CHAPTER 2

FIBRE SPINNING

2.1 Introduction

The conversion of bulk polymer into fibre form is accomplished by ***spinning*** processes. Filaments can be drawn from the melts or concentrated solutions of most high molecular weight substances, and also from those of a few low molecular weight compounds. Filament forming, then, is not a property unique to macromolecular substances. However, the filaments of low molecular weight compounds have only a low mechanical strength. If the filament material consists of long molecular chains, these will be partially oriented on stretching or drawing giving the resulting filament increased strength. Only a few of the many types of filaments known have a sufficiently high tensile strength to be suitable for use in textiles or in other industrial applications.

Fibres are usually classified according to their origin as being either natural or man-made fibres. Natural fibres can come from vegetable, animal or mineral sources. At present, all currently used vegetable fibres are cellulosic materials such as cotton, flax, hemp, ramie and jute while animal fibres are proteins such as wool, natural silk and camel hair. Asbestos is an example of a mineral fibre.

Man-made fibres include both regenerated and completely synthesized fibres. Regenerated fibres are fibres produced from materials of natural origin. The material undergoes some chemical process or modification (viscose silk, acetate silk, nitrocellulose, alginate fibres, etc.). Synthesized fibres, on the other hand, are synthetic fibres which are synthesized from other raw materials.

In addition, fibres can also be classified according to their application as either textile or industrial fibres. Textile fibres are used for yarn, weaves and knitted fabrics, whereas industrial fibres are used for nets, cloths and ropes [20].

In most cases, spinning processes require solution or melting of the polymer. If the polymer can be melted under reasonable conditions, the production of a fibre by ***melt spinning*** is preferred over solution processes. When melt spinning cannot be carried out, a distinction as to type of process is made depending upon whether the solvent is removed by evaporation ***(dry spinning)*** or by leaching out into another liquid which is miscible with the spinning solvent but is not itself a solvent for the polymer ***(wet spinning)***.

The conversion of spun polymer melt or solution into a solid fibre involves cooling, solvent evaporation, or coagulation, depending on the type of spinning used. The rates of these processes decrease in the order listed. Cooling of a fine filament from the melt is normally very rapid and can only be controlled within relatively narrow limits. Solvent evaporation involves simultaneous outward mass transfer and inward heat transfer, the rate-controlling step invariably being outward diffusion of solvent. Coagulation involves two-way mass transfer, the coagulating agent (e.g., acid) diffusing in and the products of coagulation (e.g., salt, H_2S) diffusing out.

As a consequence of these factors, it is very easy to obtain a melt-spun fibre which possesses uniform properties throughout its cross-section but almost impossible to do so with solvent-spun or coagulated fibres [21].

2.2 Wet Spinning [21, 22]

Solution-spinning methods comprise the oldest processes used for the preparation of synthetic fibres. The wet-spinning process requires the coagulation of a filament of the viscous polymer solution in a non-solvent for the polymer.

As with dry spinning, the polymer is dissolved or suspended in a solvent to form a viscous "spin dope" and filaments are formed by extrusion through tiny holes in a spinneret plate. Some polymers will degrade thermally if attempts are made to melt them (e.g., chitosan) and thus a solvent must be used. With wet spinning, the term more accurately depicts the process than with dry spinning because the solvent is extracted or, perhaps more appropriately, leached from the filaments by another liquid. In most cases, the second liquid is an aqueous medium.

Thus, in the wet-spinning process, a concentrated solution of the polymer or polymer derivative is spun through a spinneret into the coagulating liquid (Figure 2.1a). The chemical reaction to convert a derivative to the final polymer can take place simultaneously or later. Wet spinning is commonly

FIBRES SPINNING PROCESSES

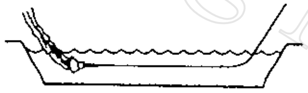
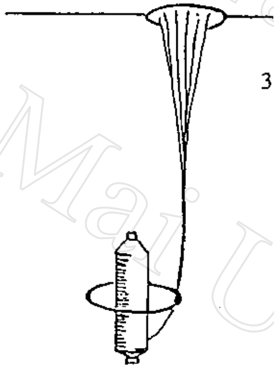
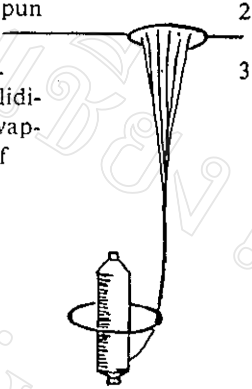
Wet Spinning	*Dry or Solvent Spinning*	*Melt Spinning*
Rayon Creslan acrylic Acrilan acrylic Zefran acrylic	Acetate Vinyon Orlon acrylic Modacrylic	Nylon Saran Polyester Olefins
1. Raw material is dissolved by chemicals. 2. Fiber is spun into acid bath.  3. Fiber solidifies when coagulated by acid.	1. Resin solids are dissolved by solvent.  2. Fiber is spun out into warm air. 3. Fiber solidifies by evaporation of solvent.	1. Resin solids are melted in autoclave.  2. Fiber is spun out into air. 3. Fiber solidifies on cooling.
Oldest process Most complex Weak fibers until dry Washing, bleaching, etc., required before use	Direct process Solvent required Solvent recovery required No washing, etc., required	Least expensive Direct process High spinning speeds No solvent, washing, etc., required Fibers shaped like spinneret hole
(a)	**(b)**	**(c)**

Figure 2.1: Schematic diagrams of the three principal types of fibre spinning processes [23]:

(a) wet spinning (b) dry spinning (c) melt spinning used for viscose cellulose and some synthetic fibres such as polyacrylonitrile spun from aqueous salt solutions.

The essential feature in wet spinning is to transfer the mass of the solvent from the polymer to the coagulating bath. This transfer is not accompanied by heat of solidification of the polymer, as in melt spinning, or heat of evaporation of the solvent, as in dry spinning. A heat of chemical reaction may be present but is not an essential part of the process.

As in other types of spinning, the surface or interfacial tension forces around the filament are quite strong so that it is difficult to produce at the spinneret a filament with a cross-section other than circular. These forces, however, also tend to make the filament break up into drops. This tendency is opposed by the viscosity of the solution; hence, more viscous solutions are easier to spin.

During coagulation, several processes take place simultaneously including diffusion, osmosis and salting out. Because of the interplay of these processes, coagulation occurs in rather different ways for different fibre-solvent systems. Usually, coagulation is rapid and the fibres cannot be stretched greatly during this step. The outer skin of the fibre sets to a gel and, later, the volume of material in the core is reduced as the rest of the solvent is removed. The skin then has to fold to accommodate the reduced volume. This give a characteristic wrinkled cross-section to some fibres such as viscose rayon. It is therefore often difficult to produce fibres with perfectly circular cross-sections despite the fact that the initial product at the spinneret is in this shape. As a result of the shrinkage, the skin of the fibre is oriented much more than the core. Wet-spun yarn may be collected on a bobbin or as a loose cake which is then subjected to chemical treatments, washing and drying. Alternatively, these steps may be carried out continuously, as indicated in Figure 2.1a.

A major difference between wet spinning and either melt or dry spinning is that one is spinning into a low viscosity non-solvent a polymer solution with a much higher viscosity. Because this higher viscosity can translate into high shearing stresses on the surfaces of the filaments, the tension in the filaments can become quite high.

Another difference is the capability of using many more spinneret holes in the case of wet spinning. The total number can approach 60,000 in a single spinneret plate if the spinning is done directly into a coagulating or extracting liquid. Because the liquid is present, the filament forms a type of skin almost immediately and the potential for the filaments to touch and fuse is practically eliminated compared with dry or melt spinning.

2.3 Dry Spinning [24, 25]

Like wet spinning, dry spinning uses solvents in which the polymer dissolves (see Figure 2.1b). The resulting solution or suspension is a viscous “spin dope”. This process necessarily introduces another species (the solvent) which is subsequently removed and is therefore more expensive than conventional melt spinning processes. It is used in cases where the polymer degrades thermally if attempts to melt it are used or in cases where certain surface characteristics of the filaments are desired - melt spinning produces filaments with smooth surfaces and dry spinning produces filaments with rough surfaces. The rougher surface may be desirable for improved dyeing steps or for special yarn characteristics. The term ***"dry spinning"*** is a bit misleading, since the polymer is certainly wet by a solvent. Presumably, the intent here was to distinguish the two methods of solvent removal for the two cases of dry and wet spinning. The solvent in dry spinning is a volatile organic species and starts to evaporate immediately after the filament is formed. Whereas melt spinning involves solidification by cooling, dry spinning produces solidification of the polymer by solvent removal.

As the fibres progress downward to the drawing rolls, a countercurrent stream of warm air evaporates the solvent. In this process, the cross-section of the fibre is determined not only by the shape of the spinneret holes but also by the complex nature of the diffusion-controlled solvent evaporation process because of the considerable shrinkage as the solvent evaporates. Acrylic fibres including polyacrylonitrile are produced by dry spinning. In the case of polyacrylonitrile (trade name: 'Orlon'), the polymer is dissolved to a concentration of 20-30 wt. % in dimethylformamide as solvent.

2.4 Melt Spinning [21, 22]

The process of melt spinning is inherently simple. The molten polymer, such as polyamide (nylon), polyester or polypropylene, is pumped at a constant rate under high pressure through a spinneret plate containing one or more small holes. The molten polymer streams emerge downward from the face of the spinneret, usually into air. They solidify and, in the case of multifilaments, are brought together to form a thread and wound up on bobbins. A subsequent drawing step is necessary to orient the fibres.

The polymer is melted by contacting a hot grid in the form of steel tubing which is heated by an electric current or by hot vapors (Figure 2.1c). It is usually necessary to protect the polymer melt from oxygen by blanketing it with a stream of an inert gas such as carbon dioxide or nitrogen. If the viscosity of the molten polymer is low, it may pass directly to the metering (constant-rate) pump. For melts of higher viscosity, a booster pump may be used. Other methods of melting have been proposed including the use of an extrusion-type screw, one section of which can serve as its own metering pump. Methods in which the metering pump is replaced, for example, by a source of gas pressure or other device, do not appear to offer sufficiently precise control to hold the denier (diameter) of fine yarns constant.

While the polymer is molten, certain physical and chemical changes in the polymer may take place. For example, in polyesters, ester interchange reactions can occur, changing the polymer's molecular weight average and distribution and, hence, the melt viscosity. Thermal decomposition may lead to the formation of gas bubbles which interfere with the spinning process or lead to chain branching and crosslinking reactions.

As the molten filament emerges from the spinneret face into air and begins to cool, an air blast may be used to speed up the cooling process. After the filaments have travelled far enough to become solid, the filaments (if more than one) are brought together and wound up. Take-up speeds of about 2500 ft/min are usually employed in industry. To be suitable for melt spinning, a polymer must be stable at the melt extrusion temperature which is generally at least 20°C above its melting point.

The advantages of the melt spinning process are that (1) the spinning process is extremely rapid and (2) the fibres have a uniform, circular cross-section. The main disadvantage of melt spinning is that some polymers are not sufficiently thermally stable above their melting temperature to survive the spinning process without at least some degradation occurring, especially in the case of polyesters.

2.5 Chitin and Chitosan Fibres

There is a long history of attempts to produce fibres from chitin and chitosan. With chitin, the main difficulty has been to find suitable solvents. The first attempt to make chitin fibres was made in 1926 by Kunike who spun fibres from 6-10% chitin solution in cold concentrated sulphuric acid. A number of other workers also produced chitin fibres in the 1920s and 1930s (see Table 2.1). For example, Knecht and Hibbert made fibres by extrusion of chitin solution in cold concentrated hydrochloric acid. Other attempts were also made by producing fibres from chitin xanthate, similar to the viscose rayon process.

These early attempts provide some basic information on the production of chitin fibres. However, after the discovery of synthetic fibres in the late 1930s, research work on chitin fibres diminished, mainly as a result of the shift of attention to the commercially more attractive synthetic fibres. There was relatively little further work on the study of chitin fibres until the 1970s when a number of unique properties were discovered for chitin and chitosan. Since then, as can be seen in Table 2.1, a number of attempts have been made to produce chitin fibres by using a wide variety of different solvents.

Table 2.1 The production of fibres from chitin and chitosan [3].

Authors	Year	Solvents Used	Fibre Tenacity* (gf/dtex)
CHITIN FIBRES			
Kunike	1926	H_2SO_4	2.5
Knecht & Hibbert	1926	HCl	
Clark & Smith	1936	Aqueous NaSCN	
Thor & Henderson	1939	Chitin xanthate	
Austin & Brine	1977	40% Cl_3CCOOH 40% Chloral hydrate 20% CH_2Cl_2	4.5
Balassa & Prudden	1978	Chitin xanthate	0.81-1.37
Tokura et al.	1979	HCOOH	0.61-1.43
Nakajima et al.	1984	DMAc-LiCl	3.57
Agboh	1986	DMAc-LiCl	0.7-2.2
CHITOSAN FIBRES			
Mitsubishi Rayon	1980	0.5% Aqueous acetic acid	2.2
Mitsubishi Rayon	1980	1% Aqueous acetic acid	
Fuji Spinning	1984	Dichloroacetic acid	
Fuji Spinning	1984	Urea-acetic acid mixture	
Tokura et al.	1987	2-4% Aqueous acetic acid	
East and Qin	1993	2% Aqueous acetic acid	0.61-2.48

*__*Tenacity*__ is a measure of the fibre's tensile strength. It is usually expressed in units of ***gf/denier*** or ***gf/dtex*** where:

gf = grams force at break (= ultimate tensile load)

denier = weight in g of 9000 m of fibre (1 denier = 1.111 x 10^{-4} g/m)

tex = weight in g of 1000 m of fibre (1 denier = 10^{-3} g/m)

dtex = decitex = 0.1 tex = 0.9 denier

Denier and ***tex*** are therefore each an indirect measure of the fibre's size diameter.

Despite the more soluble nature of chitosan, chitosan fibres were developed much later than chitin fibres (Table 2.1). The first reported attempt was made in 1980 when chitosan fibres were made by extruding a 3% by weight chitosan solution in 0.5% aqueous acetic acid into a 5% aqueous NaOH solution. A fibre tenacity of 2.2 g/dtex and an elongation at break of 10.8% were reported. A few other attempts were also made using different solvent systems such as an acetic acid / urea mixture. Fibres were also produced using different coagulating baths, typical examples being aqueous solutions of sodium lauryl sulphate and aqueous alkali solutions containing $CuCO_3$-NH_4OH. With baths containing Cu(II) ions, the fibres obtained were chitosan containing chelated Cu(II) ions. A typical schematic arrangement used for the wet spinning of chitosan is shown in Figure 2.2.

In a recent study, East and Qin [17] found that chitin fibres can be more easily made by spinning chitosan fibres first and then acetylating them in fibre form to produce chitin fibres via an indirect route. Since chitosan fibres can be easily made by dissolving chitosan in 2% aqueous acetic acid solution, and the fibres can also be easily acetylated with acetic anhydride, this route provides a more economic way of producing chitin fibres. It was found that the acetylation process was affected by the treatment conditions such as reaction time, temperature and the ratio of anhydride to fibre weight. The acetylated fibres gained both dry and wet strength while losing the chelating ability of the original chitosan fibres.

There are many procedures reported in the literature for producing chitosan fibres from wet spinning. For example, East, McIntyre and Qin [26] found that chitosan fibres could be spun by wet spinning using 2% acetic acid as solvent and 5% aqueous sodium hydroxide as coagulant. At best, fibre

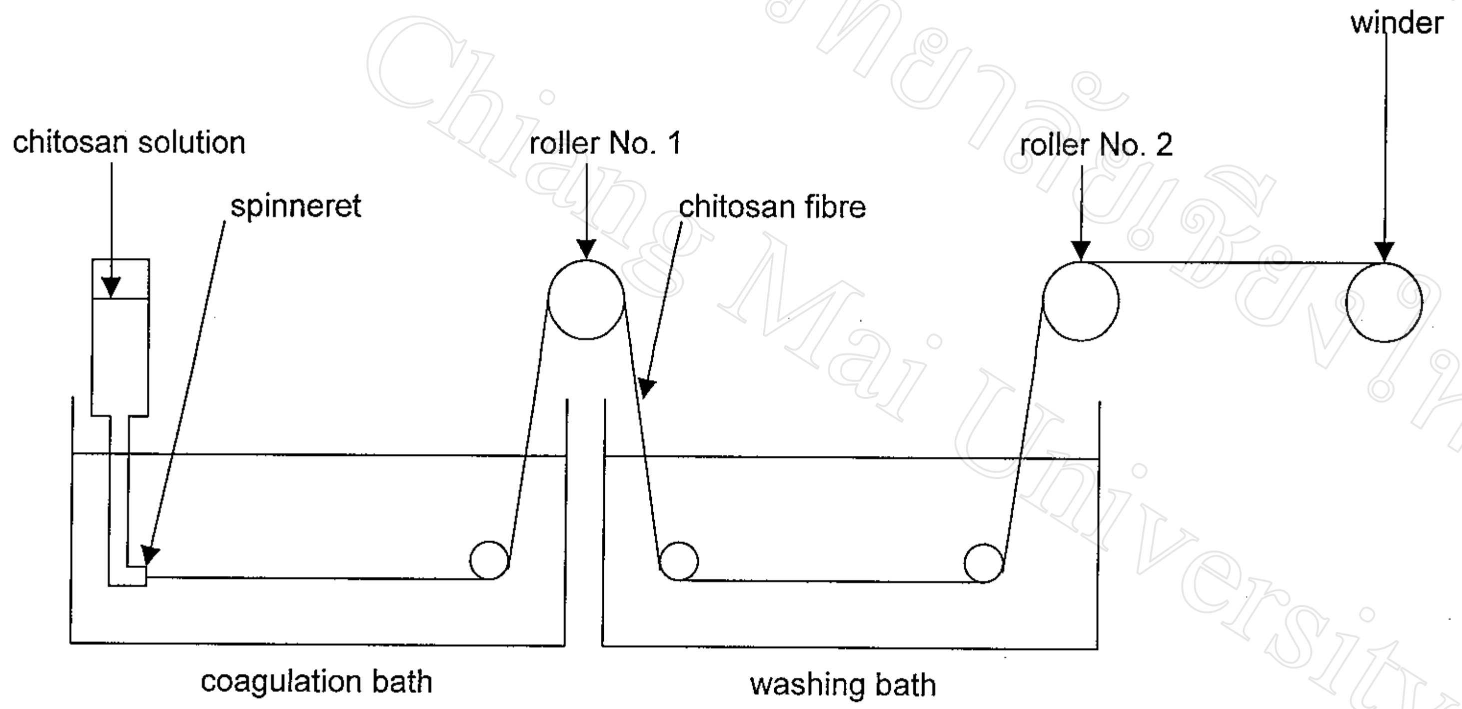


Figure 2.2: Schematic diagram of a typical wet spinning apparatus used for producing chitosan fibres [27].

strengths of up to 2 g/dtex could be obtained with extensibilities of 5-15%. Drawing of the wet fibre during production was possible but was limited to 60%. Other examples include the method of Knaul et al. [27] who reported that chitosan fibres could be wet spun from a 6% by weight chitosan solution in 3% by volume acetic acid. The coagulating bath employed a 1 M NaOH solution. Similarly East and Qin [14] also wet spun chitosan fibres by dissolving 50 g chitosan in 950 ml of 2% (v/v) aqueous acetic acid solution. The filaments were coagulated in a dilute NaOH bath.

In a method similar to the xanthate process for viscose rayon, Ming [5] dissolved chitosan in carbon disulphide and precipitated the suspension in dilute acetic acid. The precipitate was then re-dissolved in a dilute alkali solution and spun. The coagulating bath components were 14% $(NH_4)_2SO_4$ and 5% H_2SO_4. Finally, Sakurai et al. [5] spun chitosan fibres from lyotropic liquid crystalline solutions. The chitosan was first dissolved in formic acid to give a 5% solution. The solution was then stored for 10 days to let some of the formic acid evaporate to give 25 wt. % solutions which were found to develop liquid crystalline order.