insoluble in common solvents, or only dissolve very slowly after considerable swelling. Their solubility depends upon the degree of crystallinity and the molecular weight.

The extent of chain orientation along the filament axis influences the degree of crystallinity. Orientation increases on extending the filaments under tension. The process is called drawing. It causes the molecular chains to slide by one another as the plastic filament extends and increases in length. This promotes chain orientation and therefore crystallisation. Drawing is an important operation for improving the mechanical properties of artificially made filaments.

All fibres exhibit their own characteristic morphology. They may have crystalline and amorphous zones. They may be non-porous, or have porous structures in which the fibres themselves are constituted of bundles of much smaller fibre-like units called fibrils. They may have pronounced differences between the fibre skin and core. Molecular organisation in fibres has many different forms and fibres cannot be considered to be homogeneous materials. The following chapters review the morphology and properties of different types of individual fibres.

3.3 INTERMOLECULAR FORCES

In the preceding section, we saw that polymer molecules will form crystalline structures if they arrange themselves so that the position of each type of atom has an exact repeated pattern in three dimensions. The proximity of the molecules allows intermolecular attractive forces to operate that stabilise the crystalline arrangement. What is the nature of this kind of force? It is a kind of bonding. Like covalent and ionic bonding, these forces originate from the mutual attraction of negatively charged electrons in an atom in one molecule for positively charged nuclei of atoms in a neighbouring molecule. These attractive forces, however, only operate over short distances and are generally quite weak. They therefore lack the relative stability of ionic and covalent bonds. These weak intermolecular bonding forces are responsible for many phenomena in textile chemistry, including the coherence of the crystalline regions in fibres, and even the dyeing process itself.

Ionic bonds are the simplest to understand since they involve the attraction of oppositely charged ions that have atoms with more or less than the required number of electrons for electrical neutrality. In wool, ionic bonds between adjacent protein chains arise from interaction between carboxylate anions attached to one chain and ammonium cations to another (Figure 3.7). As we saw in Section 3.1, covalent bonds between polymer chains lead to the formation of network structures that are not conducive to fibre formation. The only fibrous polymer with significant covalent inter-chain bonds is wool. These crosslinks come from the incorporation of the double amino acid cystine into two separate protein chains (Figure 3.7). Such inter-chain bonding is deliberate during crease-resist finishing of cotton materials. The crosslinked cellulose chains are less easily displaced when the material is folded (Section 25.4.1).

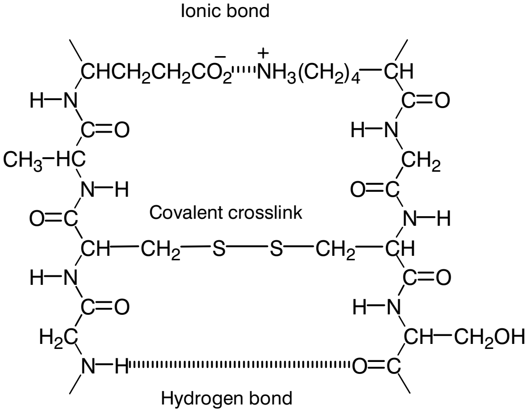


Figure 3.7 Some inter-chain bonds between protein chains in wool

Another type of much weaker intermolecular bond is that occurring between permanent dipoles. Such dipoles arise from the unequal sharing of electrons in covalent bonds between atoms of different electronegativity. The result is a bond with one end somewhat electron deficient and therefore more positive than the other electron rich and relatively negative end. The separated partial charges represented by $\delta+$ and $\delta-$ constitute a dipole, and attraction between the opposite ends of the dipoles in molecules results in weak bonds. Figure 3.8 illustrates dipole–dipole attraction between the cyano groups in polyacrylonitrile. In some cases, molecules with permanent dipoles can exert attractive forces on neighbouring non-polar molecules by polarising their electrons. The electropositive end of a dipole attracts and polarises the electrons in a bond between two atoms in a neighbouring molecule while the electronegative end of the dipole becomes attracted to the neighbouring atom's more exposed nucleus. Dipole–dipole and dipole-induced dipole bonds are weak and only significant when molecules are in close contact. They are therefore continually being broken and reformed as molecules collide.

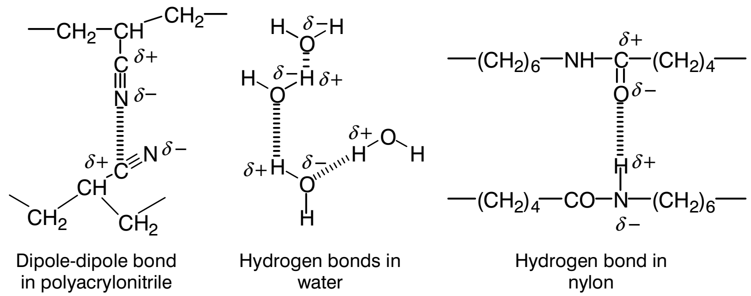


Figure 3.8 Dipole and hydrogen bonds in water and some fibres

A special kind of dipole–dipole interaction occurs between the pronounced dipoles of covalent bonds between electronegative atoms such as oxygen or nitrogen and a hydrogen atom. This type of bond is called a hydrogen bond because the interaction or bond energy is about 10 times stronger than that of a typical dipole–dipole bond (See Table 3.1). Even at its boiling point, water is a highly associated liquid in which clusters of water molecules associate together by hydrogen bonding (Figure 3.8). Cellulose is a polyalcohol. It is insoluble in water because water molecules are unable to penetrate into the crystalline regions and break the hydrogen bonds between the hydroxyl groups of the ordered cellulose molecular chains. Hydrogen bonds between amide groups are important in proteins and nylon (Figure 3.8).

The weakest intermolecular forces are those that exist between all types of molecules, even those without particular ionic or dipolar sites. These forces involve the attraction of the electrons of an atom in a given molecule for the partially exposed nucleus of an atom in a neighbouring molecule. They are a

Table 3.1 Approximate energies of various types of chemical and intermolecular bonds

Type of bond	Typical bond energy (kJ mol^{-1})
Ionic	700
Covalent	400
Hydrogen bond	40
Dipole–dipole	5
Dispersion forces	5

consequence of the unequal distribution of electrons around atoms at any given instant. The attraction will only exist for a short time since the electron arrangement is continuously in flux, the atoms are in constant motion, and the energy of interaction decreases dramatically with increasing molecular separation. These instantaneous attractions are called dispersion or London forces. They have a significant influence on molecular properties. Even the completely non-polar polyethylene has a fairly high melting point because of the cumulative effect of dispersion forces at many locations along the polymer molecules. The weak dipole and dispersion intermolecular forces discussed above, often collectively referred to as van der Waals forces, are responsible for the non-ideal behaviour of all gases and are intimately involved in the interaction between dye and polymer molecules during dyeing.

3.4 THERMAL PROPERTIES OF POLYMERS

The different polymers used as fibres have varied responses to heat. Natural polymers, such as cellulose and proteins, have high average molecular weights but invariably decompose before they reach their melting temperature. During drying or curing, temperatures as low as 150 °C can cause fabrics from natural fibres to become yellow and more brittle. The thermal damage is greater the longer the exposure to the high temperature. The consequences of this are quite obvious on dry pressing wool or cotton fabrics with an over-heated iron.

Synthetic fibrous polymers consist of unbranched molecules. They are usually thermoplastic. This means that materials made from them tend to soften and deform on heating, but become rigid again on cooling. Cellulose diacetate and acrylic fabrics require careful treatment during dyeing to avoid deforming the fabric structure. They become quite plastic at temperatures below 100 °C. A hot iron can melt cellulose diacetate and produce a hole in a fabric made from it. To avoid creasing and over-extension of the fabric, cellulose diacetate materials must be dyed at no higher than 85–90 °C, in open width, and with a minimum of tension. High-bulk texturised acrylic fibres usually give fabrics with good crease resistance. Such materials are, however, quite plastic when hot and excessive tension must be avoided during dyeing. Rapid cooling of the goods by flooding a hot dyebath with cold water causes a sudden change from plastic to rigid behaviour and will set creases in the fabric. Slow cooling of the bath and gentle motion of the material are essential.

For thermoplastic materials, the glass transition temperature (T_g) is that at which molecules in the solid, glassy state, characteristic of the amorphous zones of the polymer, have sufficient energy for entire segments of the polymer chains to become mobile. At temperatures below T_g, the molecules are frozen in position and the polymer is rigid. Above this temperature, the available thermal energy is sufficient to cause bond rotations allowing segments of the polymer chain to move into new positions. This results in significant changes in the physical properties of the polymer. For example, above the T_g, the specific volume of a thermoplastic polymer increases more rapidly with increasing temperature and the stress required to deform a sample of polymer will be less than at lower temperatures. The changes in such properties can be used to measure T_g, although the values obtained tend to be dependent on the actual experimental conditions (Figure 3.9).

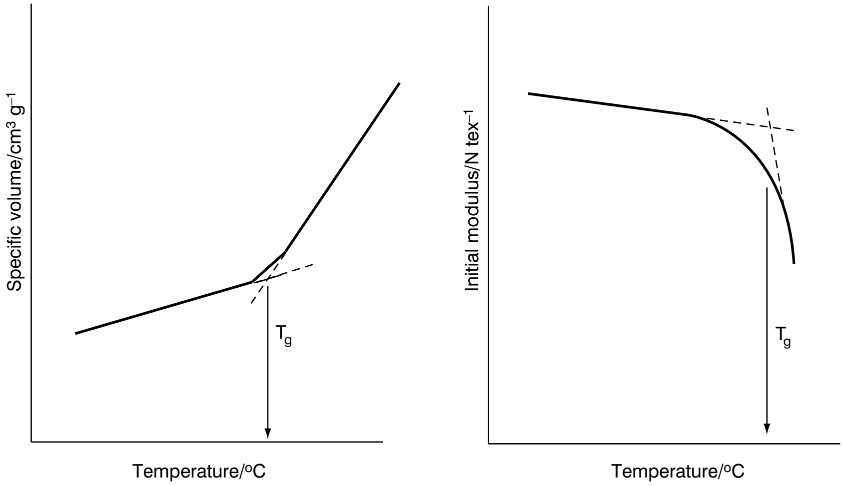


Figure 3.9 Variations of specific volume and initial elastic modulus with temperature

Usually, T_g is not a sharp, well-defined temperature and the changes in temperature dependent properties occur over a range of values around T_g.

As the temperature increases, the volume of a rigid polymer sample expands in the usual manner. This involves proportionate increases in the actual volume occupied by the molecules, as they vibrate, and that of the voids between molecules in the amorphous zones and around the chain ends. These voids are called the polymer free volume. Molecular packing in the crystalline state is very compact and ordered so the free volume is a characteristic of the amorphous regions of a polymer. At temperatures above the T_g, bond rotations allow sections of the polymer chains to move into voids with increasing ease and thus create new voids. Segmental motion increases rapidly with increasing temperature above T_g, increasing the free volume and the coefficient of expansion. Eventually, on continued heating, chain mobility becomes so pronounced that the true liquid state forms at the melting point.

The T_g has considerable significance in textile processing. Two of the most important processes that depend upon a synthetic filament having some plasticity are drawing and texturising. In drawing, newly formed continuous filaments are first wrapped several times around a rotating feed cylinder, and then around a second one running at 4–5 times the linear speed of the first. Provided that the polymer is not at a temperature too far below its T_g, the stress applied by the faster running cylinder causes the polymer molecules to unfold and slide by each other in the filament as it extends in length. This aligns the molecules in proximity, increasing the degree of molecular interaction and therefore the strength of the filament. It is in this way, in varying degrees, that the orientation of the molecules of all artificially made fibres improves the filament tenacity and rigidity. If the filament is at a temperature too far below T_g, it is too rigid to be drawn uniformly and may even break on application of stress. At temperatures around T_g, the filament is sufficiently plastic for drawing to be practicable.

In texturising, the filaments are deformed by application of a transverse stress. The objective is to buckle the initially straight filament so that it develops a permanent crimp. Several technologies for texturising depend on bending the filaments while they are warm and plastic, and then stabilising the crimp by rapidly cooling. The degree of crimping determines whether the fabric handle will be smooth or rough. Texturising increases the bulk of an assembly of filaments trapping more air and improving the insulating power.

When a fabric made from thermoplastic fibres such as nylon or polyester is heated to a temperature around T_g, the mobility of the polymer chains allows the relaxation of any tension. This causes deformation of the shape of the material, usually with considerable shrinkage. It can occur in hot water. The tensions in the polymer molecules can be present from the original drawing of the filaments immediately after their production, from texturising, or from stresses introduced during winding, weaving or knitting. The strained polymer molecules, held in place in the rigid, glassy structure, become mobile once the temperature is above T_g. Their movement in the plastic condition eases the stress on them.

Fabric deformation or shrinkage on heating is minimised by a process called heat setting. The speed and separation of two moving parallel chains, which grip the fabric edges as it passes through the setting oven, determine the final dimensions of the relaxed fabric. The setting temperature used is above T_g. In heat setting, inter-chain bonds, such as hydrogen and dipole bonds, break. This allows the molecular chains to move and adopt new, stress-free positions. New intermolecular bonds then form with the fabric in a relaxed condition at the setting temperature. After cooling, the polymer molecules in the filaments become frozen in place. The new bonds are stable up to the heat setting temperature. The reorganised internal polymer structure, and the material's dimensions, will be stable, provided the material is not heated to temperatures above the heat setting temperature.

Most synthetic fibres cannot be dyed at temperatures below the T_g existing under the dyeing conditions. This is because the dye has no mechanism for diffusion into the fibre. The dye can only penetrate into the polymer structure when motion of the polymer chain segments creates sufficient free volume with adequate mobility to allow dye molecules to penetrate into the polymer. The temperature at which polymer chain segment mobility allows a significant increase in the rate of dye diffusion is called the dyeing transition temperature, T_d. Dyeing of thermoplastic synthetic fibres always requires temperatures above T_d. This poses no problems with nylon and acrylic fibres that have quite low values of T_g and T_d. The T_g of polyester, however, is around 80–90 °C. The diffusion of dyes into polyester filaments is therefore quite slow at 100 °C and dyeing must be carried out at temperatures well above this, by dyeing in water above 100 °C under pressure. Because of the higher T_g, polyester drawing requires warm filaments. Cellulosic and protein fibres do not have a T_d. Unlike most synthetics, natural fibres are quite porous, being constituted of many long fibrils laid side by side along the fibre axis. Dyes are able to penetrate into the bulk of these fibres along the many narrow channels permeating them.

This introduction to natural and synthetic polymers briefly outlines the nature of their chemical structures and molecular arrangements. The nature of intermolecular attractive forces and the glass transition temperature were introduced because so many of the properties of synthetic polymers, including their dyeing behaviour, depend upon them. This chapter therefore sets the stage for the following discussions of specific fibres.

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CHAPTER 4

Synthetic Fibres

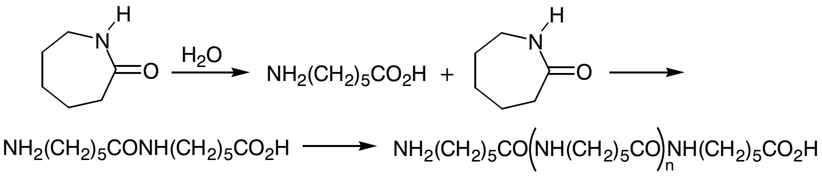
4.1 SYNTHETIC FIBRES

This chapter on the manufacture and properties of synthetic fibres reinforces the principles of polymer chemistry introduced in Chapter 3. Synthetic fibres are produced from simple organic chemicals, obtained mainly from petroleum. They are thus distinct from natural fibres and those made from regenerated natural polymers such as cellulose. In particular, the dyeing of synthetic fibres is quite different from that of natural fibres and the progress of each synthetic fibre has involved new dyeing technologies.

The major polymers used for synthetic fibres are polyamides (nylons), polyesters and polyacrylonitrile. The first two are products of polycondensation reactions, and the latter of radical addition polymerisation. Figures 3.2 to 3.4 show the structures of these polymers. Synthetic fibres have many excellent textile properties and comprise over 40% of all fibres consumed (Figure 1.9). Each type is available in a wide variety of modifications to suit market requirements. These include mono- or multi-filaments, or staple fibre, of any denier or length, and with a variety of different physical and chemical properties. One of the advantages of synthetic fibres is the relative ease with which physical and chemical modifications are possible. The favourable economics of the mass production of nylon, polyester and acrylic fibres are the result of solving many technical problems for their production and use. The introduction of new types of synthetic fibre in the foreseeable future is often considered unlikely, but such pessimism may not be warranted [1].

Research on polymer formation at DuPont, under the direction of W H Carothers in the 1930s, led to the first fully synthetic textile fibre of commercial significance: nylon 6.6, introduced in 1940. This polyamide is prepared by condensation of the bifunctional monomers adipic acid (1,6-hexanedioic acid) and hexamethylenediamine (1,6-hexanediamine) (Figure 3.3). Both these compounds have 6 carbon atoms per molecule, hence the name ‘nylon 6.6’. Very shortly thereafter, nylon 6 was produced in Germany by polymerisation of caprolactam. Caprolactam is the lactam (cyclic amide) of 6-aminohexanoic acid, a single monomer with just 6 carbon atoms (Scheme 4.1). After the Second World War, polymer chemistry and engineering rapidly developed and the unbranched polyester polyethylene terephthalate (PET,

Figure 3.4), produced from terephthalic acid (1,4-benzenedicarboxylic acid) and ethylene glycol (1,2-ethanediol), came on the market in 1948, followed by polyacrylonitrile copolymers in 1950.



Scheme 4.1

All synthetic fibres are produced by extrusion of continuous filaments, either of the molten polymer or of its solution in a solvent, through tiny holes in a metal plate. This is called a spinneret. Extrusion of polymer filaments is called spinning, but must be distinguished from the spinning of yarns of staple fibres by drawing and twisting. In melt spinning, the solid polymer filaments are obtained by rapidly cooling the extruded molten polymer, whereas in solution spinning they remain after evaporation of the solvent, or coagulation in a bath of suitable chemicals.

4.2 NYLON FIBRES

4.2.1 Production of nylon 6.6

Heating the salt of adipic acid and hexamethylene diamine (**1**, Figure 4.1) in concentrated aqueous solution in the presence of a little acetic acid gives nylon 6.6, or polyhexamethylene adipamide. Once most of the volatile diamine has reacted, water is gradually removed by distillation. Finally, the molten mixture is heated to 280 °C under nitrogen to avoid oxidation. Figure 3.3 illustrates the sequence of condensation reactions. The final liquid polymer is extruded as a thick ribbon, cooled to solidify it, and cut into chips. Using the exact 1:1 stoichiometric ratio of the monomers (from the diacid-diamine salt), and forcing the polycondensation to a high conversion, are important for obtaining the desired high molecular weight of the product. Low values of molecular weight give weak filaments but too high a value results in a more viscous molten polymer that is difficult to extrude. Addition of a small amount of acetic acid in the polymerisation assists in controlling the final molecular weight of the nylon. The added acetic acid functions as a chain stopper by

$$NH_2(CH_2)_6NH_3^+ \; {}^-O_2C(CH_2)_4CO_2H$$

1

Figure 4.1 Salt of adipic acid and hexamethylene diamine

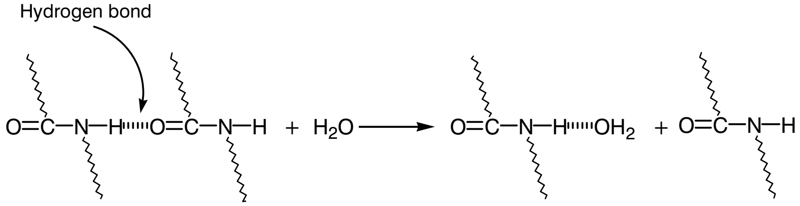
$$\text{—}CONH(CH_2)_6NH_2 + CH_3CO_2H \longrightarrow \text{—}CONH(CH_2)_6NHCOCH_3 + H_2O$$

Scheme 4.2

reducing the number of terminal amino groups in the polymer (Scheme 4.2). The nylon is then less likely to undergo further polycondensation when molten.

The nylon chips are re-melted and the molten polymer extruded to form fine filaments. The melting point of nylon 6.6 is around 250 °C. Melt spinning directly from the polymerisation reactor requires very long holding times at a temperature above the melting point. This changes the polymer molecular weight distribution, as free amino and carboxylic acid groups can continue to react. There is also the risk of thermal and oxidative degradation causing yellowing and liberation of carbon dioxide gas. In melt spinning from nylon chips, the molten polymer is kept under nitrogen. The amount of liquid is so small that the polymer is only molten for a short time. The hot liquid nylon is filtered to prevent particles of polymer from blocking the holes in the spinneret. It is also important to avoid gas bubbles in the molten polymer since their passage through a spinneret hole gives a broken filament. After cooling, the nylon filaments are bone dry and are conditioned in steam before winding onto bobbins. This avoids the slight expansion that occurs when dry filaments absorb water from the atmosphere and which results in unstable bobbins.

The next process is drawing. The nylon filaments are drawn by passing them around and between sets of rotating cylinders of increasing speed (Section 3.4). The newly extruded filaments are relatively easy to extend to about four-fold their original length before the stress begins to increase sharply. Drawing decreases the filament diameter. The elongation causes folded polymer chains to unfold and the chains to slide past each other, gradually increasing the degree of orientation of the polymer molecules along the filament axis. Because of this, there is an increase in crystallinity, giving higher tenacity and reduced elasticity. The glass transition temperature of completely dry nylon 6.6 is probably over 100 °C, but drops considerably in the presence of small amounts of absorbed water. Water will form hydrogen bonds with both the hydrogen and oxygen atoms in the amide groups, breaking the existing hydrogen bonds between amide groups in different polymer chains (Scheme 4.3). The chains therefore have greater mobility, since the water is acting as a plasticiser. In air at room temperature, the filaments are sufficiently plastic for cold drawing.



Scheme 4.3

Nylon 6.6 fibres are available in many diverse physical and chemical forms for different applications. These include mono-filaments, multi-filaments, regular and high tenacity types (the latter being more extensively oriented by drawing), and a number of varieties with different dyeing characteristics (Section 4.2.4).

Changing the shape of the holes in the spinneret gives filaments with different cross-sections. Filament cross-sections with flatter surfaces, such as trilobal sections, reflect more light and give high lustre and a smooth silky handle. Titanium dioxide pigment added to the molten nylon before extrusion gives filaments with reduced or no lustre. Filaments for staple nylon, which will be blended with other fibres such as cotton, will normally have been texturised before cutting the filaments into short lengths. The crimp improves the adhesion between fibres in a spun yarn. After spinning, chemicals such as lubricants and anti-static agents are applied to the filament surface. Scouring before dyeing effectively removes these spin finishes.

Both nylon 6.6 and 6 are susceptible to degradation by ultraviolet light resulting in yellowing and loss of strength. Lustrous filaments have better ultraviolet resistance than those dulled by pigmentation with titanium dioxide. Ultraviolet stabilisers, which protect the polymer by strongly absorbing ultraviolet light and converting the energy into heat, are added to the nylon before spinning.

4.2.2 Production of nylon 6

Nylon 6 is manufactured similarly to nylon 6.6 by heating caprolactam with a little water, a chain stopper such as acetic acid, and an acid catalyst, gradually removing the water by distillation. The water initially hydrolyses some caprolactam to 6-aminohexanoic acid. This then reacts with caprolactam, opening the ring and generating a new amino end group. This amino group then undergoes the same addition reaction with more caprolactam so that the forming polymer chain always has amino and carboxylate end groups (Scheme 4.1). The polyamide obtained is in equilibrium with about 10% of unreacted monomer and low molecular weight oligomers. These are removed by water washing after extrusion.

The melting point of nylon 6 is about 215 °C. Molten nylon 6 is therefore more stable than molten nylon 6.6. The lower melting temperature of nylon 6 allows filament spinning directly from the polymerisation reactor without undue decomposition or changes in properties. Nylon 6 may also be extruded as a thick band, chipped and processed as for nylon 6.6. The chips are preferred for continuous filament spinning because the denier is more uniform. Direct spinning from the reactor is satisfactory for staple fibres where denier variations are less important because the fibres will be well-blended. As for nylon 6.6, the conditioned filaments have a sufficiently low T_g to be cold drawn to increase the molecular orientation and crystallinity, giving improved mechanical properties.

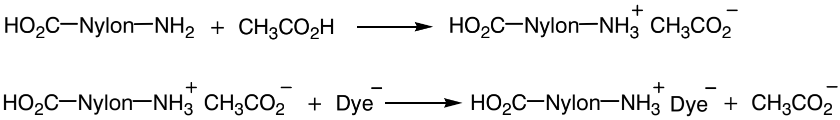
4.2.3 Properties of nylon 6.6 and 6

The numbers of repeat units along the polymer chains of nylon 6.6 and nylon 6 are about 65 and 130, respectively, corresponding to molecular weights of about 15 000 g mol^{-1}. They have similar chemical structures and therefore many common characteristics and end-uses. There are, however, some important distinctions.

These nylons are not totally hydrophobic and do absorb water at room temperature. The standard regains of both nylon 6.6 and 6 are around 4%. These relatively low moisture contents do not allow effective dissipation of accumulated static electric charge, which causes handling and soiling problems. This must be controlled by application of appropriate anti-static chemicals to the fibres, and grounding devices on machinery may be necessary.

Both types of nylon contain weakly basic amino and weakly acidic carboxylic acid end groups. The number of terminal amino groups in a nylon can vary from 30 to 100 mmol kg^{-1}. If each nylon molecule with a molecular weight of 15 000 g mol^{-1} had one amino end group, the number of such groups would be 67 mmol kg^{-1}. The actual number is usually less than this since some terminal amino groups will have reacted with the acetic acid chain stopper (Scheme 4.2). Therefore, the number of carboxylic acid groups in a typical nylon (90 mmol kg^{-1}) is usually greater than the number of amino groups, but, in a regular nylon, the sum of amino (40 mmol kg^{-1}) and acetylamino end groups (55 mmol kg^{-1}) approximately equals that for the carboxylic acid groups.

Nylon is usually dyed with anionic acid dyes in weakly acidic solution. This process can be considered as a simple anion exchange process in which a counter ion such as acetate, associated with a protonated amino group in the nylon, is exchanged for a dye anion (Scheme 4.4). In many instances, the number of available ammonium ion groups limits the amount of anionic dye taken up by a nylon fibre and direct dyeing of deep shades and blacks becomes impossible. On the other hand, the amino and carboxylic acid groups do not influence dyeing with disperse dyes. The nylon acts as a solid solvent in which the disperse dye is soluble, so the nylon extracts it from the aqueous bath. This mechanism is identical to that for dyeing cellulose acetate and other synthetic fibres with disperse dyes (Section 1.1.2). Nylons, however, tend to absorb many kinds of dyes to some extent, so that staining of the nylon component in fibre blends by dyes intended for the other fibres is a problem. Such staining is undesirable since stained fibres have poor fastness properties and may subsequently be difficult to dye on shade with the correct type of dye selected for them.



$$HO_2C\text{—Nylon—}NH_2 + CH_3CO_2H \longrightarrow HO_2C\text{—Nylon—}\overset{+}{N}H_3\ CH_3CO_2^-$$

$$HO_2C\text{—Nylon—}\overset{+}{N}H_3\ CH_3CO_2^- + Dye^- \longrightarrow HO_2C\text{—Nylon—}\overset{+}{N}H_3\ Dye^- + CH_3CO_2^-$$

Scheme 4.4

Nylons are polyamides and are therefore susceptible to hydrolysis. They are hydrolysed by boiling solutions of strong acids. For this reason, dyeing is rarely carried out at pH values below 3.0. They are resistant to short treatments with hot alkaline solutions.

Nylon 6 and nylon 6.6 are strong fibres with moderate elasticity, even after drawing. Nylon 6 has a somewhat lower elastic modulus and better elastic recovery than nylon 6.6 and therefore gives more flexible fabrics of softer handle. Both nylons are available in high tenacity variations for industrial uses. In fact, the mechanical properties can be varied considerably by changes in the polymerisation and drawing conditions.

Nylon fibres and filaments appear remarkably uniform in appearance. This can be misleading. Each nylon filament has a particular heat and tension history arising from polymer production and textile manufacturing processes. We have already seen that heating nylon to a temperature above its T_g causes rearrangement of the molecular chains in the amorphous regions of the material, and a reorganisation of the intermolecular attractive forces (Sections 3.4 and 4.2.1). Because the nylon polymer molecules are still potentially reactive, strong heating may establish a new polycondensation equilibrium with a new molecular weight distribution and more or fewer amino end groups. Level dyeing with anionic dyes is difficult if thermally induced changes in polymer structure have not been uniform. Filaments under tension undergo a drawing effect that can change the orientation and crystallinity of the polymer. During weaving and knitting, nylon filaments under prolonged mild stress elongate but do not recover their original length on releasing the tension. Variable mechanically and thermally induced stresses can build up in the filaments and may not relax until the fabric is subsequently wetted or heated. This can result in undesirable changes in shape from the shrinkage of filaments. Processes such as drawing, bulking (texturising) and heat setting, in which it is difficult to ensure uniform treatment, can result in physical and chemical variations along the length of filaments that only become visible after dyeing with anionic acid dyes. These effects are the origin of a phenomenon called barré. The extreme case of this is the occurrence of individual filaments in a woven or knitted nylon material that have absorbed less dye than neighbouring filaments and show up as a pale streak on the material surface.

Heat setting of nylon materials may be carried out under dry conditions in hot air at 190 °C for nylon 6, or 205 °C for nylon 6.6. Alternatively, setting is achieved in steam at 120 or 135 °C, respectively. As explained in Section 3.4, this allows relaxation of any strain in the filaments or fibres introduced during manufacture and improves the wrinkle resistance and dimensional stability of a material, avoiding shrinkage when it is heated in water, as in dyeing, or in hot air as in drying. It also stabilises the yarn twist and filament crimp. Heat setting is carried out after dyeing unless the fabric has a tendency to form crease marks.

It is very difficult to obtain accurate data for the T_g values of nylons. In particular, absorption of small amounts of water significantly depresses the value of T_g, but it also depends on the extent of drawing and the method of heat setting, and therefore on the degree of orientation and crystallinity. Nylon 6 has a lower T_g than nylon 6.6 for comparable conditions. It also has a less compact internal structure. At a given temperature, nylon 6 will usually have greater and more mobile free volume and therefore it usually has a higher rate and degree of dye absorption. Although dyes diffuse more rapidly into nylon 6 fibres during dyeing, they also diffuse out more readily on washing. This type of generalisation is useful but it may not always be valid as there are considerable variations of each type of nylon, all with different dyeing and fastness characteristics.

4.2.4 Other nylons

Nylon is also used for a number of speciality fibres such as 'core and mantel' and bicomponent varieties (Figure 4.2). In the former, a nylon filament core may be wrapped with a different filament or staple fibre. Combining extruded streams of two different molten nylons, with different characteristics, during spinning produces bicomponent fibres. They form a single filament but have the different nylons on each side. These show different shrinkage when wetted or heated producing a crimped filament. In Chapter 7, we shall see that wool fibres have a similar bicomponent structure that is responsible for its natural crimp.

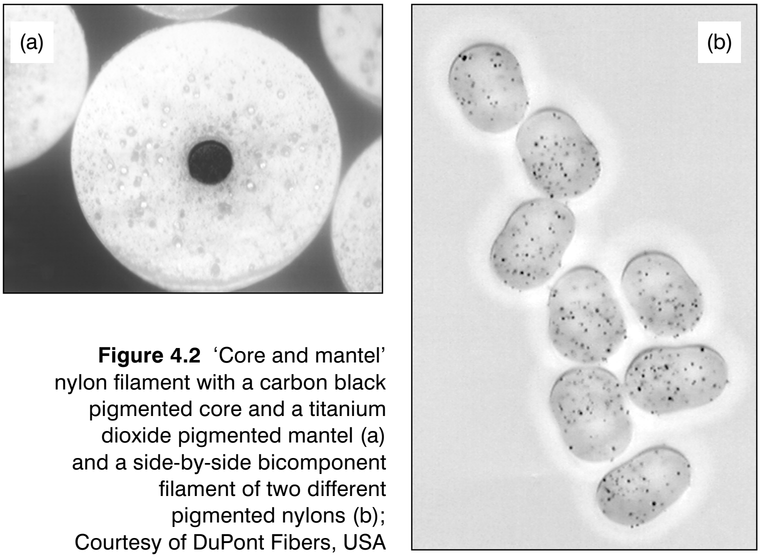


Figure 4.2 'Core and mantel' nylon filament with a carbon black pigmented core and a titanium dioxide pigmented mantel (a) and a side-by-side bicomponent filament of two different pigmented nylons (b); Courtesy of DuPont Fibers, USA

Normal nylon filaments have a terminal amino group content of around 45 mmol kg^{-1}. In addition, there are varieties with more than double this number of amino groups, which are therefore able to absorb increased quantities of anionic acid dyes. These so-called deep-dyeing nylons have amino groups that are protected during polycondensation by salt formation using p-toluene sulphonic acid or phosphoric acid derivatives.

Nylons dyeable with cationic dyes, but which resist acid dyes, have a smaller number of amino groups. They come from polymerisation of adipic acid with hexamethylene diamine in the presence of 5-sulpho-isophthalic acid (5-sulpho-1,3-benzenedicarboxylic acid; **2**, in Figure 4.3). This gives a polymer with a number of anionic sulphonate groups along the molecular chain capable of binding cationic or basic dyes by cation exchange (Section 1.1.2). The deep-dyeing and basic-dyeable nylons are often used in mixtures with regular nylons for the production of two-colour or two-tone effects for carpets and some fabrics. With disperse dyes, these modified nylons usually dye to the same depth as regular nylons since the absorption of this type of dye does not involve any ionic interactions.

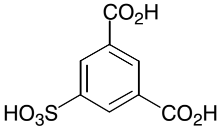


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Figure 4.3 5-Sulpho-1,3-benzenedicarboxylic acid

4.3 POLYESTERS

The first commercial fibre-forming polyester was developed by Dickson and Whinfield working at the Calico Printers' Association in England in 1941. It was produced by condensation of ethylene glycol (1,2-ethanediol) and terephthalic acid (1,4-benzenedicarboxylic acid) (Figure 3.4). Rights to manufacture this product were bought by ICI and DuPont but, because of the Second World War, fibres were not marketed until 1948. The ICI product was named Terylene and the DuPont product Dacron. This type of polyester, and several variants, are now produced by a number of manufacturers.

4.3.1 Production of PET fibres

The polyester from ethylene glycol and terephthalic acid is called polyethylene terephthalate (PET). Terephthalic acid sublimes on heating and is difficult to purify because it is not particularly volatile or soluble in common solvents. The actual polymerisation process is, in fact, a transesterification reaction starting with ethylene glycol and the ester dimethyl terephthalate. The latter is easily purified by distillation. Initially, dimethyl terephthalate reacts with an excess of ethylene glycol, in the presence of sodium methoxide as catalyst, forming bis(2-hydroxyethyl)-terephthalate. Distillation removes the methanol produced. Subsequent heating induces further transesterification of the bis(2-hydroxyethyl)terephthalate forming the polymer and releasing ethylene glycol, which is removed under vacuum at 280 °C and recovered (Figure 4.4).

Filament production is very similar to that for nylon 6.6. The molten product is extruded as a thick band, cooled and chipped. The blended chips are then re-melted under nitrogen and spun into fine filaments.

The PET filaments are then drawn to about 4–5 times their original length, but at 70 °C rather than at room temperature as for the nylons. This improves the polymer chain orientation and promotes crystallisation. The T_g of PET is around 80–90 °C and less uniform filaments result on cold drawing because of their low plasticity at

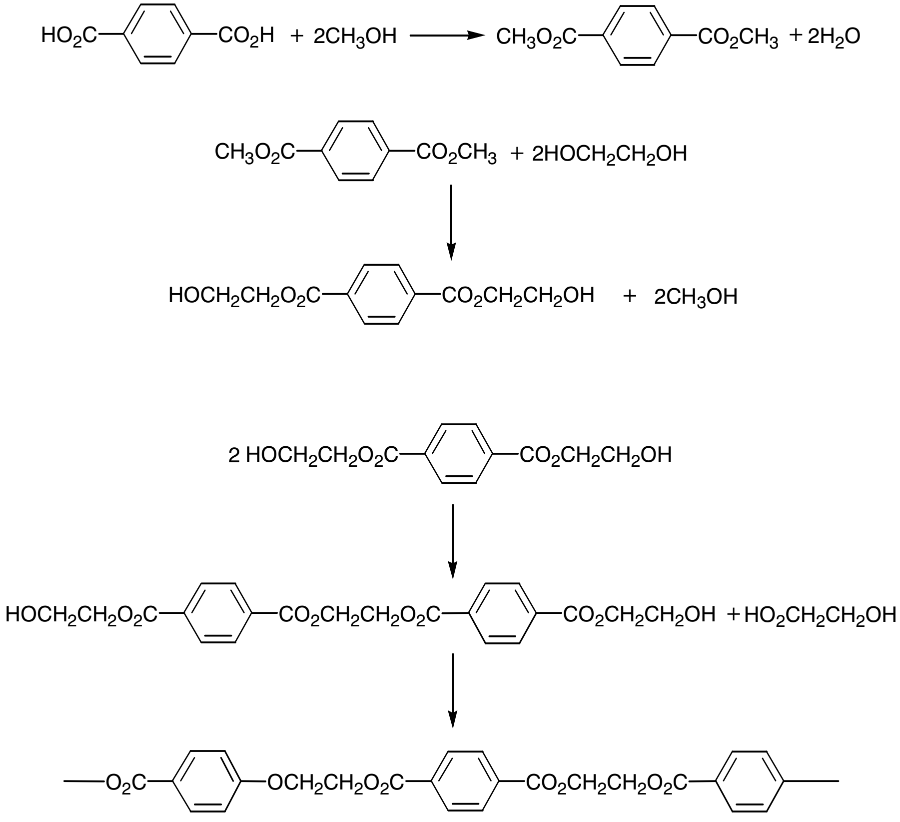


Figure 4.4 Transesterification reactions in the formation of PET

room temperature. Like other hydrophobic fibres, accumulation of static electric charge poses some problems in handling and promotes accumulation of dirt. Antistatic spin finishes are invariably applied by the fibre manufacturer. The three major types of PET fibres are high tenacity (highly oriented by drawing), regular tenacity and staple fibre. Large amounts of texturised staple polyester fibres are produced for blending with cotton.

4.3.2 Properties of PET fibres

The standard regain of PET is only 0.4% and so it is a hydrophobic material. Even above the T_g, water penetration is minimal. Because of this, PET is unaffected by aqueous solutions of ionic dyes. The many ester linkages make it slightly polar and the fibres can be dyed with non-ionic disperse dyes as for cellulose acetate and nylon. Disperse dyes only have very limited water solubility. The dye in the bath is so finely divided that the high specific surface area of the particles allows a rapid equilibrium with the small amount of dye in true solution. This dyeing process involves the fibre extracting the small amount of dye dissolved in the aqueous bath, and more dye dissolving from the reservoir of dispersed particles. At 100 °C, the temperature is not more than 10–15 °C above the value of the T_g, the rate of diffusion of dyes into the polyester is very low and dyeing is slow. This is because polymer chains in the amorphous regions of the polymer still do not have adequate mobility to continually create large enough voids into which dye molecules can diffuse. Increasing the dyeing temperature from 100 °C to 130 °C, however, has a very favourable effect on the dyeing rate and dyeing of PET under pressure has become the accepted practice. Even under these conditions, however, the dyes used are invariably of small molecular size in comparison with other types of dyes to ensure an acceptable rate of diffusion into the fibres.

Dyeing at the boil is possible if the T_g of the PET has been lowered by absorption of a swelling agent or carrier. Dyeing carriers are liquids present in emulsified form in the dyebath, which absorb into the PET causing swelling. They act as plasticisers and assist chain movements and create free volume. The use of dyeing carriers is now in decline because of their odour, the difficulties of removing them from the fibres after dyeing, and their adverse effect on the light fastness of some dyes.

Small amounts of cyclic oligomers, such as the cyclic trimer with three glycol and three diacid units, are always bi-products of the polycondensation reaction. These oligomers cause complications in dyeing. Although they are not very soluble in water, they leech out of the polyester during high temperature dyeing. On cooling the dyebath, there is a risk that the oligomers will deposit on the fibre and machine surfaces. For this reason, the exhausted dyeing bath is often drained while still hot.

In PET, the molecular chains are fully extended and relatively rigid because of the repeating benzene rings and the short chains separating them. PET filaments therefore have a higher elastic modulus than the nylons and are less extensible and flexible. They are therefore not suitable for the manufacture of ladies' silk hose but provide fabrics with good dimensional stability, crease resistance and shape retention, even when wet. Such properties are also improved by heat setting. Because PET is a thermoplastic material, permanent pleats can be introduced by hot pressing. Polyester fibres are strong, easy to dry, and relatively stable to processing conditions. Much of their value is attributable to the excellent textile properties of fabrics of both 100% PET and those in which cotton and polyester are blended.

Even though PET is less extensible than nylon, unset filaments will shrink by relaxation when exposed to dry or wet heat. This is a consequence of the relaxation of tensions built up in the filaments during processing. It can cause consolidation problems with packages of yarn and uneven dimensional changes in fabrics. Materials are usually heat set before exposure to high temperatures. Steam setting can be used for packages, but hot air is preferred for woven fabrics using a pin stenter. In this, small pins mounted on two parallel continuous chains pierce and hold the selvages of the fabric as it passes through a hot air oven. The setting temperature may be as high as 220 °C. If pin marks on the selvages are undesirable, setting on heated cylinders is possible but does not allow width control. Heat setting after dyeing usually involves lower setting temperatures and care in dye selection to ensure that the non-ionic disperse dyes do not vaporise from the fibre surface.

Being an ester, PET is susceptible to hydrolysis but under normal conditions this does not limit its use as a textile. It is, for example, unaffected by treatment with cold, aqueous 20% NaOH solution in the mercerisation of cotton in cotton/polyester blends (Section 5.4.6). PET does hydrolyse and slowly dissolve in hot alkaline solutions, however. Treatment with 3–5% NaOH for 30–60 min at 95 °C gives a considerable weight loss and filaments of decreased denier and softer handle. This type of process led to the deliberate manufacture of fine microfibres (Section 4.3.4). The polymer is reasonably stable to solutions of dilute acids and is stable to pressure dyeing at 130 °C at pH 4.5–6.0, apart from the leeching out of low molecular weight oligomers. PET is more stable to sunlight than nylon and has good resistance to the chemicals used in textile processing. This is partly a consequence of its hydrophobic nature. It is not particularly soluble in common solvents although it may swell somewhat. Methylene chloride (dichloromethane) or aqueous *N*,*N*-

dimethylformamide can be used to extract disperse dyes without influencing PET filaments.

Pilling is the name given to the undesirable formation of small bundles of knotted fibres on a fabric surface. These are formed by the matting together of fibre ends that have been rubbed up from the fabric surface by abrasion. This is much easier for the smooth surfaced synthetic fibres than for natural fibres. Because of the high tenacity of synthetic fibres, these knots of matted fibres do not easily break off, as do those of the weaker natural fibres. The balls of fibres therefore accumulate on the fabric surface and produce an unattractive appearance. This can be quite pronounced in fabrics made from 100% PET staple fibre. Decreased fibre tenacity reduces the pilling, as does singeing after dyeing. Optimising the yarn and fabric construction, heat setting, and chemical finishes all help to minimise pilling.

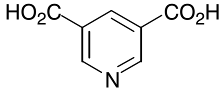
4.3.3 Modified polyesters

As for the nylons, PET type fibres are available in a considerable number of different physical and chemical forms. Besides ethylene glycol and terephthalic acid, other monomers may be added in the polymer-forming reaction. Copolymers produced with ethylene glycol plus other diols (such as 1,4-butanediol), or diacids (such as suberic acid, 1,8-octanedioic acid), have a lower melting point and T_g, and improved dyeing properties. The introduction of longer alkyl groups into the polymer chain gives it greater flexibility and the fibres absorb disperse dyes at the boil without use of a carrier. They also give less fibre pilling on abrasion. Incorporation of halogenated or phosphonated derivatives gives polyesters with improved flame resistance.

Polyester dyeable with cationic acid dyes has some terephthalic acid units replaced by 5-sulphoisophthalic acid (**2**, Figure 4.3). This again decreases the regularity of the PET chains and also the crystallinity and orientation so that dyeing can be carried out at the boil by a cation exchange mechanism. Similarly, dyeing with anionic dyes is possible if an acid such as 1,5-pyridinedicarboxylic acid (**3**, in Figure 4.5) is used as a comonomer. Basic and acid-dyeable PET are used for special colour effects.

All these chemically modified PET fibres have lower T_g values. They all absorb disperse dyes at the boil without the use of a carrier.

Kodel fibres (Eastman Chemical, USA) are also polyesters produced by ester exchange between dimethylterephthalate and a mixture of cis- and trans-1,4-bis(hydroxymethyl)cyclohexane. The polymer is called poly-1,4-cyclohexylene-dimethyleneterephthalate or PCDT (**4**). In many respects, this polymer is very



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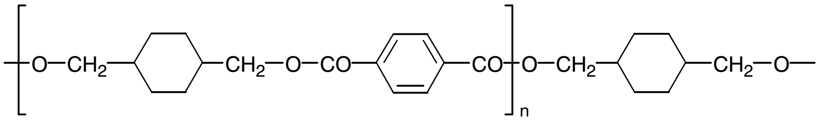

4

Figure 4.5

similar to PET in its physical and chemical properties. It is also produced by melt extrusion and drawing. PCDT fibres have lower tenacity than PET and are more elastic, with superior recovery. They give less pilling and are useful where resilience and bounce are required.

Shell have recently introduced a new polyester fibre called Corterra. This is a polyester called polytrimethylene terephthalate (PTT) based on terephthalic acid and 1,3-propanediol [2]. This development came about as a result of a new, efficient method of synthesis of the diol in which ethylene oxide reacts with carbon monoxide and hydrogen. It is produced similarly to PET and can be spun into filaments from pre-melted polymer chips. Its properties are similar to those of other polyesters. Because of the somewhat longer trimethylene unit between the benzene rings along the polymer chain, PTT gives filaments that are more elastic than those from PET and the fabrics produced from them are softer and have good elastic recovery. In addition, the increased chain flexibility permits dyeing with disperse dyes at lower temperatures than for PET, typically at 100–110 °C.

4.3.4 Microfibres

The usual definition of a microfibre is one that has a count of less that 1.0 denier or decitex. A typical PET yarn might contain 30–50 filaments, each with a denier in the range 2.0–3.0. A microfibre yarn may have well over a hundred filaments of 0.5 denier. A number of manufacturers are now producing such microfibres. In fact, there has been a continuing trend of denier reduction from around 7 to 2–3 dpf (denier per filament) for polyester filaments since the early 1980s. Low denier filament fabrics have been most popular in Japan, where the name *Shin Goshen* meaning 'new synthetic fibre' is used. Microfibres only have a small share of the total polyester market but this is growing quite rapidly.

As outlined in Section 4.3.2, the treatment of PET filaments with hot aqueous NaOH solution hydrolyses and dissolves the filament surface, reducing the filament diameter. Copolymers of PET hydrolyse more rapidly, but the reaction of the homopolymer can be catalysed with cationic auxiliary products. The resulting fabrics of denier-reduced PET have a warm silky handle with increased scroop (the attractive sound that silk fabric gives when it is compressed and released). In Japan, where this technique has been most popular, weight losses of as high as 40–50% are not uncommon, but are in the range 10–20% in other countries.

Some microfibres can be spun directly while others are bicomponent or matrix types (Figure 4.6). After spinning of the filaments, the individual microfibres are liberated by splitting, or by chemical treatments to remove the supporting matrix.

Microfibre filaments give lightweight fabrics with a soft handle and good drape. The fabrics produced are attractive and comfortable for fashion and sports applications. Because of the high number of filaments in each yarn, closely woven microfibre fabrics have high covering power. A variety of finishing processes enhances their natural properties. The fabric can be made to be breathable with adequate permeability to air and moisture, but yet easily waterproofed. Finishing

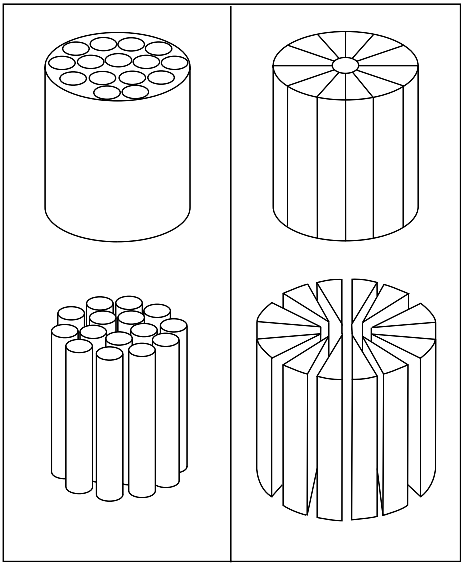

Figure 4.6 Cross-sections of some microfibres showing matrix type (left) and split type (right) [3]

processes (such as differential shrinkage of warp and filling filaments, sanding or sueding to give the fashionable ‘peach skin’ look, or napping and shearing) produce special surface appearances. A variety of chemical finishes are used to impart water or oil resistance, soil release, and resistance to pilling. The application of anti-static lubricants is common.

Fabrics of microfibres are delicate and require careful treatment. They also pose a number of problems in wet processing and dyeing not found with those produced from higher denier filaments. The extra fine filaments have a much higher specific surface area than regular filaments. A major consequence of this is the much higher reflection of light from the filament surface. A higher dye concentration in the filaments is therefore needed to produce a given depth of shade. The greater fibre surface area also results in higher rates of dyeing at lower temperatures, and decreased fastness to light, crocking (fastness to rubbing), water and ozone. These problems will be more fully discussed in Section 15.7.5.

4.4 ACRYLIC FIBRES

4.4.1 Polyacrylonitrile

Radical polymerisation of acrylonitrile (cyanoethene) in aqueous solution, using sodium persulphate ($Na_2S_2O_8$) and bisulphite ($NaHSO_3$) as initiators, gives polyacrylonitrile (PAN) with sulphate (SO_4^-) and sulphonate (SO_3^-) end groups (Figure 3.2). The homopolymer decomposes on heating before it melts. Melt spinning, as carried out for polyamide and polyester fibres, is therefore impossible. In addition, the homopolymer has limited solubility in common solvents so solution spinning of filaments was not a simple option for commercial fibre production. Pure PAN also proved to be very difficult to dye because of its compact, crystalline structure and a T_g above 100 °C.

Commercial acrylic fibres are copolymers obtained by polymerisation of acrylonitrile in the presence of other monomers, usually in aqueous solution or emulsion. An acrylic fibre consists of polyacrylonitrile containing at least 85% by weight of acrylonitrile units. The presence of other types of monomer unit along the polymer chain destroys the regularity of the structure and decreases the crystallinity. Non-ionic comonomers such as vinyl chloride or acetate, or methyl esters of acrylic or methacrylic acids (propenoic and 2-methylpropenoic acids), lower T_g to around 75 °C and considerably improve the dyeability of the polymer. The disruption of the regular repeating structure by a different comonomer not only increases dye diffusion rates but also renders the copolymers more soluble in solvents such as dimethylformamide (DMF; **5**, in Figure 4.7) or ethylene carbonate (cyclic ester of 1,2-ethanediol and carbonic acid; **6**). Such solutions can be spun into filaments either by evaporation of the solvent (hot DMF) in steam or hot nitrogen, or by coagulation of the polymer in an aqueous bath of appropriate chemicals. The filaments may then be stretched in steam or hot drawn.

$HCON(CH_3)_2$

5

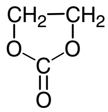

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Figure 4.7

The anionic sites in the polymer arising from the sulphonate and sulphate end groups give a fibre that can be dyed by an ion exchange mechanism using cationic dyes (Scheme 4.5).

$$\text{PAN—SO}_3^{-}\ \text{Na}^{+} + \text{Dye}^{+} \longrightarrow \text{PAN—SO}_3^{-}\ \text{Dye}^{+} + \text{Na}^{+}$$

Scheme 4.5

Surprisingly, dyeings of PAN fibres with cationic dyes show much better fastness to light than these dyes give on natural fibres. In fact, today, PAN dyeing is the major textile consumer of cationic dyes, despite some difficulty in obtaining level dyeings. The early types of PAN were difficult to dye and a special dyeing technique, in which cuprous ion was absorbed by the fibres, was developed so that it could be dyed with acid dyes capable of forming a complex with the metal. This procedure is obsolete partly because of the problem of copper in the dyehouse effluent.

Some PAN fibres contain anionic comonomers such as allyl sulphonate (2-propenylsulphonic acid; **7**, in Figure 4.8) or acrylic acid (propenoic acid; **8**) to improve the uptake of cationic dyes by ion exchange. Others have added vinyl chloride (chloroethene), or vinylidene chloride (1,1-dichloroethene) to improve the flame resistance. Potential cationic comonomers, such as 2-vinylpyridine (2-ethenylpyridine) that promote substantivity for anionic dyes by ion exchange have also been used but have been less successful (Acrilan, Chemstrand Corp.). Coagulated filaments are more porous and accessible to dyes than those obtained by evaporation of the solvent in solution spinning. There is a wide range of acrylic fibres that differ in dyeability. PAN fibres are hydrophobic (regain 1–3%) and can also be dyed with disperse dyes by the solution mechanism. The disperse dyes, however, only build up to give pale or medium shades of moderate fastness properties.

$CH_2{=}CH{-}CH_2{-}SO_3H$ $\qquad$ $CH_2{=}CH{-}CO_2H$

7 $\qquad$ **8**

Figure 4.8

PAN fibres do not have the high tenacity of nylon and polyester, but the strength is sufficient for most textile applications. PAN fabrics can be heat set but, unlike nylon and PET, this does not increase the crystallinity. The filaments are easily stretched when hot. This causes increased chain alignment but not much plastic flow since the latter is limited by the polymer crystallites. Hot stretching thus builds up some tension in the filaments. On heating, these tensions relax and there is shrinkage to the length that existed before hot stretching. This leads to considerable bulking of the fibres. Vast quantities of high-bulk acrylic fibres are produced by initial hot stretching and subsequent steam relaxation. Bicomponent fibres with each component having different shrinkage on heating are used for some bulked fibres. To take advantage of the effects of chain alignment on hot stretching of acrylic filaments, they must be annealed to give fibres of high tenacity. Although PAN fibres come way behind polyester and nylon in consumption, the bulked fibres give fabrics with a warm, soft handle that provide good thermal insulation. Because of this, and the relatively easy care required, they have largely replaced wool for knitted goods. Carpets and non-woven blankets are also significant outlets.

The large number of possible variations in manufacture has resulted in a large number of commercial acrylic fibres with different properties. These depend upon the type and amount of the comonomer used, the spinning method (wet or dry) and the drawing. The base polymers are produced by different polymerisation methods and may then be dry or wet spun, the latter giving better dyeability. The wet spun fibres produced by coagulation have more pores and are therefore more accessible to dyes and chemicals. They will be drawn, heat set, bulked or textured by different methods. A wide range of physical forms is available. Most products are of low crystallinity but have a high order of polymer chain orientation. They have good mechanical properties and have excellent resistance to light showing little or no yellowing on exposure. PAN fibres are generally inert and have good resistance to chemicals including dilute solutions of acids and alkalis. They are, however, soluble in polar aprotic solvents such as DMF.

4.4.2 Modacrylic fibres

Modacrylic fibres have between 35 and 85% acrylonitrile units in the polymer chain. Fibres with such high relative proportions of comonomers such as vinyl chloride (chloroethene), along with the acrylonitrile, provide specific properties such as improved flame resistance or chemical resistance. Because of the wide variations in comonomer type and proportions, fibres with a wide range of properties can be produced. The dyeing characteristics of modacrylics are much like those of regular PAN. They are usually more soluble in common solvents such as acetone, which may be used for solution spinning. Some of the fibres of this type, with a high proportion of a comonomer, may have lower softening temperatures and care is required to avoid creasing in dyeing.

4.5 OTHER SYNTHETIC FIBRES

The three major synthetic fibre types are the nylons, polyesters and acrylics, with polyesters predominating. In addition, there are a number of other kinds used to a much lesser extent in textiles. These include a variety of addition polymers made from vinyl compounds. Fibres from polypropylene are relatively cheap but quite difficult to dye. Large quantities are coloured by pigmentation of the molten polymer before spinning. This provides cheap coloured filaments of good fastness properties but only in a restricted range of colours. Additives can be incorporated into the polypropylene before spinning that are capable of increasing dye substantivity and the rather poor heat and light resistance of this polymer.

Polyvinyl fibres have limited textile application. Polyvinyl and polyvinylidene chlorides are valued for their high resistance to chemicals and their low-flammability, and have specialised applications. They tend to have low softening temperatures and shrink on heating. This polymer is soluble in water and filaments of it are used as support yarns in the construction of delicate materials. Washing the final article dissolves out the polyvinyl alcohol leaving the delicate structure of the other yarns behind.

Polyurethane elastomeric fibres are being used more and more. The generic name of such fibres is Spandex. They have the unusual characteristic of high elasticity and elastic recovery. Such elastomeric fibres are essentially block copolymers consisting of strong, rigid polymer segments among weaker more flexible segments. The flexible segments are composed of low molecular weight aliphatic polyesters or polyethers. These are reacted with a di-isocyanate and the resulting product is reacted with an appropriate diamine (Figure 4.9). The urethane and urea type groups produced are

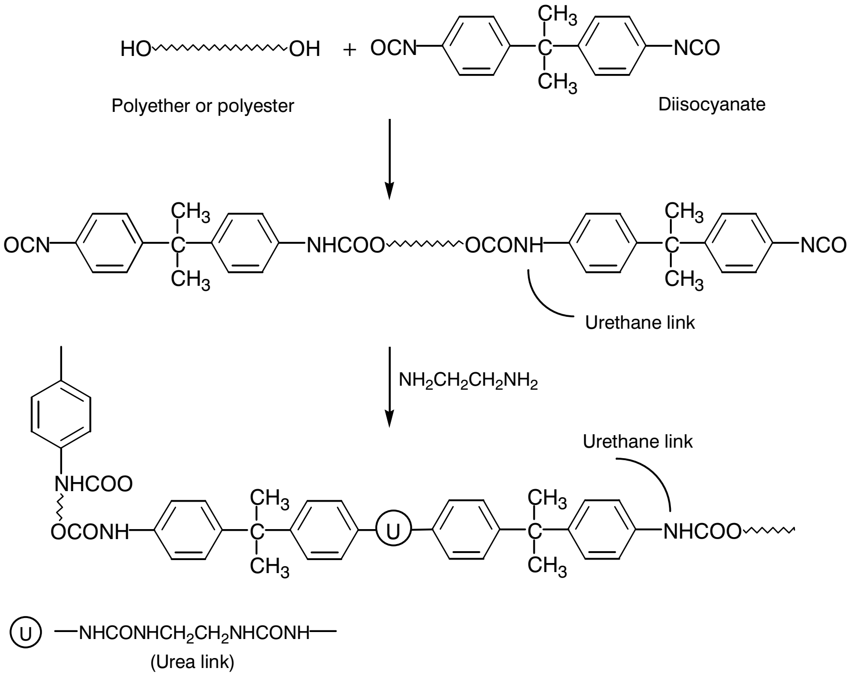

Figure 4.9 Formation of a segmented polyurethane

capable of strong inter-chain hydrogen bonding and provide the strong rigid segments of the matrix. On initial stretching, the flexible coiled segments of the polyester or polyether uncoil, but the bonded urethane segments remain immobile. On releasing the stress, the flexible chains recoil, and since the rigid segments have not permitted any extensive chain slippage, the flexible chains return to their original positions. Since they have amino end groups derived from the diamine, the dyeing of segmented polyurethane fibres is similar to that of the nylons.

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CHAPTER 5

Natural cellulosic fibres

5.1 INTRODUCTION

Cotton is, by far, the most important textile fibre. This chapter discusses the chemical and physical properties of cotton, related to the preparation, dyeing and finishing of fabrics containing this fibre. In Sections 1.1.2 and 3.1, we saw that cotton consists of cellulose, a polymer of glucose. Cellulose is the basic building material of all types of vegetation and many different plants are sources of cellulose fibres. Linen and ramie are cellulosic fibres of lesser importance than cotton. Purified cotton consists almost exclusively of cellulose, whereas fibres such as linen and ramie contain other materials besides this polymer. Other types of cellulosic fibres, such as hemp and jute, are used for sacks and cord but these are not usually dyed.

Chapter 6 deals with regenerated cellulose (viscose) and cellulose acetate, mentioned in Section 1.1.2. Although cotton and viscose are almost pure cellulose, they have quite different physical properties because of their distinctive morphologies and molecular arrangements. Even though cotton and viscose fibres can be dyed with the same types of dyes, using similar methods, their dyeing characteristics are different.

5.2 COTTON [1,2]

5.2.1 Production of cotton

Cotton comes from the seed pod of plants in the *Gossypium* family cultivated in a number of subtropical climates. The fibres grow out of the seeds in the closed pod. In the initial phase, they form long, thin-walled cells filled with protoplasm. Later, as the growth in length ends, the cell walls increase in thickness as rings of cellulose are deposited on the inner surface of the cell wall. When the pod or boll bursts, the cotton fibres, whose function is to aid seed transport in the wind, dry out. Once the remaining protoplasm has evaporated, the cotton bolls are harvested mechanically and the fibres removed from the seeds by a process called ginning. This must be carefully controlled to avoid over-cutting of the fibres. Cotton ‘linters’, the short lint hairs not removed from the seeds by ginning, are also an important source of pure cellulose. Pressing the residual seeds gives cotton seed oil.

5.2.2 Structure and constituents of cotton fibres

Microscopic examination of cotton fibres reveals that they are single cells with a closed tip but open at the end where they were cut from the seed. They have the appearance of flat, twisted ribbons. This characteristic shape develops as the cotton fibres dry out and collapse in the open boll. The fibre cross-section has a bean shape and often shows the presence of a central canal or lumen.

The morphology of a cotton fibre is extremely complex. The cuticle, or outer cell wall, is relatively hydrophobic. It contains some cellulose but accompanied by fats and waxes. It will be broken and more or less removed during processing to render the fibres more water-absorbent. Beneath the cuticle is the primary cell wall composed of criss-crossed fibrils of cellulose and containing some pectins. The next layer inside this, the secondary wall, constitutes the bulk of the fibre. It is built up of successive layers of fibrils. These are long structures, in each growth layer, that spiral around the fibre in a helical manner. From time to time, the spirals reverse direction and are responsible for the characteristic convolutions of the cotton fibre that develop on first drying. The fibrils, in turn, are composed of smaller microfibrils, the smallest being a combination of cellulose molecules. The numerous channels between the fibrils result in a fibre porosity of about 6% and an internal specific surface area of the order of 100 $m^2\ g^{-1}$. The lumen, the cavity that may remain after the protoplasm in the cell interior has evaporated, has proteins, colouring matter and minerals deposited on its walls.

Figure 5.1 Scanning electron micrographs of raw cotton fibres (Source: BTTG, Manchester)

The complex arrangement of cellulose fibrils leads to a fibre structure of uneven accessibility. Dye absorption tends to be greatest on the inside surface of the curved bean-shaped cross-section and least on the ends. These differences in dye absorption are evident on microscopic examination of cross-sections of dyed fibres and illustrate the great heterogeneity of cotton. Fortunately, they are not visible to the human eye [3].

Table 5.1 Typical composition of raw cotton

Component	Main location	Relative amount (%)
Cellulose	Secondary wall	86.8
Oils, waxes	Cuticle	0.7
Pectins	Primary wall	1.0
Carbohydrates	Primary wall	0.5
Proteins	Lumen	1.2
Salts	Lumen	1.0
Water		6.8
Other		2.0

Table 5.1 shows a typical composition of raw cotton. During manufacture of cotton materials, they are boiled with solutions of NaOH, which serves to emulsify waxes, hydrolyse fats and proteins, and solubilise mineral salts. Some low molecular weight non-cellulosic carbohydrates are also removed. This alkaline treatment gives a loss in weight of around 7%. Subsequent bleaching eliminates the natural yellowish colour of cotton. Dry, purified cotton therefore consists of essentially pure cellulose. Alkali boiling and bleaching always involves some degree of cellulose hydrolysis and oxidation, decreasing the average molecular weight of the polymer. Process conditions must minimise this, while ensuring adequate removal of those impurities such as waxes that make the fibres difficult to wet.

5.2.3 Properties of cotton

Cellulose is a polyalcohol, but the strong hydrogen bonds between hydroxyl groups in neighbouring polymer molecules do not easily break, even in the presence of water. In fact, water does not penetrate into the compact, crystalline regions of cellulose and therefore it is not soluble in water. Cotton is, however, a relatively hydrophilic, water-absorbent fibre. Its porous structure allows ready penetration of water molecules between the fibrils and into the amorphous regions of the polymer where they can easily form hydrogen bonds with free cellulose hydroxyl groups. The standard regain is about 8% and rises to around 25–30% water at 100% relative humidity, at room temperature. Water absorption causes swelling of the secondary wall but little fibre elongation. The wet fibres become softer and more pliable. Cotton is unusual in that water absorption increases the fibre strength. Although absorbed water acts as a plasticiser, it also cements the cellulose chains and fibrils together by hydrogen bonding.

Cellulose shows remarkable stability towards strongly alkaline solutions in the absence of oxygen, even at high temperatures. This is significant in the alkali boiling process mentioned above. Cellulose is, however, very sensitive to mineral acids. These catalyse hydrolysis of the bonds between the glucose units and cause depolymerisation eventually leading to the monomer, glucose (Section 5.3.2).

Cellulose is a carbohydrate and, despite its alkali stability, it is a sensitive biopolymer. On heating, cotton's behaviour is like that of sugar. Browning and hardening of the fibres becomes more pronounced at temperatures above 150 °C. If processing requires higher temperatures, shorter treatment times avoid thermal damage. Unlike synthetic fibres, damp cotton readily supports the growth of bacteria and moulds. These first generate an unpleasant odour and leave coloured marks on the fabric that are often difficult to remove. In bad cases, the fibres may become substantially weakened. Warm, damp conditions foster the growth of mildew, but application of an appropriate anti-fungal agent to the cotton material prevents this problem.

Cotton is a natural vegetable fibre and exhibits considerable variability in properties, even among fibres from the same seed. Cotton is available in a variety of qualities based on the fibre length or staple, and the colour. The longest fibres are usually the finest. Cotton fibre fineness is often evaluated by measuring the pressure drop across a pad of cotton fibres of given weight that is required to produce a given air flow rate. The pressure drop is related to the total fibre surface: the finer the fibres, the greater the pressure drop [4]. Cottons from different geographical regions are quite distinctive. The top quality cottons, such as Sea Island, are 25–65 mm long (12 μm diameter). The bulk of the cotton produced consists of medium quality fibres 12–33 mm long (15 μm diameter). The courser Asiatic grades are only 10–25 mm long (18 μm diameter). The major producing countries are the USA, Russia, China and India.

Cotton fibres from the same harvest do not all have the same degree of maturity. The thickness of the secondary wall of cellulose, deposited during the second phase of growth of the fibres, can vary over a wide range. Mature fibres will have a thick secondary wall and more convolutions per unit fibre length. Immature fibres are those with thinner secondary walls, because of restriction of their growth, and so-called dead fibres have essentially only the primary cell wall. Because of their higher elasticity, immature and dead cotton fibres readily form small bundles of entangled fibres during the mechanical processes producing yarns. These are called neps. The thin secondary wall of nep fibres makes them more opaque and they appear much paler than mature cotton fibres after dyeing. Dead fibres remain undyed. Neps can therefore be readily seen on the fabric surface. Dyeing tests are frequently used to evaluate the content of dead and immature fibres in a cotton sample. Such fibres are always present, typically constituting about 20% of the total weight. Immature cotton fibres will swell in 20% NaOH solution during mercerisation (Section 5.4.6). This decreases the colour contrast between the dyed neps and mature fibres.

5.3 CELLULOSE

5.3.1 Molecular structure of cellulose

Careful hydrolysis of cellulose gives an almost quantitative yield of glucose, confirming that the former is a polymer of this sugar. 2,3,6-Trimethylglucose (Figure 5.2) is the predominant product of the hydrolysis of cellulose in which all the hydroxyl groups have been initially methylated. Therefore, the hydroxyl groups attached to carbon atoms C-2, C-3 and C-6 in the glucose units in cellulose are free and the oxygen atom linking the glucose units must be between carbon atoms C-1 and C-4. The numbering of the glucose ring is shown in Figure 5.2. Cellulose is a polymer of β-D-glucose, with the specific configuration shown in Figure 5.2. This distinguishes it from starch (a polymer of α-D-glucose) in which the 1-hydroxyl group has the alternative configuration. The correct name for glucose is glucopyranose which indicates that the glucose molecule has five carbon atoms and one oxygen atom in a ring, as in pyran. α- and β-D-glucopyranose must also be distinguished from the respective L-glucopyranoses, their non-superposable mirror images (enantiomers), which are not found in natural carbohydrates.

In the cellulose molecule, each successive glucose unit is rotated 180° around the molecular axis. This gives a linear polymer chain that is almost flat. This structure allows the close approach of neighbouring cellulose molecules necessary

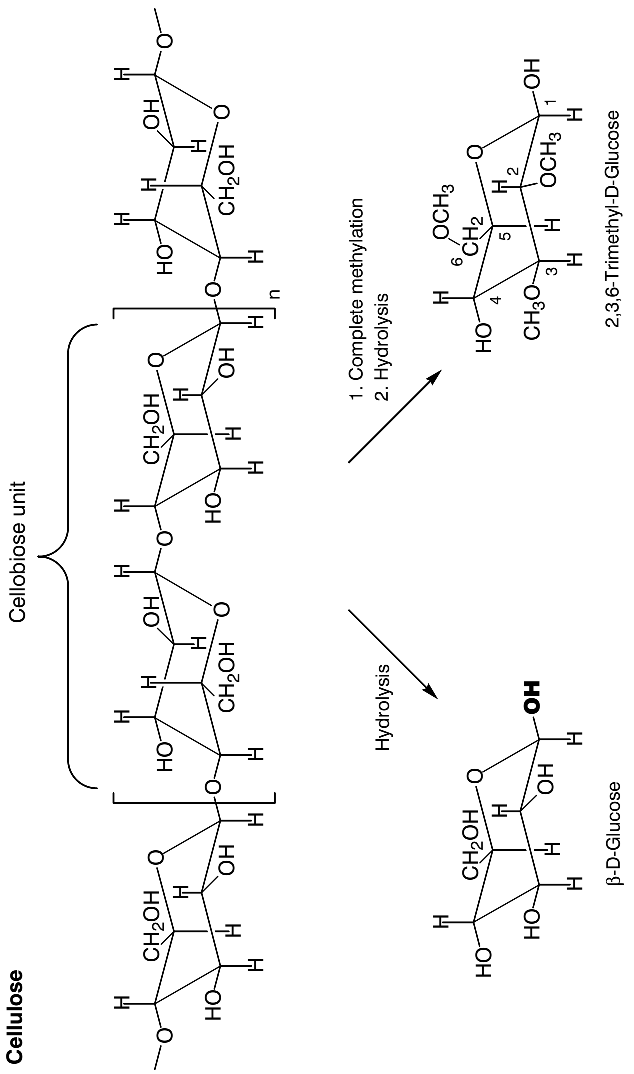


Figure 5.2 Relationships between the structures of cellulose, starch and their monomers; see next page for starch

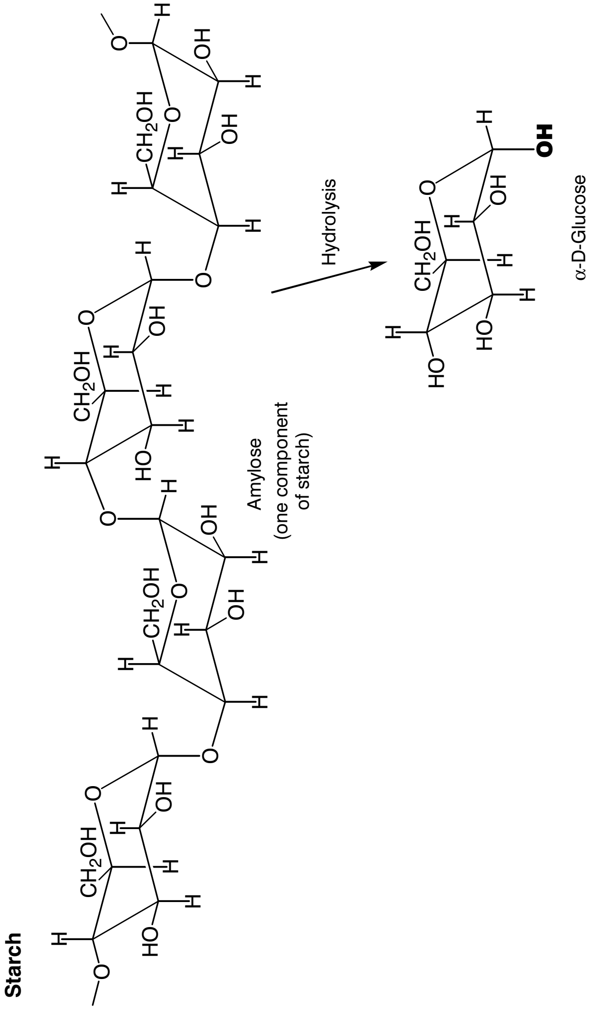


Figure 5.2 Relationships between the structures of cellulose, starch and their monomers; see previous page for cellulose

for the development of crystalline regions. In these, the cellulose molecules are held together by intermolecular hydrogen bonds between hydroxyl groups. X-ray diffraction studies of ramie fibres show that the repeat distance in crystalline cellulose corresponds very closely to the length of a cellobiose molecule. Cellobiose is the dimer of glucose (Figure 5.2). The molecules in cellulose are oriented along the fibre axis passing through regions varying from fully crystalline to amorphous. Whenever the molecules are in proximity, hydrogen bonds will form between pairs of adjacent hydroxyl groups.

The arrangement of α-glucose units in starch is less regular. Unlike cellulose, molecules of amylose, one component of starch, are not flat and crystallinity is totally suppressed. In amylopectin, the other major α-glucose polymer in starch, the polymer molecules are branched. The oxygen atom at C-1 at the end of one chain links to a C-6 in the middle of a neighbouring chain.

Cellulose is soluble in a solution of cuprammonium hydroxide, $Cu(NH_3)_4(OH)_2$. The viscosity of this solution depends on the average molecular weight of cotton cellulose and can establish if any depolymerisation has occurred during processing. The DP (degree of polymerisation) of purified cotton is around 1000–3000. The dissolution of cotton in cuprammonium hydroxide solution is quite slow and protection of the solution from light and oxidation during the procedure is essential. The quantity usually determined is the fluidity or inverse of the viscosity [5]. The higher the molecular weight or DP of the cellulose, the higher the viscosity, and the lower the fluidity of the cuprammonium solution. Any process such as hydrolysis or oxidation that reduces the length of the molecular chains, causes a loss in fibre strength and an increase in the fluidity.

5.3.2 Chemical properties of cellulose

Cellulosic fibres absorb large amounts of water (25–30% regain at 100% relative humidity and 25 °C). Water molecules, however, do not penetrate into the crystalline regions of cotton. Even though cellulose has a large number of hydroxyl groups per molecule, it is not soluble in water, unlike glucose. Even quite large molecules, such as those of typical cotton dyes, easily penetrate into the accessible interfibrillar and amorphous regions of the fibres. The high molecular weight and crystallinity of cotton cellulose are thus responsible for its good mechanical properties, and the fibrillar structure and amorphous regions for its hydrophilic character and absorptivity. Starch, in which the arrangement of glucose units prevents crystallinity, is much more accessible to water and the unbranched amylose is soluble.

Cellulose is susceptible to hydrolysis by hot dilute solutions of mineral acids. Initially, this breaks the polymer chain at the oxygen atoms between C-1 and C-4 of adjacent glucose units, causing a dramatic drop in DP, and a loss of fibre strength called tendering. The lower molecular weight insoluble celluloses obtained from such partial hydrolysis are called hydrocelluloses. If hydrolysis continues, the eventual product is the soluble monomer glucose. Because of this sensitivity towards acids, cellulose fibres are never dyed at a pH below 3–4. For the same reason, wet cellulose must never be heated, dried or stored when it contains residues of mineral acids. After treatment of a cellulosic material with an alkaline solution, acetic acid is the preferred acid for neutralisation. This is a weak acid that will vaporise during drying before it concentrates to the point at which the pH becomes low enough to result in hydrocellulose formation.

Glucose is a mild reducing agent. The α- and β- configurations of D-glucopyranose interconvert in aqueous solution by way of the open chain aldehyde (Figure 5.3). This process is called mutarotation, after the changes in optical activity that occur. In fact, glucopyranose is a hemi-acetal, formed by the intramolecular reaction of aldehyde and alcohol groups at C-1 and C-5, just as for a simple aldehyde and alcohol (Figure 5.3). Although the actual concentration of the aldehyde form is very small, the equilibrium is quite rapid in acidic or alkaline

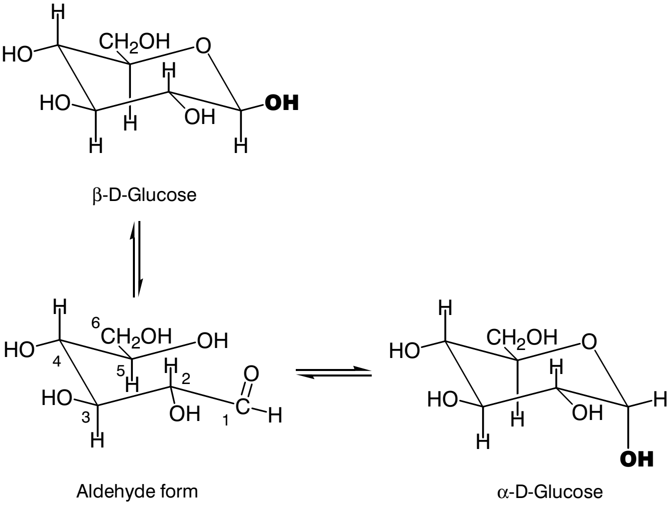


Figure 5.3 Mutarotation of glucose via the non-cyclic aldehyde form

solution. Glucose therefore readily gives some reactions typical of aldehydes, such as easy reduction of copper(II) or silver(I) ion complexes, or derivative formation with hydrazines.

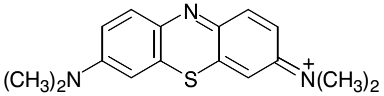
One end of a cellulose molecule ends in a C-1 hydroxyl group and can form a terminal aldehyde group like glucose. Cellulose is therefore a reducing agent, but a weak one since the number of such reducing end groups is limited. Because of this, dyeing of cellulosic fibres with some azo dyes at high temperatures under weakly alkaline conditions is not always feasible. The aldehyde of the reducing end group can reduce the azo dye, destroying its colour. This problem is more serious for regenerated cellulosic fibres since they have a considerably lower DP and therefore a higher proportion of potential aldehyde end groups. There are a number of chemical tests that are used to establish the reducing power of cellulose. They provide a measure of its DP. For example, the 'copper number' is the weight in grams of cupric ion in Fehling's solution reduced to the salmon coloured Cu_2O by 100 g of cellulose [5] (Scheme 5.1). Such tests are useful for detecting the formation of hydrocellulose.

$$\text{Cell—CHO(s)} + 2\text{Cu}^{2+}\text{(aq)} + 2\text{H}_2\text{O} \longrightarrow \text{Cell—CO}_2\text{H(s)} + \text{Cu}_2\text{O(s)} + 4\text{H}^+\text{(aq)}$$

Scheme 5.1

Cellulose is also susceptible to oxidation of the primary alcohol group at C-6 and at the linkage between C-2 and C-3. Like all alcohols, it is sensitive to oxidation by oxygen under hot alkaline conditions, such as those used in alkali boiling to eliminate non-cellulosic impurities. In such processes, oxygen must be excluded.

To destroy the natural yellowish colouring matter of cotton, and produce a white material, cotton is usually bleached. This is not necessary if it is going to be dyed in a dull or a deep shade. Bleaching agents include alkaline sodium hypochlorite (NaOCl) and alkaline hydrogen peroxide (H_2O_2) solution, both of which are quite powerful oxidising agents. Neutral solutions of sodium hypochlorite, in particular, readily over-oxidise cellulose and produce oxycellulose. This increases the number of aldehyde and particularly of carboxylic acid groups; for example, at C-6. Oxidation between C-2 and C-3 of the glucopyranose ring and subsequent hydrolytic reactions dramatically reduce the DP. Pure cellulose does not adsorb cationic dyes from solution because the fibres lack anionic sites to bind the positively charged dye molecules. When carboxylic acid groups are present, however, the cellulose will contain negatively charged carboxylate groups at pH values above 4–5 and these can bind cationic dye molecules. Staining of cotton with a cationic dye such as Methylene Blue (**1**, in Figure 5.4) is a common test for oxycellulose.



1

Figure 5.4 Methylene Blue

In the absence of oxygen, cellulose exhibits excellent stability towards alkaline solutions. Treatment with hot dilute NaOH solution at the boil, or even under pressure at higher temperatures, has no ill effects. This is extremely valuable for eliminating a number of impurities from cotton. Treatment of cotton with concentrated NaOH solution, in a process called mercerisation, causes a change in internal structure of the cellulose but no degradation (Section 5.4.6).

5.4 COTTON PROCESSING

5.4.1 Preparation of cotton [6]

In preparation for dyeing and finishing, a number of impurities must be removed from cotton fibres. Table 5.1 lists the major natural contaminants. Other chemicals present, such as warp size or knitting oil that assist manufacturing processes, must also be eliminated. Many of the natural and synthetic contaminants are hydrophobic and hinder wetting of the fibres. The objective of preparation is to remove the bulk of these impurities so that the cotton readily and uniformly absorbs the aqueous solutions used in dyeing and finishing. Complete elimination of the undesired impurities is not practical and uniformity of the prepared material is the critical requirement. Any uneven distribution of residual warp size, oil or wax will result in uneven dye absorption and be immediately visible.

Although the operations used in the preparation of cotton differ widely in practice, depending upon the type and quantity of material to be processed, the same basic principles apply. For bulk production of woven goods, fully continuous preparation of open-width and rope forms is common. A woven cotton fabric may undergo singeing, desizing, alkali boiling and bleaching treatments, followed possibly by mercerisation, before it is ready for dyeing (Section 2.4). Knitted materials do not require singeing or desizing. Because knitted fabric stretches easily, handling with minimum tension is essential to avoid excessive elongation. There are therefore many different types of equipment. For more specialised, low volume materials, and in commission dyehouses that dye only small lots, preparation is often a batch process carried out in the dyeing machine.

5.4.2 Preliminary processes for woven cotton fabric

The first process in the preparation of woven cotton materials is singeing. The full-width fabric passes rapidly through a flame issuing from a long gas burner. This burns off the short fibre ends projecting from the fabric surface without any damage to the fabric. These exposed fibres arise from the abrasion of the yarns during weaving. The result is a much smoother fabric surface.

The fabric is then ready for desizing, the removal of the sizing material covering the warp yarns [7]. Warp size consists of a film-forming polymer and hydrophobic lubricants; its effective removal is essential for rapid and uniform wetting of the cotton fibres. A sizing formulation must coat each warp yarn with a flexible polymer film and lubricants, and good adhesion of the film to the yarn surface is vital. Starch-based products are widely used for sizing cotton warps, since their chemical similarity to cellulose ensures good film adhesion. However, although starches have excellent sizing characteristics and low price, they are often difficult to remove by simple washing. The fabric is therefore usually treated with a suspension of an enzyme capable of depolymerising the starch molecules to the point at which they become water-soluble.

Like cellulose, the terminal glucose units of the starch have a reducing action. Unless the starch is effectively removed from the cotton material, it will reduce the oxidising agent used in bleaching, increasing its consumption.

Because of the sensitivity of enzymatic systems, desizing proceeds at a temperature and pH where the enzyme has high activity. The fabric is then well washed to remove the starch degradation products. Alternatively, the starch size may be degraded by oxidation with hydrogen peroxide in alkaline solution.

It is now common practice to size warps of cotton/polyester with polyvinyl alcohol. This polymer is water-soluble and easily removed by simple washing in hot water. It can even be recovered from the desizing liquor and re-used. This has the additional advantage of a low load of organic chemicals in the washing effluent. Bacteria readily metabolise starch products, rapidly consuming the dissolved oxygen in the water. Starch-based products therefore dramatically increase the biological oxygen demand (BOD) of the effluent (Section 8.5.1).

5.4.3 Alkali boiling of cotton [8]

Treatment of cotton with boiling dilute NaOH solution hydrolyses the natural fats in the fibre, producing soaps that then aid in emulsifying the cotton wax. The latter is resistant to hydrolysis. The classical method of kier boiling involves heating cotton with about 2% aqueous NaOH solution under pressure. Besides NaOH, the solution may also contain soaps and solvents such as pine oil, which aid wax removal from the fibre cuticle. Uniform plaiting of the rope of fabric into the kier boiler avoids channelling of the circulating liquor and non-uniform treatment. Before the boiler is closed to develop pressure, the steam from the boiling solution is vented, thus removing air from the system. This avoids any oxidation of the alkaline cotton. For the same reason, after several hours of boiling under pressure, oxygen must not enter the hot boiler. After the initial cooling, the dirty alkaline solution is slowly drained off but replaced with water to completely cover the hot, alkaline goods and avoid direct contact with the air. Provided oxygen is absent, the cellulose is unaffected by the hot alkaline solution.

Continuous alkali treatment involves impregnating the cotton fabric with NaOH solution and then heating it in a sealed pressurised steamer. Because continuous processes have a shorter treatment time, a more concentrated solution of NaOH is used.

The final step, after either batch or continuous alkaline boiling, is good rinsing with much hot water to remove the soluble and emulsified impurities. The process results in a 5–8% loss of weight from emulsification of the cotton wax, hydrolysis of fats, and the solubilisation of pectates, organic acids, cellulose oligomers and mineral salts, as well as any residues of sizing material. Again, the effect of these chemicals on the BOD of the effluent is of concern.

5.4.4 Cotton bleaching [9]

The objective of cotton bleaching is to eliminate the yellowish natural colouring matter in the fibres. This is only present in very small amounts and its chemical nature is not known. For the production of high quality white fabrics, and for those that will be dyed in pale or medium, bright shades, bleaching is essential. It is not necessary for dull or dark shades provided the fabric is already of adequate and uniform absorbency. The types of chemicals used include hypochlorites, chlorites and peroxides, hydrogen peroxide being by far the chemical of choice.

The traditional use of bleaching powder (calcium hypochlorite, $Ca(OCl)_2$) for cotton bleaching is now almost obsolete. Bleaching cotton with alkaline solutions of sodium hypochlorite (NaOCl) was once common. Hydrogen peroxide (H_2O_2) has taken its place. A successful continuous method of bleaching with hypochlorite was never developed. Even in a batch process, careful control of the temperature and a pH above 10 were essential to avoid over-oxidation of the cellulose. In hot, neutral hypochlorite solution, oxycellulose formation is rapid. In addition, effective alkali boiling was essential as starch residues and proteins both react with hypochlorites. The free amino groups in proteins ($R–NH_2$) react with hypochlorite, forming chloramines (R–NHCl). On heating the fabric, these groups liberate hydrogen chloride, causing rapid depolymerisation of the cellulose with a drastic loss of fibre strength (Scheme 5.2). After bleaching with chlorine-based oxidising agents, complete removal of residual chlorine and chloramines is essential, using a mild reducing agent such sodium bisulphite solution. In more recent times, there has also been concern about the presence of chlorinated organic chemicals in the bleaching plant effluent.

$$\begin{aligned} \mathrm{R{-}NH_2 + Cl_2} &\longrightarrow \mathrm{R{-}NHCl + HCl} \\ \mathrm{R{-}NHCl + H_2O} &\longrightarrow \mathrm{R{-}NH_2 + HOCl} \\ \mathrm{2HOCl + R{-}CHO} &\longrightarrow \mathrm{Cl_2 + R{-}CO_2H + H_2O} \\ \mathrm{Cl_2 + H_2O} &\longrightarrow \mathrm{HOCl + HCl} \end{aligned}$$

Scheme 5.2

Cotton and cotton/polyester materials are now invariably bleached with an alkaline solution of hydrogen peroxide. This usually involves impregnation of the goods with a stabilised, alkaline solution of hydrogen peroxide followed by steaming. The goods are finally well washed in hot water. Neutralisation of any residual NaOH in the cotton using dilute acetic acid is a key step before the final rinse and drying. For small batches of cotton fabric, bleaching with alkaline hydrogen peroxide solution may be carried out in a dyeing machine.

The active species in bleaching with hydrogen peroxide is probably the hydroperoxyl anion (HO_2^-). Hydrogen peroxide is quite unstable in alkaline solution, particularly on heterogeneous surfaces and in the presence of many transition metal ions. The bleaching liquor normally contains a silicate, polyphosphate or protein stabiliser. These probably function by sequestering (complexing) metal ions in the water, such as Fe^{3+}, and by coating rough surfaces. Thus the stabiliser suppresses catalysis of the decomposition of the peroxide.

Hydrogen peroxide bleaching of cotton offers a number of advantages:

(1) a range of continuous, semi-continuous and batch bleaching processes are possible;
(2) the complete removal of proteins from the cotton is not essential since chloramine formation is not possible with peroxide;
(3) for some materials, the combining of alkali boiling and bleaching, or even of desizing, alkali boiling and bleaching, into a single operation is possible;
(4) there is a reduced risk of over-bleaching and oxycellulose formation.

On the negative side, careful control of the bleaching pH is necessary and heavy metal ions such as those of copper and iron, which catalyse rapid peroxide decomposition, must be complexed with an appropriate sequestering agent such as a stabiliser or ethylenediamine tetra-acetic acid (EDTA) (Section 8.3.3). The use of buffers and stabilisers is rather critical. The presence of magnesium ions in the water is essential for effective peroxide stabilisation by silicates. Silicate stabilisers tend to deposit on the yarns or fabric and form silica particles on drying. These can give a rough handle to a fabric and considerable friction of yarns with their guides during knitting. Protein stabilisers are preferred over silicates for a softer, smooth handle.

In the preparation of cotton yarn packages for knitting, a one-step process is common (combined mild alkali boiling and bleaching). Pressurised alkali boiling promotes swelling of the yarns and can create excessive pressure in the package interior.

Much of the success of hydrogen peroxide bleaching is a consequence of the development of rapid processes combining some or all of the three preparation operations, allowing considerable economies in labour, time, steam and hot rinsing water. Good water absorbency only requires rupture of the cotton fibre cuticle wall and not necessarily complete removal of the cuticle so vigorous alkali boiling, as in a kier, is not always essential. On the other hand, the traditional enzyme desizing, kier boiling and hypochlorite bleaching give the whitest cotton. Continuous preparation operations, and particularly those where stages are combined, although often giving acceptable results, are less effective and give a white of lower quality. Semi-continuous pad–batch methods, with cold or hot storage, are also used. Section 21.6.6 discusses evaluation of the degree of whiteness of a fabric.

Cotton may also be effectively bleached with weakly acidic solutions of sodium chlorite ($NaClO_2$), more widely used in bleaching wood pulp. The acid liberates the toxic gas ClO_2, which is the real bleaching agent. This, however, promotes corrosion of steel and a corrosion inhibitor such as sodium nitrate is needed in the solution.

5.4.5 Fluorescent whitening agents [10]

One remarkable way of improving the apparent whiteness of a cotton fabric is to treat it with a fluorescent whitening agent (FWA), sometimes also called an optical whitener or optical bleach. These chemicals are colourless or very pale yellow. They do not absorb visible light significantly, but do absorb ultraviolet light with wavelengths around 340–380 nm. Some of the absorbed ultraviolet energy is re-emitted as blue fluorescence in the 430–450 nm wavelength range. The absorbed ultraviolet light has greater energy than the re-emitted fluorescence, the remainder being converted into heat. This is illustrated in Scheme 5.3. In this, FWA and FWA* represent the normal and excited electronic states of the fluorescent chemical, respectively, ν and λ are the frequency and wavelength of the absorbed or emitted light, *h* is Planck's constant, and *c* the speed of light.

$$\mathrm{FWA} + h\upsilon\ (360\mathrm{nm}) \longrightarrow \mathrm{FWA}^*$$

$$\mathrm{FWA}^* \longrightarrow \mathrm{FWA} + h\upsilon\ (440\mathrm{nm}) + \mathrm{heat}$$

$$\text{Energy of light} = h\upsilon = \frac{hc}{\lambda}$$

Scheme 5.3

A perfectly white material will reflect all wavelengths of white light to the same high degree. Most textile fabrics requiring bleaching, however, have a slight cream or yellowish appearance because they preferentially absorb blue light and therefore have lower reflectance in the 400–500 nm region of the spectrum. The blue fluorescence of the FWA compensates for this. In fact, it may over-compensate, and it is possible that the sum of the reflected light and fluorescence at 400–500 nm may give an apparent reflectance exceeding 100% in this wavelength region (Figure 5.5). The effect is a very bright white, the 'whiter than white' of the detergent advertisements. However, these compounds are only functional if the light source has a sufficient proportion of ultraviolet light to activate the blue fluorescence. They are therefore much less effective in light from a tungsten filament lamp (Section 21.2) than in normal daylight. The presence of a FWA is easily detected by illumination in the dark with a long-wave ultraviolet mercury lamp, when only the blue fluorescence can be seen.

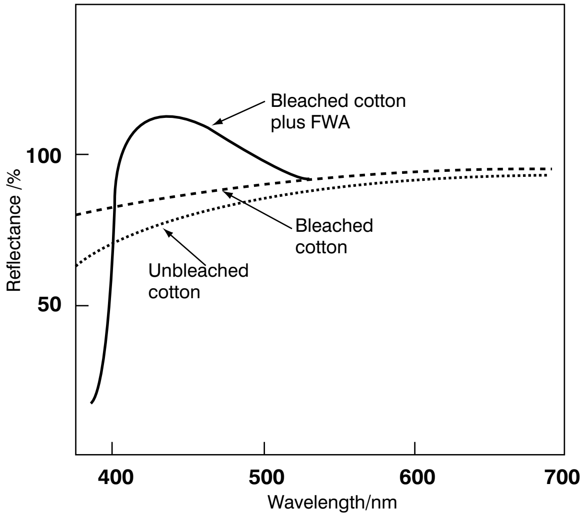
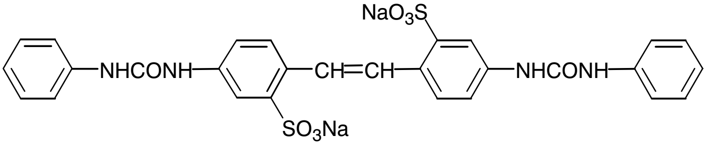
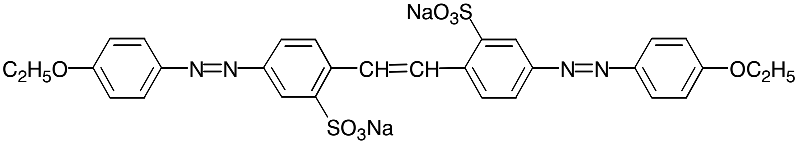


Figure 5.5 Reflectance spectra of unbleached, bleached and optically brightened cotton (treated with a fluorescent whiting agent)

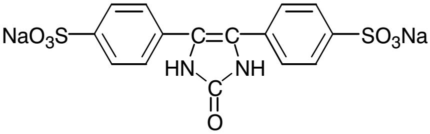
An FWA is a colourless dye, and must have some substantivity for the fibre on which it is to be used. For use with different types of fibres, therefore, there are anionic, cationic and non-ionic types available (Figure 5.6). The Colour Index lists over 250 such chemicals under the generic name fluorescent brighteners. Their chemical constitutions resemble those of dyes but they often lack electron-attracting and electron-donating groups and the direct conjugation between them. Figure 5.6 compares the chemical structures of some FWAs with various anionic,



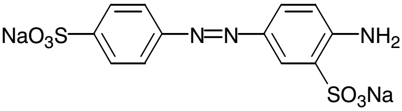
CI Fluorescent Brightener 30 (cotton)



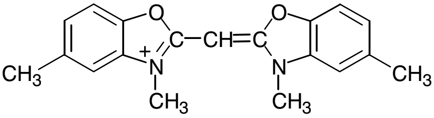
CI Direct Yellow 12



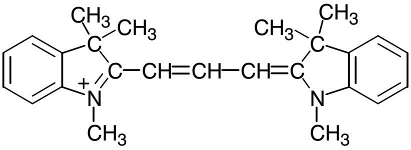
CI Fluorescent Brightener 48 (wool)



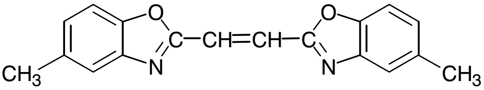
CI Acid Yellow 9



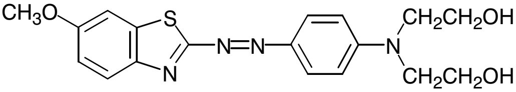
Cationic Brightener (acrylics)



CI Basic Red 12



Brightener for polyester



CI Disperse Red 58

Figure 5.6 Chemical structures of some FWAs and closely related dyes cationic and non-ionic dyes. The types for cotton behave as colourless anionic direct dyes whereas the non-ionic types are similar to disperse dyes. Use of these compounds at low concentrations of 0.1 g l^{-1} or less is usual, with application procedures closely resembling the analogous dyeing processes. Many of these compounds are stable in alkaline solutions of hydrogen peroxide commonly used in beaching and their presence in the bleaching bath allows milder bleaching conditions. They often have poor fastness to washing and light but this is not a problem since most synthetic washing detergents contain FWAs and reproduce the whitening effect after each wash.

5.4.6 Mercerisation

Mercerisation is a process named after its discoverer, John Mercer (1850). He treated cotton cloth with cold 20% aqueous NaOH solution, without any applied tension, and then washed out the alkali. This caused considerable fibre swelling and shrinkage of the fabric, but increased its strength, elasticity and ability to absorb cotton dyes. Later, around 1890, Horace Lowe showed that if the material was held under tension during the treatment, and until most of the NaOH had been washed out, no shrinkage occurred and the fibres developed an attractive, subdued lustre. The development of this lustre is still one of the purposes of modern mercerisation.

During the process, absorption of NaOH by the cotton fibres causes acidic dissociation of a significant number of hydroxyl groups. The concentration of ionic sites within the cotton fibres is high in comparison to the ion concentration in the external solution. A considerable pressure develops in the fibres as water is absorbed by osmosis and the fibre swells, loosing the characteristic convolutions. After washing out of the alkali, the fibres have a much rounder cross-section and therefore higher lustre. Today mercerisation is also appreciated because mercerised cotton absorbs larger amounts of dyes and gives a higher rate of dyeing. The more uniform swollen fibres absorb more and scatter less light so that a given amount of dye produces a deeper shade than on regular cotton. This is significant when the dyes are expensive. In addition, the swelling of immature fibres, with thin secondary walls, during mercerisation results in improved dye absorption and a depth of colour close to that of normal fibres, so that the paler dyed neps are less obvious.

The effects on the dyeing properties and the changes in mechanical properties are a consequence of the fibre swelling and changes in the crystalline structure of the cellulose, giving a more open accessible structure. Obviously, dissociation of the hydroxyl groups gives sufficient swelling for water and hydroxide ions to penetrate into the crystalline regions. The cellulose chains then rearrange into a new, more stable pattern, which is preserved after washing out the alkali.

Identification of mercerised cotton is quite easy by microscopic observation of its characteristic rounder fibres, without convolutions. Alternatively, a small region of a fabric sample may be wetted with 20% NaOH solution for a few minutes. After washing, the whole sample is dyed with a direct cotton dye such as Benzopurpurine 4B (CI Direct Red 3). If the treated zone dyes deeper than the remainder of the sample, the cotton was not mercerised. The greater accessibility of mercerised cotton is also evaluated from the increased absorption of chemicals such as iodine and barium hydroxide.

Large quantities of bleached cotton fabric, and to a lesser extent cotton/polyester, are mercerised by a technique called chain mercerisation. The wet fabric coming directly from bleaching is mangled, and possibly vacuum extracted. The objective is to remove as much water as possible from the goods, but to ensure a uniform distribution of the residual water. The material then passes into the first bath of the mercerisation unit, containing 22% NaOH. The solution may contain an alkali-stable wetting agent to assist penetration of the solution into the cotton yarns. It is squeezed, to remove excess liquid, and then passes over a series cold metal cylinders to allow time for the solution to absorb into the fibres. This impregnation is repeated with a second bath and series of ‘timing cans’. Then, clips grip the selvages of the fabric and pull it to the required width. The clips run down each edge of the fabric in continuous chains. The tension in the fabric is determined by the speed of the chains and their separation. Further along the chain, the washing process begins, using dilute NaOH solution originating from the countercurrent flow of the wash water that enters at the chain end. Suction boxes below the fabric pull the washing solution through it and circulate the liquid upstream. The NaOH in the cotton is diluted to a concentration below 5% before the clips release the fabric at the end of the chain. Further washing in a wash box, neutralisation with acetic acid solution and final rinsing and drying complete the series of operations. The entire process must be conducted under conditions giving uniform mercerisation from side to side and end to end of the fabric. The residual alkalinity should be negligible. Table 5.2 lists some of the effects of this process.

Cotton yarn, in hanks held by a pair of rollers, can also be mercerised under tension. This is usually a batch operation. In the Prograde process, cotton yarn is treated under tension with liquid ammonia at its boiling point (–34 °C), washed

Table 5.2 Effects of the chain mercerisation of cotton fabric

Property	Effect
Fabric lustre	Increased
Dye uptake	Increased
Dye consumption	Economy of 30–50%
Fibre strength	Increased
Standard regain	Increased from 6 to 10%
Fibre cross-section	Increased and rounder

with hot water, and dried in a continuous process. The effects are similar to those of mercerisation. Ammonia treatment also gives improved strength, elasticity and dye uptake, but the degree of fibre swelling is less. There are also processes in which cotton fabric is treated with liquid ammonia and the bulk of the ammonia is allowed to evaporate. The liquid ammonia treatments may take place after dyeing, give softer fabrics with a more resilient handle, and allow use of lower amounts of crease-resist agents.

5.5 OTHER VEGETABLE FIBRES

In addition to cotton, there are a number of minor vegetable fibres, the most important being linen, which is derived from flax. The stalks of the plants are harvested and soaked in water under various conditions, in a process called retting. This softens the ligneous material holding the stalk fibres together. A considerable amount of processing is required to produce clean linen fibres. Linen materials also tend to crease easily. For finishing with crease-resist chemicals, mercerisation of the linen helps to minimise the decrease in resistance to abrasion (Section 25.4.1).

Ramie, from China grass, is another vegetable fibre used for textiles. These different types of cellulosic fibres have different morphologies to cotton and are a less pure form of cellulose. They have similar dyeing behaviour but will not dye to the same depth of shade as cotton with a given amount of the same dye.

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CHAPTER 6

Artificially made fibres based on cellulose

6.1 THE FIRST REGENERATED CELLULOSE FIBRES

The first artificially made filaments of regenerated cellulose were produced by Chardonnet in 1884. These were named artificial silk because of their form and appearance. The production method involved extrusion of a solution of cellulose nitrate and regeneration of the cellulose by hydrolysis, as outlined in Section 1.1.2. Although this fibre was produced commercially until 1949, the quantity was always limited by the difficulties of controlling the reactions involved and the high flammability of nitrocellulose and the solvents used. Nevertheless, Chardonnet was the first to demonstrate that extrusion of a polymer solution and evaporation of the solvent, a technique now called dry spinning, was a feasible method of fibre production on a large scale.

Cuprammonium viscose (then called cuprammonium rayon) was first manufactured commercially in 1899. According to the US Federal Trade Commission, a rayon (viscose) is a fibre of regenerated cellulose in which other substituents have replaced not more than 15% of the hydroxyl groups. Cuprammonium viscose is also called cupro or Bemberg viscose. Purified cotton linters, or wood pulp, are dissolved in a solution of cuprammonium hydroxide and sulphate. This is a mixture of copper sulphate, ammonia and sodium hydroxide (Scheme 6.1). Before this solution can be forced through the holes in the spinneret plate to form filaments, the usual filtering and degassing are necessary (Section 4.2.1). The filaments are produced by a wet spinning technique, extruding the cuprammonium solution into running water. This dilutes the solution and coagulates the cellulose filaments. They pass down a converging funnel and the shear forces developed by the concurrent flow of water stretch the still plastic filaments. This increases the orientation of the cellulose chains along the filament axis and thus improves the fibre strength. A bath of dilute sulphuric

$$\mathrm{CuSO_4 + 2NaOH + 4NH_3 \longrightarrow Cu(NH_3)_4(OH)_2 + Na_2SO_4}$$

Scheme 6.1

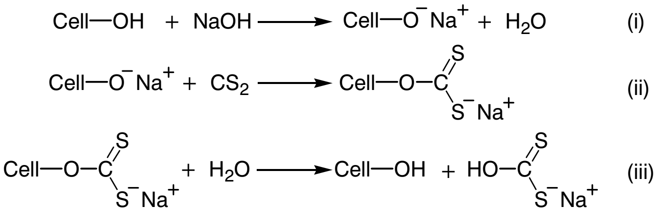
acid washes out the remainder of the copper and neutralises the ammonia. Copper salts are sufficiently expensive to make recovery and recycling of the copper necessary. The filaments are finally well washed and dried.

The smooth, round filaments of this viscose tend to adhere together so that twisting is not necessary. This adhesive quality is used in forming slub yarns. These have thicker areas along the even yarn consisting of an accumulated mass of fibres. For these, the filaments running continuously from one spinneret are intermittently combined with accumulated filaments from another, to produce yarn with slubs. The physical and chemical properties of cuprammonium viscose are very similar to those of viscose fibre discussed in the next section. Despite the silky appearance, fine denier, soft handle and good draping properties of fabrics made from it, cuprammonium viscose has always been a minor fibre compared to regular viscose.

6.2 VISCOSE FIBRE [1,2]

6.2.1 Production of regular viscose fibre

Cross and Bevan in the UK discovered the viscose method for the production of regenerated cellulose in 1892. This was later developed by Courtaulds Ltd. After wet spinning of a dilute NaOH solution of the xanthate ester of cellulose into an acidic spinning bath, the cellulose filaments reform by coagulation and hydrolysis of the ester. Scheme 6.2 outlines the basic chemistry of this process.



Scheme 6.2

The major starting material for viscose fibre is high-grade wood pulp in the form of pressed sheets. These consist mainly of cellulose with a reasonably high DP. Treatment of the sheets with warm 18% aqueous NaOH solution causes dissociation of some of the hydroxyl groups in the cellulose and the formation of its sodium salt, called alkali- or soda-cellulose (Scheme 6.2(i)). Pressing out the excess NaOH solution removes some soluble carbohydrates, and the moist, solid product is next broken up into crumbs and allowed to age. During this period, oxidation in the presence of air causes some depolymerisation. The crumbs of alkali-cellulose are then churned with about 10% of their weight of carbon disulphide, forming sodium cellulose xanthate (Scheme 6.2(ii)). Addition of dilute aqueous NaOH gives a viscous, brown solution, from which the name ‘viscose’ was derived.

The viscose solution is then left to ripen. The viscosity gradually increases as some of the xanthate ester groups hydrolyse back to hydroxyl groups (Scheme 6.2 (iii)). The degree of substitution (DS) of the hydroxyl groups of cellulose represents the number of hydroxyl groups per glucose unit that have undergone chemical substitution. The value of the DS varies from 0, for cellulose, up to a maximum of 3.0. The initially formed sodium cellulose xanthate has a DS of just less than 1.0 but during ripening this falls to about 0.33. Too large a decrease in the DS results in precipitation of cellulose.

During ripening, the average DP also decreases further. The depolymerisation of the cellulose in the ageing and ripening stages of viscose production determines the viscosity of the final spinning solution. This is important for controlling the filament integrity on initial extrusion into the coagulating bath. The low DP of the final cellulose is, however, the major reason for the weakness of this fibre.

The ripe viscose solution is finally degassed and filtered in preparation for wet spinning. Extrusion of the solution into a bath containing acid and salts first coagulates the cellulose xanthate, which then hydrolyses to reform cellulose (Scheme 6.2(iii)). The still plastic filaments pass around and are stretched between rotating pulleys. Stretching produces finer filaments, but also orients the cellulose molecules along the filament axis so that they begin to interact with each other by hydrogen bonding. Without such orientation, viscose filaments would be too weak for textile use. The drawn filaments may be collected in a Topham box (a rotating cylindrical container in which the filaments press against the walls as a result of centripetal force), or wound up on perforated tubes to form bobbins.

The filaments produced require a number of aftertreatments such as desulphurising, bleaching if necessary, washing, drying and oiling. The aftertreatment and washing processes are carried out on batches of cakes or bobbins. Washing with Na_2S solution removes any precipitated elemental sulphur from the filaments, which tends to cause a yellow coloration. Like bleaching, this is not always necessary. Thorough washing finally eliminates all the residual chemicals. The cakes or bobbins may also be dyed at this stage, before drying.

Manipulation of numerous cakes and bobbins is time-consuming and these batch operations limit the rate of production. Fully continuous aftertreatment and washing, immediately after spinning, is much more productive. For each treatment, the extruded and stretched filaments wind around, and advance along, a pair of rollers with convergent axes while being sprayed with the appropriate washing solution.

Wood pulp, and the other chemicals used, are relatively cheap and viscose has become the predominant regenerated cellulose fibre. However, viscose production involves an extremely lengthy series of operations requiring strict control. Large volumes of water are necessary and the alkali, soluble carbohydrates and sulphur compounds in untreated effluent pose an environmental problem. A newer type of regenerated cellulose (called lyocell) is now being manufactured by a process generating less water pollution (Section 6.2.4).

6.2.2 The morphology, properties and uses of viscose

The cellulose in cotton has a DP of around 2000 and a degree of crystallinity of up to 70%. For regular viscose, the DP (250–400) and crystallinity (25–30%) are much lower. The crystallites in viscose are also 4–5 times smaller than in cotton and have a lower degree of orientation. It is therefore not surprising that viscose is a much weaker fibre than cotton. Crystalline zones in a fibre are responsible for strength and rigidity, whereas the amorphous regions provide accessibility, flexibility and extensibility. Wet spinning involves extrusion of a solution of free, individual cellulose molecules. These tend to orient themselves along the filament axis during extrusion and this continues during stretching after coagulation. The molecules are not, however, aligned to the same extent as in cotton.

Regular viscose fibres are weaker than those of cotton, particularly when wet (Figure 6.1). They are much less rigid and much more plastic. Elongation under a stress of more than 2% can cause displacement of the cellulose molecules and therefore permanent elongation. The strength of viscose filaments is improved by stretching them after extrusion, while they are still plastic. Even so, the strength of wet viscose may be as much as 50% lower than when dry. Because the filaments have low crystallinity and high accessibility, water absorption causes fibre swelling and increases the extensibility by 20%. Swelling of viscose filaments can be a

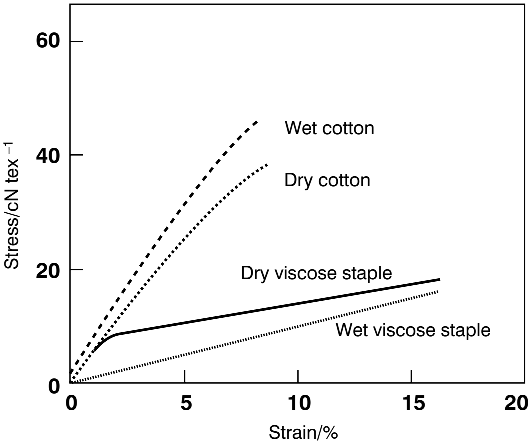


Figure 6.1 Stress–strain data for cotton and viscose fibre

problem when treating wound packages. The swelling tends to close the channels through which dye or chemical solutions are flowing and thus increases the internal pressure.

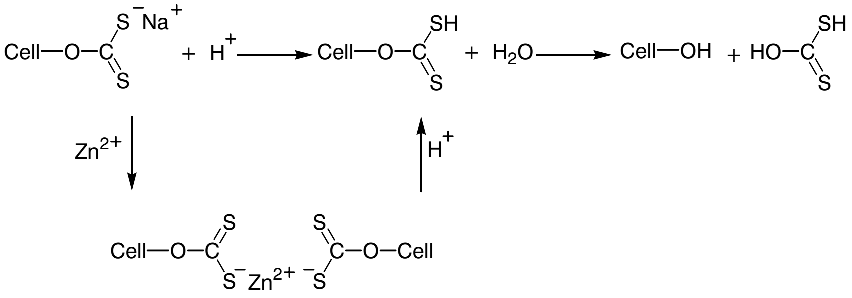
These properties are in direct contrast to those of cotton, which is much stronger and only swells slightly in water. Cotton fibres are still quite rigid even when wet. Fabrics of viscose do not, therefore, have the good resistance and washability of those made with cotton. During processing and use, viscose fabrics must be handled with care to avoid stretching, creasing and even tearing. The limp handle of fabrics made from viscose contrasts sharply with the crisp handle of cotton materials. Resin finishes are widely used on viscose materials to improve the poor wet strength and provide better dimensional stability (Section 25.4).

The low DP of viscose results in a much higher number of reducing end groups and therefore a higher copper number than for cotton (Section 5.3.2). Because of this, the problem of dye reduction, when dyeing under hot alkaline conditions, is more pronounced for regenerated cellulosic fibres. The low DP and crystallinity of viscose fibres make them much more accessible to solutions of chemicals than fibres of cotton. Viscose has about the same accessibility as mercerised cotton, as shown by the regain values at 25 °C and 100% relative humidity (cotton 25%, viscose 45% and mercerised cotton 50%).

Since it is essentially pure cellulose, viscose has the same chemical properties as cotton. In its chemical reactions, it will, however, react more rapidly than cotton.

Because of its lower DP and crystallinity, and higher accessibility, viscose even tends to be reactive under conditions where cotton is quite stable. For example, cold, concentrated or hot dilute NaOH solution will attack and tend to dissolve viscose, so it requires milder processing conditions. Viscose also has a higher number of carboxylate groups than cotton and will absorb cationic dyes by ion exchange.

The composition of the aqueous coagulating bath significantly influences the properties of the viscose filaments. A typical bath might contain dilute sulphuric acid, sodium sulphate, glucose and zinc sulphate. The salts promote rapid coagulation and dehydration of the coagulated sodium cellulose xanthate by osmosis. The acid present in the bath catalyses hydrolysis of the cellulose xanthate back to cellulose. Cellulose is generated either by transformation of the sodium cellulose xanthate into cellulose xanthate, and its subsequent hydrolysis, or similarly by the slower reaction of the zinc cellulose xanthate. Scheme 6.3 shows the two different routes by which cellulose is reformed.



Scheme 6.3

In regular viscose filaments, there is a distinct difference between the skin and the core of the filament. Since the acid in the spinning bath penetrates into the core of the coagulated sodium cellulose xanthate more rapidly than zinc ions, the cellulose skin is formed via the zinc salt and more slowly than the cellulose core forms from the sodium salt. Rapid coagulation of the filament surface, using a higher concentration of zinc sulphate in the bath, produces a pronounced filament skin. During these processes, the more rapidly regenerated cellulose core shrinks and the skin becomes wrinkled, giving the filaments of viscose their characteristic serrated cross-section (Figure 6.2).

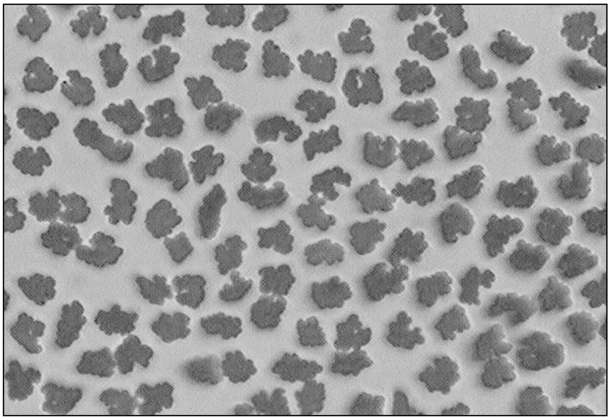


Figure 6.2 Cross-section of dyed viscose filaments (courtesy of Acordis Fibers)

The cellulose molecules in the skin layer are more highly oriented along the filament axis than those in the core and the crystallinity is therefore higher. This is partly because of the friction of the solution with the walls of the spinneret hole. The core of a regular viscose filament therefore absorbs dyes faster than the skin. Dyes also tend to bleed more rapidly from the core on washing. These effects provide a means of seeing the skin thickness on microscopic examination of cross-sections of dyed fibres.

Viscose filaments from wood pulp are relatively cheap and available in large quantities. The normal filaments have an attractive lustre. Titanium dioxide is added to the viscose solution during ripening to give matte filaments. Alternatively, coloured pigments may be added. Despite a limited choice of colours, pre-pigmented or dope-dyed viscose filaments are useful when high fastness to washing and light are essential. As for other artificially made fibres, a wide variety of forms and properties are available. These differ in denier, cross-section, lustre, tenacity, and so on. In addition, hollow filaments or filaments containing air bubbles are produced. These give high bulk and good thermal insulating power. They have high moisture absorption. A number of modified viscoses have non-cellulosic polymers or crosslinking agents added to the viscose solution before spinning.

Large quantities of viscose are produced as staple fibre. Blending with other fibres such as polyester provides cost-effective water absorbency and softness. Because of the blending of staple fibres, they do not need to have the same uniformity as continuous filaments and large scale production of staple fibre gives better economics. For staple fibres, combination of the output of several spinnerets forms a band or tow of filaments, which can then be cut into short lengths. Before cutting, the filaments may be crimped to improve the adhesion of the short fibres for yarn spinning. Crimping may be achieved mechanically or by coagulating under conditions that produce an asymmetric cross-section, with more skin on one side of the filament than the other. When wet, the asymmetric fibres swell more on the thin-skinned side and tend to curl. Bicomponent fibres of two different kinds of viscose behave similarly.

6.2.3 Improved forms of viscose

As we have seen, the cellulose skin in regular viscose has better orientation and strength. So, to produce high tenacity viscose, less acid and a high concentration of zinc sulphate in the spinning bath are used. Then, all the cellulose is regenerated slowly and the filament is all skin. These filaments have no core, do not shrink during regeneration of the cellulose, and have a uniform cross-section. Alternatively, regeneration of the cellulose is delayed by using a very dilute acid bath. This allows time for better stretching and improved orientation.

High tenacity viscose fibres are used for tyre belts, hoses, and industrial applications. They are rarely dyed. There are various ways of controlling the coagulation process with bath additives. A higher degree of stretching produces filaments with greater orientation and crystallinity. This gives filaments that may be up to three times stronger than regular viscose, but still with acceptable extensibility. High tenacity viscose has lower water absorption and swelling but higher wet strength.

A variety of other high-strength viscose filaments are also produced whose mechanical properties are much closer to those of cotton. These are called high wet modulus (HWM), modal and polynosic viscoses but there are various definitions of these names. The word ‘polynosic’ is presumably derived from ‘polymer’ and ‘cellulosic’ and refers to viscoses with a fine micro-fibrillar structure resistant to cold 8% aqueous NaOH solution. The generic name ‘modal’ is used to describe viscoses having high tenacity and a high wet modulus; ‘polynosic’ usually refers to the type with the highest values of wet modulus. The elastic modulus is the stress that must be applied to produce a unit elongation. The higher the value, the more rigid the fibre. All the HWM viscoses have higher wet strength than regular viscose, increased resistance to swelling by alkali solution, a higher DP and a more fibrillar internal structure similar to cotton. Their properties are therefore much closer to those of cotton. Compared to regular viscose, they are more crystalline and oriented, imbibe less water and swell less.

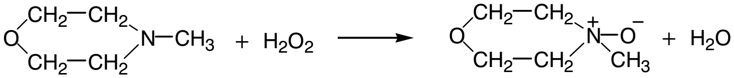
HWM viscose is used as staple for blending with other fibres using the cotton carding system. The fibres consist of cellulose fibrils and have no skin. The average DP is 500–600, and the fibres are 50–60% crystalline with larger crystallites than in cotton. Because of this, and the higher orientation than in regular viscose, HWM viscose fibres are less likely to deform under wet conditions. On water absorption, the swelling is intermediate between that of regular viscose and cotton. For many materials, HWM viscose competes with cotton, but, unlike cotton, it has a soft silky handle, with an attractive subdued lustre. It can be used for materials where regular viscose would be inappropriate because of its poor wet strength. It is blended with cotton to a large extent and also with polyester staple.

Polynosic fibres have a higher DP of around 500–700, compared to the value of 250–400 for regular viscose. The higher values of the DP for HWM and polynosic fibres are achieved by curtailing the ageing of the soda-cellulose and the ripening of the viscose solution to avoid depolymerisation. The viscose solution is prepared under much milder, neutral conditions. Regeneration is also slowed down by spinning into a dilute sulphuric acid solution without salts. Other additives are also present to retard coagulation. The filaments exhibit a high degree of internal fibrillation and their properties are much closer to those of cotton.

6.2.4 Lyocell fibres [3]

The lyocell fibres developed by Courtaulds and Lenzing appear to have solved the two major problems of viscose production: the excessive environmental pollution and the poor wet strength of the viscose filaments. The generic name ‘lyocell’ is from the Greek verb *lyein* meaning ‘to dissolve’, and is used for fibres of regenerated cellulose produced directly from a solution of cellulose rather than from a cellulose derivative. Courtaulds’ product is called Tencel.

Few details of the manufacture of this type of fibre have been divulged but the following steps seem likely. Firstly, an aqueous suspension of ground cellulose (13%) in water (20%) and *N*-methylmorpholine-*N*-oxide (67%) is prepared. The solvent is obtained by oxidation of *N*-methylmorpholine with hydrogen peroxide (Scheme 6.4). Thin film evaporation of the water then increases the cellulose solubility and a true solution is obtained in the amine oxide solvent. This solution is stabilised by an anti-oxidant such as propyl gallate (propyl-3,4,5-



Scheme 6.4

trihydroxybenzoate) and a little NaOH. After the usual filtration, the hot solution is extruded through a spinneret. Before entering the aqueous coagulation bath, the liquid filaments pass through an air gap where the final filament shape is determined. The water in the spinning bath precipitates solid cellulose filaments. The filaments are then washed to remove the amine oxide and dried. The beauty of the lyocell technology is the re-use of the recovered solvent and of much of the process water. In addition, the number of process steps is much smaller than in production of viscose.

Staple lyocell fibres can be ring or open-end spun, alone or in mixture with other natural or synthetic fibres. They can be used for clothing and also for technical textiles. In comparison to viscose, lyocell filaments have a round cross-section and are relatively homogeneous throughout. The core–skin character typical of viscose is absent. Lyocell filaments have higher tenacity and slightly greater extensibility than cotton fibres. The wet strength is 2–3 times greater than for regular viscose filaments, being comparable to that of cotton. The mechanical properties are slightly better than those of most HWM viscoses and are a consequence of the high crystallinity of the filaments and the high degree of polymer chain orientation in the amorphous regions.

The fibres have a fibrillar structure and these fibrils will separate when the fibres are wet and under tension. Fibrillation is the longitudinal splitting of a fibre into a bundle of microfibres of smaller diameter, typically 1–4 μm. This will occur predominantly on the exposed fibre surface. Because of the high transparency of the fibres, the fabric has a white or frosty surface appearance. Fibrillation usually occurs during rope wet processing, as in winch or jet dyeing (Sections 12.4.1 and 12.4.4), being much less pronounced when fabric is treated in open-width form. The degree of fibrillation can be controlled during fabric processing.

Fibrillation allows the production of very attractive fabric surface effects with a soft, pleasant handle, such as the peach skin effect. To produce these attractive effects, a number of processes is required. A typical procedure is to singe off any loose fibrils and then fibrillate by rope scouring. The surface fibrils are then removed by a cellulase enzyme treatment. Cellulase is an enzyme capable of digesting cellulose. Because the fibrils expose a large surface area, it is possible to clean them off the fibre surface without digesting the bulk of the more compact fibre. A second fibrillation is next carried out on the cleared fibre surface but only on the exposed areas. This avoids any problems of pilling and fibril entanglement. It is preferable that dyeing follow these processes. If a fabric is required with a clean surface appearance, fibrillation must be minimised by using high liquor ratios, a lubricant in the bath or by low temperature processing. To minimise fibrillation of Tencel, Courtaulds recommend the use of a proprietary chemical applied under hot alkaline conditions. It functions as a crosslinking agent and prevents fibrillation.

6.2.5 Dyeing regenerated cellulose fibres

All the various forms of viscose are composed of cellulose and therefore have similar chemical properties. The different types of viscoses, however, have different dyeing properties. They can all be dyed with the same types of dyes used for dyeing cotton, but the dyeing rate and amount of dye absorbed may vary from one type of viscose to another. If a viscose/cotton blend is dyed with a typical cotton dye, it is usual that the viscose will be more deeply coloured. Even in the case of fibrillar viscoses, which closely resemble cotton, it is unlikely that the two different cellulosic fibres in the blend will be dyed to the same depth. Dyed lyocell fibres have a colour yield (the depth of colour obtained for a given amount of dye) that is higher than that for dyed viscose, but lower than for mercerised cotton. These differences are not surprising since viscose morphology can be quite varied, depending upon the manufacturing conditions. From the dyeing point of view, all they have in common with each other, and with cotton, is their cellulosic nature. Dyeing trials are therefore recommended.

6.3 CELLULOSE ACETATES [2,4]

Cellulose acetates are esters of cellulose in which a large fraction or even all the hydroxyl groups have been esterified using acetic anhydride (Scheme 6.5). The two major types of cellulose acetate have about 55 and 62% of combined acetic acid. These values correspond to cellulose with degrees of substitution (DS) of 2.48 and 3.00, respectively. The latter is correctly called cellulose triacetate, but the name cellulose diacetate for the former is somewhat misleading, its composition being intermediate between the di- and triacetate.

These fibres in no way resemble fibres of cellulose. Both cellulose diacetate and

$$\text{Cell—OH} + (CH_3CO)_2O \longrightarrow \text{Cell—O—COCH}_3 + CH_3CO_2H$$

Scheme 6.5

triacetate are relatively hydrophobic and thermoplastic. The standard regains of cellulose di- and triacetate are 5.0 and 2.5%, respectively. They hardly swell in water. Once superficial water has been removed by centrifugation, vacuum or mangling, fabrics from these fibres are easy to dry, unlike cotton. Both cellulose acetates are resistant to dilute solutions of acids but are sensitive to alkaline solutions, which cause hydrolysis of the acetate ester to hydroxyl groups, especially at higher temperatures. The triacetate is more hydrophobic and more compact and crystalline than the diacetate and has better resistance to alkaline solutions and to solvents.

The dyeing properties of cellulose acetates are quite different from those of cellulosic fibres and different types of dyes must be used. Although much of the work on development of these polymers was carried out by Henry and Camille Dreyfus, working in England during the First World War, full commercial exploitation was not possible before the problem of dyeing these fibres had been solved. Cellulose di- or triacetates have no ionic groups. They are quite hydrophobic fibres. When introduced in the 1920s, cellulose diacetate was initially difficult to dye satisfactorily with existing ionic dyes. Fine dispersions of simple, non-ionic azo and anthraquinone compounds, of limited water solubility, however, efficiently dyed this fibre. These so-called disperse dyes are slightly soluble in water and are extracted from the aqueous solution by the solid fibre in which the dyes are quite soluble (Figure 1.7).

6.3.1 Cellulose diacetate

In the production of cellulose acetates, wood pulp is first pretreated either with glacial acetic acid or with the vapour of an acetic acid–water mixture to swell the cellulose fibres. This makes them more accessible for acetylation. The fibres are then treated with a mixture of acetic acid and acetic anhydride containing a small amount of sulphuric acid as catalyst. Cooling prevents an increase in temperature of the mixture that will promote excessive hydrolysis of the cellulose. The cellulose triacetate produced becomes soluble in the reaction medium. This initial product is called primary cellulose acetate. Cellulose diacetate is obtained directly from the triacetate by partial hydrolysis. Rather than precipitate the triacetate, by addition of a large amount of water, a small amount of dilute aqueous acetic acid is added to the cellulose triacetate solution. The water reacts with the excess of acetic anhydride and hydrolyses some of the acetate to hydroxyl groups. The final product is called secondary cellulose acetate which is synonymous with cellulose diacetate. Once the DS has fallen to the required value of about 2.5, the cellulose diacetate becomes soluble in acetone. It is then precipitated by addition of water.

Because of its good solubility in acetone, filaments of cellulose diacetate can be produced by extrusion and evaporation of this solvent. This is the dry spinning process, which has the advantage over wet spinning that no additional treatments such as washing are needed. Recovery of the evaporated acetone and of the acetic acid is required for economical operation.

For dry spinning, a filtered and degassed acetone solution, containing a small amount of water, is extruded through a spinneret. To ensure constant properties of the filaments, the acetone solution is prepared from several blended batches of the solid cellulose diacetate because of their slight variations in properties. If required, pigmentation of the solution with TiO_2 at this stage will decrease the lustre of the filaments produced. The solution is spun into a rising current of hot air at 100 °C. Some stretching occurs during this phase while the filaments are still quite plastic. Lubricants are then sprayed or wiped on and the filaments wound up.

Cellulose diacetate is available in a range of deniers, as single or multi-filaments, and as staple fibre. The denier depends on the solution pumping rate, the spinneret hole size and the filament speed that causes drawing. Staple fibre is produced by cutting a tow of mechanically crimped filaments. Slub yarns can be made by combination of two different sets of extruded filaments.

The acetylation procedure, under acidic conditions, results in a large decrease in the DP of the cellulose to about 300. This is controlled by pre-swelling of the cellulose fibres, by cooling the reaction mixture and by careful hydrolysis of the primary acetate. The large acetate side-groups prevent close packing of the polymer chains and the development of crystallinity. Even though the filaments are drawn during spinning, the degree of polymer chain orientation remains fairly low. Filaments of cellulose diacetate are therefore not particularly strong. The fibre is weaker and more extensible when wet but it does not lose as much strength as viscose when wetted. Fabrics easily deform if over-stretched. Because this polymer is thermoplastic, it requires careful handling when in contact with hot solutions to avoid stretching and creasing of the material. Fabrics from this fibre have good drape, a crisp handle, and reasonable dimensional stability and wrinkle resistance if they are handled carefully and not over-heated.

Cellulose diacetate filaments have an almost round cross-section with several lobes, with ridges between them that run along the filament length. The unpigmented filaments have high sheen that is valued for linings, lingerie and dress fabrics, ribbons, and for some furnishing fabrics. Few of these have high fastness requirements. Yarns made from multi-filaments, however, do tend to slip easily over each other and chemical finishes may be needed to avoid this effect and to stabilise a fabric. Cellulose diacetate is produced mainly as continuous filament even though it is more difficult to dye level.

The temperature of materials of cellulose diacetate should not exceed 85 °C when wet, and should be less than 140 °C in dry heat. Because bright filament is easily delustered in hot water above 85 °C, partly by surface hydrolysis of acetyl groups, dyeing temperatures rarely exceed this value, even if the filament has been delustered with TiO_2. The fibre surface is very easily hydrolysed by mild alkaline scouring. This sensitivity to heat and alkaline hydrolysis should always be born in mind. Cellulose diacetate softens on heating and fabrics can be embossed with a pattern using heat and pressure. It is produced with almost no natural colour and rarely requires bleaching. It is soluble, or swells considerably, on contact with a number of common solvents.

6.3.2 Cellulose triacetate

Cellulose triacetate is obtained as described in the previous section. Before precipitation, reaction with magnesium acetate and a little water removes any sulphuric ester groups (Cell–OSO_3H). The triacetate is then precipitated by addition of water, filtered and washed. Alternatively, acetylation procedures are used in which the fibrous wood pulp preserves its form and does not dissolve. The product is soluble in chloroform but this toxic solvent is not used for dry spinning. A solution of the triacetate in methylene chloride (dichloromethane) containing a little ethanol is used. The safety of even this chlorinated solvent is in question and the production of triacetate is decreasing because of this.

Fibres of the triacetate are more hydrophobic than those of secondary acetate and they have higher chemical resistance. They are much more stable to hot water and dilute alkali than secondary acetate. Dyeing temperatures are close to the boil and even as high as 120 °C. Because of the more regular structure, the crystallinity of triacetate is higher than that of the diacetate and it is more solvent resistant.

Cellulose triacetate is thermoplastic and fabrics can be heat set or permanently pleated using dry heat or steam. Heat setting of triacetate fabrics improves their dimensional stability so they do not shrink or wrinkle on dyeing, or on washing, but the process increases the crystallinity and the rate of dyeing is reduced. The mechanical properties of triacetate fibres are close to those of the secondary acetate but it does not lose a great deal of strength when wet. It gives fabrics with a firm crisp handle, less soft than that of the diacetate.

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