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Advances in filament yarn spinning of textiles and polymers

Edited by Dong Zhang

The Textile Institute

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Advances in filament yarn spinning of textiles and polymers

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Dong Zhang

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Contributor contact details

(* = main contact)

Editor

D. Zhang
Textile Research Associates
105 Shenandoah Street
Clarksville, TN 37043
USA

E-mail: dzhang@charter.net;
dzhang@textileresearch.org
http://www.t1extileresearch.org/

Chapter 1

V. Kandagor and G. Bhat*
Department of Material Science and Engineering
University of Tennessee
Knoxville, TN 37996, USA

E-mail: gbhat@utk.edu

Chapter 2

E. Devaux
Ecole Nationale Supérieure des Arts et Industries Textiles (ENSAIT)
Laboratoire de Génie et Matériaux Textiles (GEMTEX)
2, allée Louise et Victor Champier
BP 30329
59056 Roubaix Cedex 01, France

and

Centre Européen des Textiles Innovants (CETI)
41, rue des Métissages
CS 40303
59335 Tourcoing, France

E-mail: eric.devaux@ensait.fr

Chapter 3

J. Hagewood
J Hagewood LLC
209 Connors Cir
Cary, NC 27511, USA

E-mail: john@jhagewood.com

Chapter 4

A. Rawal* and S. Mukhopadhyay
Department of Textile Technology
Indian Institute of Technology Delhi
Hauz Khas
New Delhi 110016, India

E-mail: amitrawal77@hotmail.com

Chapter 5

C. J. Kuo* and W. L. Lan
Department of Materials Science and Engineering
National Taiwan University of Science and Technology
43, Sec. 4, Keelung Rd.
Da'an Dist.
Taipei City 106, Taiwan

E-mail: jeffreykuo@mail.ntust.edu.tw

Chapter 6

S. Mukhopadhyay
Department of Textile Technology
Indian Institute of Technology Delhi
Hauz Khas
New Delhi 110016, India

E-mail: samrat@textile.iitd.ac.in

Chapter 7

Q. Q. Ni*, X. D. Jin, H. Xia and F. Liu
Faculty of Textile Science and Technology
Shinshu University
Ueda 386-8567, Japan

E-mail: niqq@shinshu-u.ac.jp

Chapter 8

W. Oxenham
College of Textiles
North Carolina State University
2401 Research Drive
Raleigh, NC 27695-8301, USA

E-mail: william_oxenham@ncsu.edu

Chapter 9

B. Ozipek* and H. Karakas
Istanbul Technical University
Faculty of Textile Technologies and Design
Inonu Cad. No: 65
Gumussuyu/Taksim
Istanbul, 34437, Turkey

E-mail: ozipek@itu.edu.tr

Chapter 10

Y. Imura and M. Jaffe
Department of Biomedical Engineering
New Jersey Institute of Technology
University Heights
Newark, NJ 07102-1982, USA

E-mail: jaffe@njit.edu

R.M.C. Hogan
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Introduction

The use of fibres is one of the most important inventions of human history. From earliest times, people have planted cotton and ramie from which to extract fibres for clothing as a substitute for animal skins, though the quality was often crude and unrefined. The Chinese extracted silk to produce high-quality apparel. The invention of rayon in 1903 triggered a revolution which led to the first synthetic fibre in 1935, so setting in train the rapid development of the synthetic fibre industry. To date, the most commonly used spinning methods include, but are not limited to, melt spinning, dry spinning and wet spinning, with nanofibre technologies emerging more recently.

The history of man-made fibres dates back to the 19th century, and has evolved over the years into a complex field of technology. During the past 50 years, the need for an understanding of the fundamental theory of fibre formation, combined with a market-driven requirement for fibrous materials, has increased interest and attracted attention from scientists, thus enhancing knowledge of these materials.

The inherent qualities of natural fibre-forming materials have limited their useful applications. Silk, cotton and wool have been in use for thousands of years, but their inherent deficiencies (for example, the tendency of cotton to wrinkle, the delicacy required in handling silk, and the shrinking characteristics of wool) limited their application, and the lifetime of such products was therefore short.

In 1903 rayon, the first manufactured fibre, was developed. Advances in the understanding of fibre chemistry for many applications had begun to emerge. By 1950, over 50 different types of man-made polymeric fibres had been produced. This historic advance in fibre technology was preceded by the modification of naturally occurring polymers, enabled by advancing understanding of the background chemistry and physics of polymers.

Since the discovery of natural silk, technology has sought to imitate nature whilst also attempting to produce artificial and synthetic materials with properties similar to those of the natural textile. The exceptional mechanical and handling characteristics of natural silk have remained the reference points in this field. The synthetic fibre invented and patented in 1884 by Bernigaud de Chardonnet, often called 'artificial silk', is considered to be the first significant result in the development of man-made fibres. Development

of such materials followed the appearance of plastics at the beginning of the twentieth century and the work done by Hermann Standinger in understanding the macromolecular structure of polymers. Polyamide 6.6 fibre (nylon) developed by DuPont de Nemours in 1938 revolutionised clothing manufacture, as well being used for military applications. The functional characteristics of this fibre closely resemble those of silk. It has exceptional strength, flexibility and lightness and was the first in a long series of synthetic fibres whose properties continued to diversify with progress in macromolecular chemistry.

There are three principal methods of producing polymeric fibres: melt spinning, wet spinning, and dry spinning. Although there are several methods of filament production, melt spinning is the preferred method, and is one of the most economical, mainly due to the simplicity of the process, which does not require solvents. Most commercial synthetic fibres are produced from crystalline polymers by the melt spinning process. For polymers without a stable melt phase, it is necessary to spin the fibre from solution. Dry spinning uses a highly volatile solvent (with a high vapour pressure), so the fibre forms during spinning by solvent evaporation. Wet spinning is used only if the potential polymer solvents are of low volatility. The fibre must be spun in a non-solvent bath to remove the spinning solvent and coagulate the fibre.

As requirements for the performance offered by fibre products increases, the development of reinforced fibre has become a key focus. In the US during the 1970s, DuPont successfully developed an aramid with strength above 17.6cN/dex, leading to the development of high-strength fibres. The main types of high-strength fibres include PPTA fibre, UHMWHP fibre, and carbon fibre.

As the demands made on fibre product performance increased, many special spinning methods were researched and developed. Methods including gel spinning, electrostatic spinning, and integrate composite spinning have been applied in industrial production. Gel spinning has been widely used for the production of fibres with high strength and high mechanical properties. Bi-component fibres are a class of poly-blend fibres, manufactured by special spinning techniques, the aim of which is to overcome the limitations of conventional single-component spinning. The blending of polymers for specialised spinning improves processing and properties for specific end uses.

Electro-spinning is a relatively simple and inexpensive method for producing fibres with diameters in the nanometer range. In recent years, many different kinds of polymer nano-fibres have been produced by this technology. While electrospinning technology is simple, it has a high potential for applications using nano materials. Nano-composite fibres are fabricated by electrospinning technology. These fibres are expected to be multi-functional and are based on the selection of particles and polymers which may have

a high potential in engineering applications such as sensing and electroactive actuators. The development of bi-functionality nanocomposite fibres is therefore a challenge for the wider application of nanofibres. However, the production rate for electro-spinning is relatively low when compared to other spinning methods.

Integrated Composite Spinning (ICS) is based on the concept of combining filament yarns with staple fibres to produce a composite yarn. It differs from other yarn formation systems in being designed to integrate a staple fibre component into semi-molten polymer. The concept has aroused considerable interest due to its high production speed when compared to other staple spinning processes. The potential applications for such a system are mainly technical, performance, and medical textiles.

Today, synthetic fibres are ubiquitous. They surround us in clothing, bedding and home furnishings. They are also found in applications such as dust covers for use under sofas and beds, air and liquid filtrations, sound absorbers in car doors, insulation materials in buildings, and as fillings in pillows and cushions. They are primary materials in diapers, cleaning wipes and many window treatments. They are used in dental brushes and floss, and for stitching and bandaging wounds. Many surgical procedures would not be possible without the use of biodegradable synthetic fibre sutures which hydrolyse and dissolve in the body. These fibres are often used as reinforcement materials in plastic parts, automobile tyres, and even in concrete. Much of modern life depends upon our understanding, production and use of synthetic fibres.

Dr Dong Zhang
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Part I

General issues

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1

Synthetic polymer fibers and their processing requirements

G. BHAT and V. KANDAGOR,
The University of Tennessee, USA

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Abstract: In order to understand the structure and properties of the desired polymer products, we should have a comprehensive knowledge of the process optimization conditions and materials characteristics. The fundamentals that determine the structure and properties of polymeric fibers include the composition, the molecular structure of the polymer, and morphological features such as crystallinity and orientation. Understanding these factors will be the key to determining correctly the manufacturing process from polymerization to fiber spinning, drawing, and post treatment of manufactured fibers. The inherent qualities of existing natural fiber-forming materials, their limitations and applications, are also discussed.

Key words: polymerization, fiber spinnability, rheology, natural fibers, synthetic fibers, high performance fibers.

1.1 Introduction

The history of man-made fibers dates back to the nineteenth century and has evolved to become one of the most widely-researched fields of technology. During the past 50 years, the need to understand the fundamental theory of fiber formation, combined with the demand for high quality fibers, has attracted the attention of many polymer scientists. For thousands of years, silk, cotton, and wool had been successfully used as textiles, but some drawbacks, for example the tendency of cotton to wrinkle, the delicate handling of silk, and the shrinking characteristics of wool, limited their application. But in 1903, rayon, the first manufactured fiber, was developed. Advances in the understanding of fiber chemistry across a wide spread of applications began to emerge. By 1950, over 50 different types of man-made polymeric fibers had been produced. This historic advance in fiber technology was preceded by the modification of naturally occurring polymers. An advancing and deepening understanding of the background chemistry and physics of

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polymers has enabled the manipulation of polymers, making possible end products driven by consumer needs.[1]

In order to understand the relationship between processing conditions and the characteristic properties of desired polymer products, a comprehensive knowledge of optimal conditions and material characteristics is necessary. This can be achieved only by understanding the fundamentals of polymers and polymer technology. The fundamentals determining the structure and properties of polymeric fibers include the composition, the molecular structure of the polymer, and morphological features such as crystallinity and orientation. An understanding of these factors is the key to determining the manufacturing process from synthesis of the monomer to polymerization, fiber spinning, and drawing through to the final product.

1.1.1 Types of fiber

Fibers are materials with a very high aspect ratio, or elongated continuous structures, similar to the lengths of thread and varying in diameter from millimeters to nanometers. Most of the commonly used fibers, whether natural or synthetic, tend to be polymeric in nature. Fiber-forming polymers can be categorized as synthetic and natural fibers, and commodity and specialty fibers. Polymers are macromolecular and in their simplest form consist of basic chemical structural units that are identical and linked together by well-defined bonds. The specific type of bond is particularly important in determining the molecular structure and architecture of the polymer. In polymer structure, the number of repeating units in a chain, or the molecular weight of the polymer, is very important in determining its characteristics and applications. The molecular weight of a fiber-forming polymer is not monodispersed, but is rather an average of the molecular weights of the chains that exist in a polymer sample. The molecular weight of the sample is an important property of the polymer, because it determines the tensile strength and influences the physical properties of the material.

Natural and synthetic fibers

Natural fibers originate in geological processes, plants, or animals, and are generally degradable, mainly as a function of time and the environmental conditions to which they are subjected. Synthetic fibers are made from materials that are chemically synthesized and may sometimes imitate natural products. Following World War II, global advances in technology enabled the fabrication of materials equal in strength, appearance, and other characteristics to natural materials. They were also lower in cost. Synthetic fibers

can be made from polymers, metals, carbon, silicon carbide, fiberglass, and minerals. This book focuses mainly on polymeric fibers.

The majority of fiber-forming polymers, like common plastics, are based on petrochemical sources. Polymeric fibers can be produced from the following materials: polyamide nylon, polyethylene terephthalate (PET) or polybutylene terephthalate (PBT) polyesters, phenol-formaldehyde (PF), polyvinyl alcohol (PVA), polyvinyl chloride (PVC), and polyolefins (polypropylene (PP) and polyethylene (PE)) among others. Because of the different chemical structures of fiber-forming polymers, their applications vary widely according to the temperature and chemical conditions which they can withstand. For example, polyethylene melts into a viscous liquid at temperatures equal to or less than that of a domestic dryer and therefore its application in a product that will require normal laundering is not possible. However, its fibers can be used in making disposable non-woven products.[2]

Commodity, specialty, and engineered fibers

Most nylons, polyesters and polypropylenes are commodity fibers and have the required properties for apparel and upholstery applications. Specialty polymer fibers are made from plastic materials and have unique characteristics, such as ultra-high strength, electrical conductivity, electro-fluorescence, high thermal stability, higher chemical resistance, and flame retardancy. PE, for instance, a polymer commonly used in the manufacture of disposable shopping bags and refuse bags, is a cheap, low friction coefficient polymer, and is considered a commodity plastic. Medium-density polyethylene (MDPE) is used for underground gas and water pipes; ultra-high molecular weight polyethylene (UHMWPE) is an engineering plastic used extensively for glide rails in industrial equipment and for the low friction sockets in implanted hip joints. It is also used to produce Spectra® or Dyneema®, the fiber having the highest specific strength.

Another industrial application of this material is the fabrication of composite materials consisting of two or more macroscopic phases. Steel-reinforced concrete is one example, and another is the plastic casing used for television sets and cell-phones. This plastic casing is usually of composite materials consisting of a thermoplastic matrix such as acrylonitrile-butadiene-styrene (ABS) to which calcium carbonate chalk, talc, glass fibers, or carbon fibers have been added to enhance strength, bulk, or electro-static dispersion. These additions may be referred to as reinforcing fibers or dispersants, depending on their purpose.

It should be noted here that the dividing line between the various types of plastics is not based on the materials, but rather on their properties and applications.

1.2 Chemistry of fiber-forming polymers

To manufacture useful products from polymers, it is necessary to shape them. This can be achieved by changing the characteristics of a polymer from hard to soft. The two kinds of polymers mainly applied in manufacturing are thermoplastics and thermosets. Thermoplastics, which can easily be melted by subjecting them to the right combination of heat and pressure without necessarily changing the chemical structure, are the most widely used polymers for fiber products. Thermoplastics consist of individual polymer chains that are connected to each other physically rather than chemically. When heated, these chains slide past each other, causing the polymer to become rubbery, eventually causing a flow that enables easier processing. Examples include polyethylene for making milk containers and grocery bags, and polyvinyl chloride for making house wall sidings.

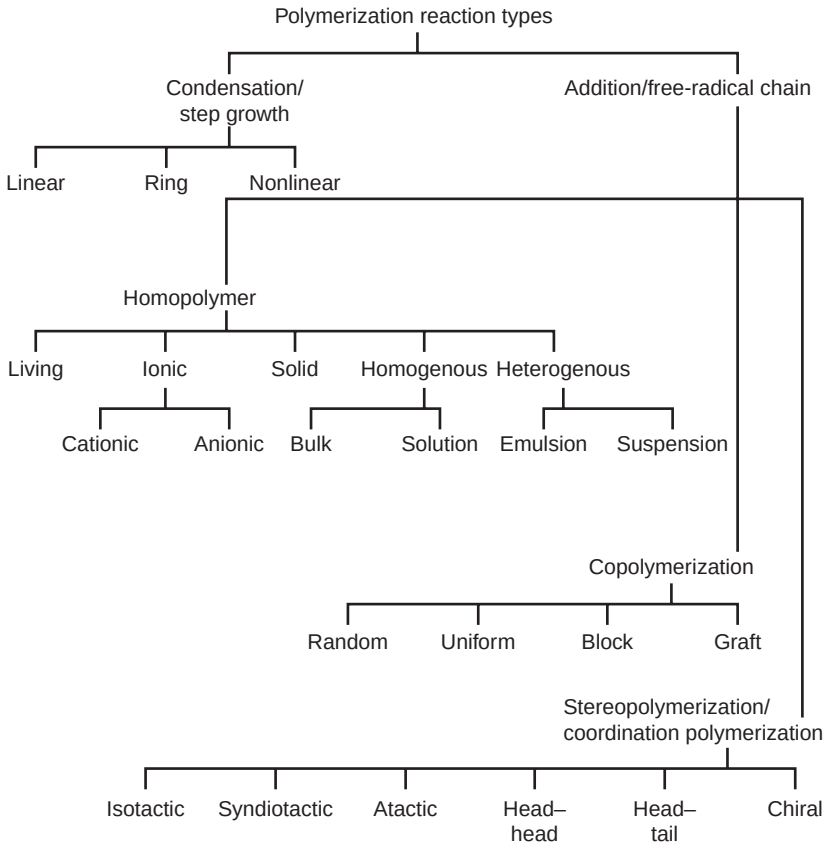
Thermosets consist of interconnected chains with a fixed position relative to each other. These polymers disintegrate into char when subjected to heat because they cannot flow. Examples of thermosets include epoxy resins, Bakelite, and vulcanized rubber, where the individual polymers are chemically interconnected. The chemical crosslinks prevent reorganization of the polymer when subjected to heat, and break only when the thermal energy exceeds the bonding energy between the crosslinks, thus causing disintegration and charring at higher temperatures.

1.2.1 Polymerization

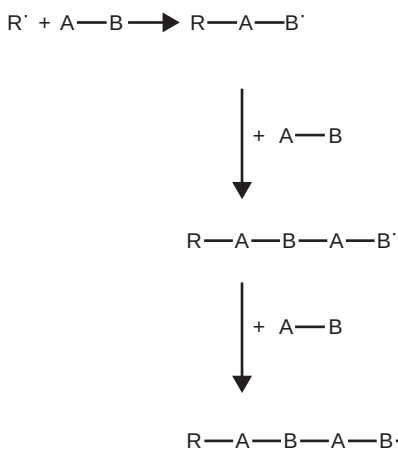
Polymerization is the process of converting a starting chemical, called the monomer, to a long chain molecule, the polymer, which is the basic structure of almost all fibers. The polymerization process will differ according to the chemical composition/structure of the starting monomer. Figure 1.1 below shows the different kinds of polymerization reactions.[3–5] It is obvious that there are many choices, and selection of the polymerization process depends on several factors. Some of these aspects are discussed in the following sections.

1.2.2 Addition polymerization

Addition polymers, also referred to as chain growth polymers, are normally formed by a chain addition reaction process. When an adjacent monomer molecule reacts with an active site of the monomer, chain addition is said to have occurred. Here, the active site is considered the reactive end of the polymer or monomer, which participates in the polymerization process. A schematic representation of a typical chain addition mechanism is shown in Fig. 1.2.



1.1 Polymerization reactions.



1.2 Schematics of a typical chain addition mechanism.

Commodity polymers, which are typically found in most consumer products, are usually formed by chain growth. These include polyethylene, polystyrene, and polypropylene. Polymerization in chain growth begins with a reaction between a monomer and a reactive species, which results in the formation of an active site. This chain growth polymerization occurs via four mechanisms: anionic, cationic, free radical, and coordination polymerization. These are the most common synthesis mechanisms for the formation of commodity polymers. The details are beyond the scope of this chapter, and can be found elsewhere.[6]

In addition to polymerization, the desired final product may be obtained through three principal steps: (1) initiation: how a polymerization reaction is started; (2) propagation: the polymerization is kept going by the ongoing addition of new monomers to the reactive end; and (3) termination: the means used to stop the reaction. The quality and characteristics of the desired polymer and the choice of the necessary monomer for the reaction process often dictate the choice of the polymerization path. In knowing and understanding the system and the components used in the polymerization process, it is possible to produce a polymer of required molecular weight and molecular weight distribution for specific products.

1.2.3 Condensation polymerization

Polycondensation is the term used to describe polymers formed as a result of reactions involving the condensation of organic materials in which small molecules are split out. In condensation polymerization, molecules of monomer and/or lower molecular weight polymers chemically combine, producing longer chains that are much higher in molecular weight. The polymers usually formed by this mechanism have two functional groups, where functionality is defined as the average number of reacting groups per reacting molecule. The kinetics of polycondensation is usually affected by the formation of a lower molecular component generated during the polycondensation reaction. The molecular component will have a concentration and mass that negatively affects the reaction mechanism. The remedy is to perform the reaction at a higher temperature and to maintain a deep vacuum, which will efficiently and effectively remove the by-products generated during the reaction, thereby favoring the production of higher molecular weight polymer. Polymers typically formed by the polycondensation reaction mechanism include polyesters, nylons, and polyurethanes.[7]

1.2.4 Polymers for specialty and high performance fibers

High performance polymers are slowly replacing traditional materials because of their strength-to-weight ratios and other economic advantages

over aluminum or other metals. Polymers used in military applications and the aviation and automobile industries are designed to resist a wider range of thermal, chemical, and physical stress. The orientation of the fibers or polymers for this kind of application is such that it will exhibit superior strength and stiffness to polymers used in conventional applications. The success in developing high performance polymer fibers lies in a deeper understanding of non-crystalline polymer matrix.[8]

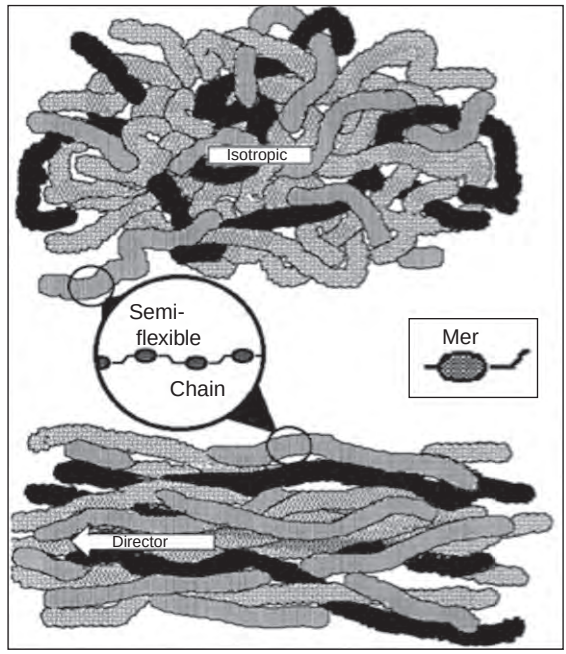
Glass fibers have been commercially manufactured since the 1930s and have found relevant application in insulation, fire-resistant fabrics, and reinforcement for fiberglass composites such as bathtub enclosures and boats. Carbon fibers are most widely used in military applications, especially for aircraft and other armored applications, because they can be engineered for strength and stiffness, with varied electrical conductivity, thermal, and chemical properties. These factors are determined by the orientation of the layered carbon planes.[9]

Organic fibers are generally characterized by high modulus and tensile strength. They are used in textiles, aerospace, mechanical, biomedical, geotextile, and electrical applications because of their performance in high thermal environments and stability over a wide range of chemical environments when compared to other conventional fibers. These specialty organic fibers generally possess one or more of the following properties: excellent fire resistance, suitable chemical resistance, higher thermal resistance, wear resistance, increased modulus and strength, and very low density. These polymers typically have an aromatic or cyclic structure, and most of them are produced by polycondensation type reactions.[10,11]

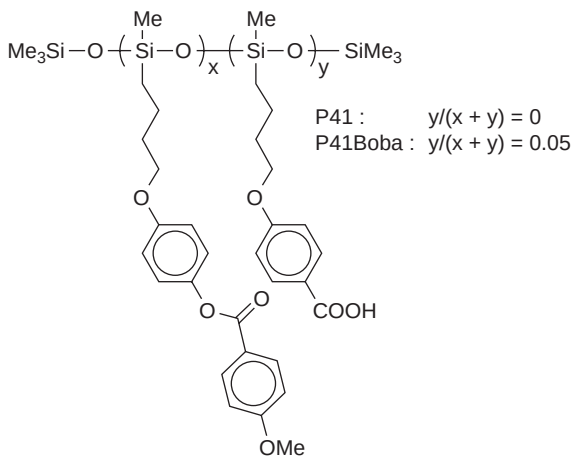
1.2.5 Liquid crystalline/rigid rod polymers

Liquid crystal polymers (LCPs), also known as mesophases, were initially traced in low molar mass compounds over a century ago. LCPs gained recognition in the technological field because of their unique electro-optical properties. Macromolecule LCPs consist of highly ordered oriented polymer chains that introduce crystal-like orientation in the liquid phases. Although the orientation can be very subtle on the local scale, time-averaged fluids are anisotropic and therefore uniquely different from the same attributes that exist in ordinary anisotropic fluids. Figures 1.3 and 1.4 below give a schematic representation of the difference between the melt of a conventional random coil polymer (top) and that of a liquid crystalline polymer.[12]

LCPs have recently become increasingly popular in specialty and high performance applications, and are categorized into two types depending on the principal means of achieving fluidity. Lyotropic LCPs originate from the action of a solvent and are therefore multicomponent polymer solvent



1.3 Schematics difference between the melt of a conventional random coil polymer (top) and that of a liquid crystalline polymer.



1.4 Structure of a liquid crystalline polymer (*Source*: Copied with permission from the author Polymers 2012, **4**(1), 448–462).

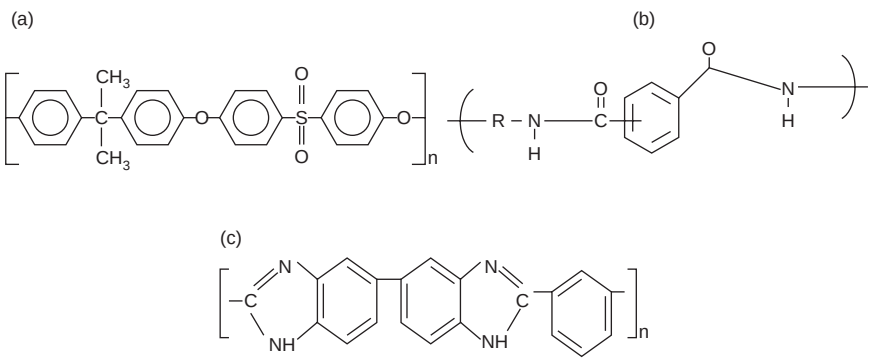
systems. Thermotropic LCPs demonstrate anisotropy in the melt and may be single or multicomponent polymer melts.

The properties of LCPs are uniquely dependent on their final physical forms and the mode of processing. Conventional polymers have been processed by the extrusion of the polymer melt into a stream of evaporating gaseous streams, also known as dry spinning, or by precipitation into liquid medium, which is referred to as wet spinning.

Compared to ultra-high strength conventional polymers, the temperature stability of LCPs is a defining characteristic that makes them effective in many applications. Like other organic polymers, they are characterized by very low densities when compared to inorganic materials such as glass and metals. This means that the tensile strength-to-mass ratios are very favorable for composite applications, and they can therefore be used in aerospace applications.[13]

1.2.6 High strength, high modulus fibers

There is an increasing demand for high temperature fibers, especially in military and aerospace applications where operation in high temperature environments for an extended period of time is critical. Experimental data have shown that incorporating aromatic segments during polymer production significantly increases the thermal stability and melt temperatures of polymers. Most of the synthetic high temperature stable and high strength aromatic fibers are categorized into aromatic polyimides, aromatic polyamides, aromatic polybenzimidazoles, and polybenzimidazolimides. Their structures are shown in Fig. 1.5 below.



1.5 Chemical structure of (a) aromatic polyimides, (b) aromatic polyamides, and (c) aromatic polybenzimidazoles.

Table 1.1 Fiber properties of the four classes of high temperature synthetic fibers under decomposition in a nitrogen environment

Polymer type	Fiber properties		TGA decomposition temperature (°C)	
	Tenacity (gpd)	Elongation (%)	Air	Nitrogen
Aromatic polyamides	5.5	15	425–450	450–470
Polyimides	7	13	450–500	500–535
Polybenzimidazoles	5	15	300	600
Polybenzimidazolimides	4.5	4	600	600

TGA: thermo-gravimetric analysis

In order to differentiate them from aliphatic polyamides, aromatic polyamides are designated by the generic name 'aramid'. They include three categories based on their composition: aliphatic–aromatic, aromatic–heterocyclic, and wholly aromatic. It has been shown that there is no significant difference in the thermal stability and fiber properties of the four classes of high temperature synthetic fibers. It is only when they decompose in a nitrogen environment that a difference in the thermal properties can be observed in the increasing order of polyamides, polyimides, polybenzimidazoles, and polybenzimidazolimides, as shown in Table 1.1.[14,15]

The term 'high performance,' when used in describing fibers, refers to certain acceptable levels of performance under extraordinary conditions involving temperature, hostile environments, high tensile or compressive exposure, electrical conductivity, or dimensional stability. Since the 1970s, advances in materials engineering technology have led to the development of new synthetic fibers with high strength, high thermal stability, high modulus, chemical and solvent resistance, and low-weight properties. This opens up opportunities in various markets for high performance applications, especially in military, aerospace and several other technological applications. Market penetration for these high performance fibers is increasing exponentially, although volumes are still relatively low. The market is characterized by high prices and complex production processes.

Biopolymers

Polymers from renewable sources offer an alternative solution for maintaining sustainable economic development that will also attract and promote emerging ecologically friendly technologies. Although not all biopolymers are biodegradable, development and innovation in polymers from biobased materials offers a solution for waste disposal problems. In addition,

biological degradability, a drastic reduction in carbon dioxide released into the atmosphere, and increased utilization of agricultural sources for the production of biopolymers will help to reduce concern over the detrimental effect of plastics on the environment. Biodegradable materials are defined as those which degrade through the action of naturally occurring microorganisms, such as bacteria and fungi, over a period of time. Bio-plastics comprise both biodegradable plastics and bio-based plastics. The source of biopolymers is mainly living organisms, and examples include cellulose, starch, chitin, proteins, peptides, and DNA. Most natural biofibers are used as reinforcement by being embedded in another polymeric matrix system that is intended to hold the fibers together, thus providing stability for the required shape in the composite structure. This can transmit the shear forces between mechanically high quality fibers and protect them when subjected to extreme force and vibration.[16,17]

The properties of natural origin polymers can also be chemically or physically modified to allow them to be processed as thermoplastic resins. Polymers from starch and cellulose, for example, may be processed using adjuvants such as water and glycerol. Polylactic acid (PLA), manufactured from completely renewable sources, may be processed into linear aliphatic polyesters and its polymer matrix is compostable. This makes PLA useful in different fiber applications and in packaging, due to its transparency and resistance to water. These properties derive from PLA being made from corn and sugars, which are a 100% renewable source. The formation of PLA is through direct condensation of lactic acid or by cyclic intermediate dimer, a process allowing the removal of water by condensation and by using solvents at high temperature in high vacuum environments.[18]

The properties and characteristics of PLA fibers are very similar to those of many other thermoplastic fibers, especially those of polyester. At room temperature, the polymer is stiff. The glass transition temperature is in the range of 55–65°C. These characteristics and other unique properties, combined with ease of processing, and the fact that PLA can be sourced from renewable products, make it an attractive and acceptable option in several commercial applications. For example, PLA has recently been used for making ski jackets, because of a lower specific gravity and higher resilience than natural fibers, thus making the fabric light with a padded feeling. The potential of PLA extends further than just developing high performance fibers for different applications. It is also a sustainable product, with reduced negative environmental effects than are caused by non-biodegradable polymers. Another polymer currently being developed and marketed by Avantium is the 2,5-Furandi carboxylic acid (FDCA)-based polyester. Although it is in an early stage of its development, this polymer is likely to become another substitute for PET in bottles, fibers, etc.[19–21]

1.3 Polymerization processes

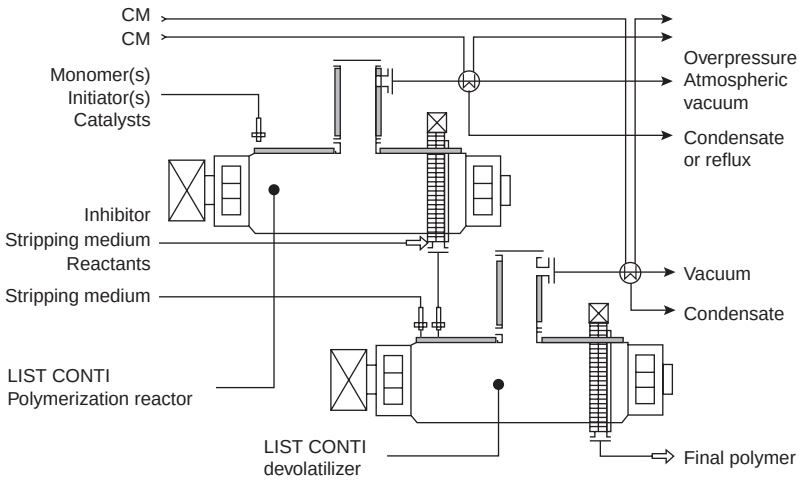
Polymerization is a chemical process in which two or more monomers are combined to form a large repetitive polymer molecule. The polymerization process or path is determined by the required characteristics and application of the end product. If the resulting polymer has more than one molecule in the chain, it is usually referred to as a copolymer. Polymers such as PVC, which consist of repeating long chains of the same monomers, are known as homopolymers. Since the polymerization process can be exothermic in nature, it can result in a hazardous polymerization, which may cause an explosion if the process begins prematurely. Natural polymerization is also known to occur when enzymes polymerase to form nucleic acids, carbohydrates, and proteins.

1.3.1 Criteria for determining the polymerization process

The industrial scale polymerization process is determined by a combination of many factors, both technical and non-technical. A clear understanding of constraints and objectives is needed to choose the right polymerization path. A manufacturer will, for example, determine production rate and the specific chemical and physical properties of the end product. This will determine the molecular weight and molecular weight distribution, copolymer composition and distribution, morphology, particle size distribution, and other factors that will then be used to choose the polymerization process for the desired characteristics. Although polymers are not necessarily sold on the basis of the manufacturing process and structural characteristics, but rather on the end user needs, there remains the challenge of relating the structural features to the properties of the polymer and the polymerization process. The toxicity of the monomers, as well as the flammability of the solvents and other reactants and catalysts necessary for the initiation of polymerization, will also determine the choice of the polymerization process. A clear understanding and choice of the polymerization path will offer the manufacturing industry considerable benefits both in direct and indirect costs. It should be noted that while most initial processes are carried out in a laboratory setting before being implemented commercially, the environment in which industrial scale polymerization is carried out is such that there will naturally be a considerable degree of difference, which will translate into the final product variability.[22]

1.3.2 Bulk polymerization

Bulk polymerization, which may also be referred to as mass polymerization, involves a monomer and an initiator as the main components, without a

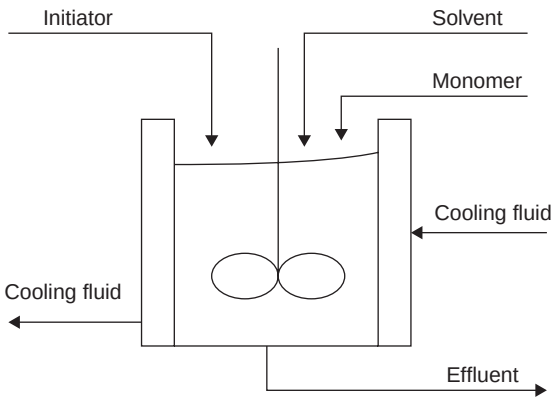


1.6 Kneader reactor concept for bulk polymerization (*Source*: Adapted from Bartke and Diener).[71]

solvent. The polymerization conforms to the fixed shape of the reaction vessel when solidification occurs. The real challenge concerns the dissipation of the heat produced by polymerization. Bulk polymerization is advantageous in the production of cast-molded products such as polystyrene scintillators. Research has shown that to improve the polymerization rate, the monomer should be distilled prior to the reaction and, where this is impracticable, the product should be rinsed with an appropriate solution. Figure 1.6 below shows the schematics of the Kneader reactor concept, which is ideally suited for bulk polymerization.[23,24]

1.3.3 Emulsion polymerization

Emulsion polymerization systems consist of water, up to 3% of surfactants and a free-radical generator soluble in water, rather than being monomer-soluble. The rate of emulsion polymerization is faster than that of the bulk of polymerization, assuming the same monomer is used under the same thermal conditions. The monomer is gradually introduced into the system from the start of the process. The average molecular weight of products obtained by emulsion polymerization is greater and the particle size is usually in the order of a 0.05–0.15 μm. The end product is in the form of emulsion in water, not a filterable suspension. In bulk polymerization by this process, recovery may be done through freezing, heating, or adding salt or acid, but the coagulants, surfactants and the initiators will normally remain as impurities in the final product.[25]



1.7 General schematics of solution polymerization (*Source*: Adapted with permission from Chemical Engineering Journal Volume **143**, Issues 1–3).

1.3.4 Solution polymerization

In this process, the polymerization reaction occurs in a solvent medium that is carefully chosen according to the chemical compatibility of the reacting monomers. Several disadvantages associated with bulk polymerization are resolved by this method. Solution polymerization makes homogeneous polymerization possible, particularly where both the polymer and the monomer are soluble in the solvent. It is also an excellent way of dissipating the reaction heat, reducing shrinkage, and minimizing side reactions in systems that are highly viscous. In ionic polymerization, the solvent medium can positively influence the stereoregularity of the final product. The solvent to be used in solution polymerization should therefore be carefully identified so that its boiling point corresponds to that of the monomer and to the temperatures at which the initiator will decompose. In the industrial production of protective coatings, it is often desirable for the solvent to remain in the paint, and therefore solution polymerization is the process of choice as a strong-polymer interaction is advantageous. Figure 1.7 shows the general schematics of solution polymerization.

1.3.5 Aqueous suspension and irradiation polymerization

In this polymerization path, the monomer droplets are suspended in an aqueous medium and are constantly stirred. Because the monomer droplets are in a water medium, the heat is easily dissipated, making this process comparable to bulk polymerization *in situ*.

Irradiation polymerization is a complex process in which a photo initiator (PI) (usually UV light or electron beam) is used to start the polymerization process. The PI absorbs the incident light in order to generate the ions or reactive radicals which result in polymerization.

1.4 Influence of chemical structure on the physical properties of chemicals and fibers

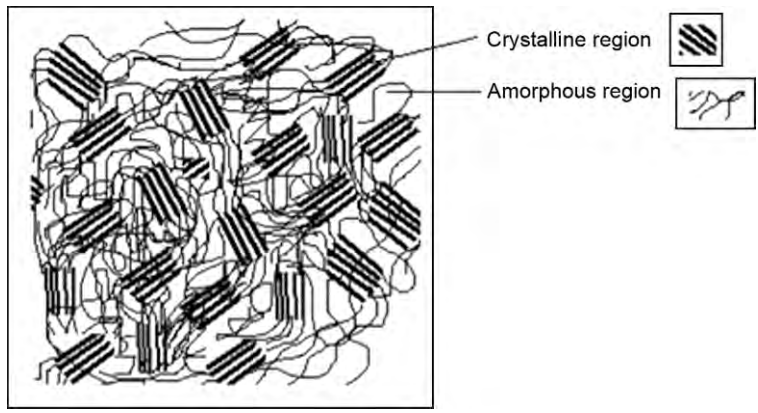
The general properties of either man-made or naturally occurring polymeric materials are substantially different from those synthesized from metallic or ceramic materials. Polymers have a large molecular weight, which clearly distinguishes them from other materials in which repeated molecules are connected in a different manner from those of the polymer molecule.[26]

Individual polymer characteristics are usually dependent on and defined by the molecular chain architecture, which is dependent on the rotational freedom of atoms around a single bond. This unique aspect of a polymer can be manipulated to obtain the characteristics required for a specific application. Bulky atoms, for example, will greatly reduce the mobility between chain elements because the degree of flexibility of the polymer is reduced — a parameter associated with the transition temperature.[27–29]

It is a fundamental property of polymeric materials that the chemical bonds must be broken and restructured to change the configuration of a particular polymer. In fiber-forming polymers, this is the means by which the desired fiber or fabric qualities, e.g., tensile strength, and stiffness, are tuned. Fibers from polymers are made by spinning or drawing, and certain molecular weight conditions have to be met to achieve predetermined fiber properties. The higher the interchange cohesive forces, for example, the lower the molecular weight at which satisfactory fiber properties are achieved, as these are determined by the molecular weight distribution of a system.[30–34]

Intermediates present during the polymerization process affect the formation of linear polymers. The chemical structure of the intermediates may cause reactions which, over time, will lead to the loss of the intended reactive groups that are important in diminishing chain growth during the polymerization process. These side reactions will also cause chain branching, which may result in cross-linking and the formation of gelled polymers that cannot be spun.

Polymers can exist in the crystalline and amorphous regions, and the crystallinity of polymeric fibers is one of the most important aspects of polymer science. Crystallinity is a measure of the percentage of crystalline regions in the polymer with respect to amorphous region. Figure 1.8 is a schematic representation of polymer chains in the crystalline and amorphous regions.



1.8 Crystalline and amorphous region of a polymer.

Most commodity fibers have crystallinity values between 20% and 60%, and crystallinity and molecular orientation together determine the physical properties of the fibers. High strength and high modulus fibers tend to have high crystallinity values, in the range of 90%.

The melting point is the temperature at which a crystallite structure is no longer stable and may be regarded as a measure of the tendency of a polymer to crystallize. The arrangement of the molecules in the structure will play a great role in determining the melting point of a semi-crystalline substance, and therefore once the crystalline structure of large polymeric materials is reached, it is possible to understand the effect of the chemical structure on the melting point. If the polymer does not have any crystallinity, then the fiber does not show a melting transition but only a glass transition temperature (T_g) which corresponds to the change from a brittle glassy to a soft rubbery state.[35,36]

The development of fiber structure is the result of several technical operations including spinning, drawing and heat setting. Each process plays an important role in determining the behavior of the polymer during the next step, thus affecting the final structure and quality of the fiber. Molecular orientation, which is the extension of macromolecules and other structural units along the fiber axis, determines the tensile strength, sorption of solvents, modulus, optical behaviors, etc.[37–39]

1.5 Effects of molecular weight on fiber spinnability, structure and properties

The molecular weight of a polymer has a significant effect on its spinnability. The word does not have a precise meaning in relation to fiber technology,

although it often means 'fiber forming,' and the definition includes the physical and chemical aspects of fiber formation from fluid threads without breakage. This means that the range of flow characteristics of the polymer in liquid form is such that no breakage occurs during the spinning process. The spinning process is important because the spinning parameters determine the elongational flow and therefore have a direct effect on the final characteristics of the fibers.[40–43]

Melt spinning has been used for many years in the polymer industry because it provides an effective means of combining two or more materials to produce fibers. Multicomponent fibers are made in this way, and each component material plays an important role in determining the end characteristics of the final product. The molecular weight of each individual material is therefore significant because the chemical and physical interaction between them is partially guided by the available quantities, which are directly linked to the molecular weight. A more complex phenomenon occurs when the different materials form phases during the process of fiber formation. Manipulating the pre-spinning conditions of a polymer or polymer composite can alter the fiber morphology as well as its mechanical and chemical structure. Other factors influencing fiber properties include time, temperature dependent molecular motion, crystallization, length and length-distribution of the molecules, and various intermolecular interactions.[44–47]

In dry spinning, the solution containing the polymer is forced through a fine jet, followed by evaporation of the solvent, which results in the formation of fiber. Dry spinning can therefore be considered a process of structure formation in a bi-component system involving polymer and solvent. This makes analysis of the dry spinning process more complex than that of melt spinning. It is treated as a single component system involving only the polymer because the evaporation rate of the solvent at the boundary between the two phases may not be easily defined. In wet spinning, a solution of polymer is forced through a nozzle into a non-solvent for the polymer. Here, the mass transfer for both the solvent and the polymer is considered. This makes the process analysis even more complex than that of dry spinning.[48–51]

1.6 Flow properties of polymers

The flow characteristics of a polymer largely determine the type of machinery used for extrusion and influence the choice of the process and processing conditions. The rheological and thermal properties of a polymer determine the flow characteristics and are discussed here. The rheological properties define the manner in which a material will deform when certain stresses are applied, a characteristic that is important in the plasticizing zone and the die-forming regions of the process. In a bulk process, the flow properties of the material are directly linked to the transport behaviors, which are

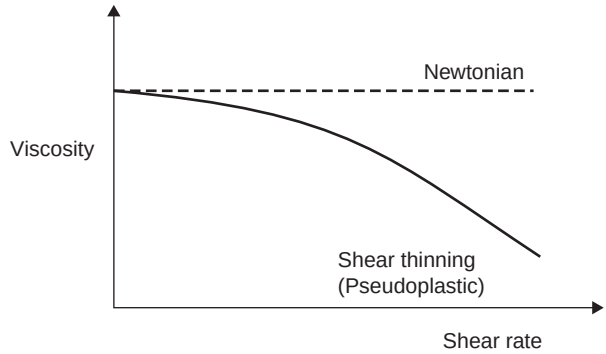
determined by the coefficient of friction, the size and shape of the particles, and the density. In polymeric melts, the shape of the molecules will in effect dictate the dynamic behaviors and rheological characteristics. It is therefore of the greatest importance to understand these flow parameters, particularly for the purpose of synthesizing new fiber-forming polymers for industrial and commercial applications.[52–54]

Rheology is generally defined as the study of flow. Polymer rheology is the scientific study of how polymeric fluids deform when subjected to external stresses. When synthesizing a polymer for a particular application, an understanding of the extruder environment in which that polymer will be used is the key to determining the properties of the polymer, so that its response matches the predetermined environment. The chemical and molecular structure of polymer melts will generally have specific effects on the dynamic behaviors and properties of the polymer rheology. It is therefore possible to engineer an end product that fits the predetermined application by manipulating the molecular composition of the polymer. Understanding the molecular structure of polymers can also provide an insight into the visco-elastic properties of polymer melt. This is essentially an understanding of how polymer energy is dissipated in the form of heat during deformation, and how the elastic nature of the polymer will store this energy and use it to restore the polymer to its pre-deformed condition. Such materials are said to have 'memory.'[29,55]

The elastic nature of polymeric materials may be attributed largely to the long chain molecules, which cause entanglements to occur at the molecular level, forming a network through Brownian motion that has a greater effect at elevated temperatures. During deformation, a polymer will alter its molecular configuration and, at the end of the deformation, will return to equilibrium due to Brownian motion.[56,57]

Because of their significance both in theory and practice, the rheological properties of solutions and melts of fiber-forming polymers have been extensively studied over the years. Several research groups and industries have pointed out that varying the viscosity of a fiber-forming polymer through the manipulation of the chemical and production parameters (such as the degree of polymerization compared with the resulting fiber structure) has proved that fiber structure and characteristics are greatly influenced by rheological properties. However, it remains difficult to formulate constitutive characteristic equations that can be precisely used to describe the connection between viscosities, shear stress and shear rate.[54,58]

In melt blowing, for example, surface tension-driven instabilities have been observed both in laboratories and in industrial processes when finer fibers are generated. These create droplets that are dispersed in the fiber mat. Systematic research has proved that altering the rheological properties of the polymer suppresses, and in some cases eliminates, their stability.[59]



1.9 Shear thinning characteristics of polymer.[60]

Shear thinning behavior, in which viscosity varies inversely with respect to shear rate, is one of the most remarkable properties of polymeric materials. When the shear rate, i.e., the rate of extrusion through a die is increased, the viscosity will decrease because molecular disentanglement and alignments of the polymer chains will occur. Figure 1.9 shows the shear thinning behavior of polymers. The higher the shear rate, the greater the force required to push the polymer melt through a die.[60] The qualities of fibers formed from different types of polymers are determined by the rheological features of the polymer during processing, and the computation of such processes will take into consideration the shear rate to optimize the process. Rheology measurements can be used for characterization and determination of material processability and can also be used as input data for computer simulations. This is because the rheology of a material is more sensitive to the structural aspects of the materials, such as branching and molecular weight tail, and is also a fast method compared to many other options of polymer liquid characterization.

1.7 Principles of solidification during fiber formation

The formation of fibers from both natural and synthetic polymers is achieved through the transformation of a polymer fluid, either molten or dissolved in a solvent, into solid filaments. The chemical process for the formation of different kind of fibers for varied applications differs, but the principle of solidification from liquid to solid remains the same. The rate of solidification of a polymer melt or solution is an important factor which determines the rate of production and the properties of the resulting fibers. It is a phenomenon that has been validated by different research groups in laboratories and industry.[61]

For solidification to occur in a polymer melt, there must be a heat transfer process. This can be done in a controlled environment where a specific shaping and stabilization of the fiber is expected. The rate of solidification is determined by the rate of heat transfer, but the thermal conductivity characteristics of the polymer may generate a larger thermal gradient within the product, causing varied polymer structure within the fiber and significant change in their physical and chemical structure. The choice of the shaping process and equipment used can also affect the solidification process. The rheological properties of the polymer, in influencing the choice of shaping process, will therefore indirectly affect the solidification process. In polymer reactions which occur in solvents, the solidification of the polymer into a desired fiber structure will be determined by the rate of evaporation of the solvents.

1.8 Fiber formation techniques

Rapid advances in the synthetic fiber industry during the 1940s led to an increase in melt spinning technology in order to improve productivity and control the quality of the end products. In melt spinning, fiber diameter may be precisely predicted based on the temperature and tension of the running filaments if the spinning conditions and rheological properties of the polymer are defined and maintained during the spinning process. Such predictions, however, will assume that no crystallization occurs during the spinning process. In cases where crystallization does occur, several parameters must be considered if an accurate mathematical simulation is to be done: the molecular orientation that results from the elongational melt flow, the influence of molecular orientation on the crystallization kinetics, significant change in the rheological properties, and the kinetics of the non-isothermal crystallization. There are several spinning techniques, each tailored to work with different kinds of polymer and/or the desired fiber end products.

1.8.1 Melt spinning

The melt spinning process has been in use since the late 1950s. The polymer melt is extruded and drawn at speeds of 1000–6000 m/min. Lower spinning speeds result in an undrawn yarn, which is then further drawn and heat-treated. At higher spinning speeds, the fiber is partially or fully drawn, and can be texturized, drawn further, or used as spun yarn. PET and nylons are examples of such polymeric fibers processed using melt spinning. The resulting fiber structure is a function of the spinning speed, the drawing mechanism, heat setting conditions etc. The stress–strain behavior of the material is also a function of the spinning speed, because the polymer chains orient and

crystallize and the fiber structure develops as the spinning speed increases. Reproducible experimental results by several research groups have shown that the molecular orientation improves much more than crystallinity with the spinning speed. However, the crystallite size will increase with spinning speed.[62]

In high speed spinning, the spinning tension is a function of inertial force and air resistance. However, it is generally agreed that the structural formation is defined mainly by inertial force and that air resistance may be ignored in speeds over 8000 m/min. But researchers have also reported that air resistance could influence the formation of the structure of fine filaments at spinning speeds between 4000 and 5000 m/min. The mechanical properties of the resultant fibers can be improved by heat-treatment of fibers in the spinline. Fibers have also demonstrated improved properties when cooled in the spinline instead of undergoing heat-treatment. Quenching immediately after necking results in highly oriented amorphous yarns. Cooling can also give precise control of the temperature of the cooling agent. In general, ultra-high-speed spinning has the potential to produce fibers with improved performance properties, and further development is needed to achieve high efficiency and high quality fibers.

1.8.2 Solution spinning

Significant developments have recently been made in the fiber solution spinning process due to increased understanding of theoretical spinning technology, especially in acrylic fibers. Solution spinning technology is primarily based on spinning a solution or suspension that precipitates or coagulates to form a solid fiber as an end product. Solution spinning is categorized into two methods: dry spinning and wet spinning. In dry spinning, the polymeric solution solidifies when evaporation of the solvent occurs. Wet spinning can be further divided into three classifications, based on physiochemical principles. In the liquid crystal process, lyotropic polymer liquid crystalline solution is solidified through the formation of a solid crystalline region in a solution. The gelation mechanism solidifies the polymer solution through formation of intermolecular bonds in the solutions. In the phase separation process, polymer rich and polymer lean phases are part of the solution.[63]

1.8.3 Highly aesthetic fiber spinning

Fibers with unique sensual characteristics, such as color, appearance, feel, bulkiness and texture, are commonly referred to as aesthetic fibers. Aesthetic fibers are highly fashionable and expensive, and their production process and advanced technology are also costly. Materials that may require

specialized finishing are processed in this manner. For example, the addition of inorganic materials in the mixed-spinning process increases the specific gravity of a fiber and improves the drapability of the fabrics. This can be varied by weight percentage of the additive, depending on the desired quality. Addition of these organic polymers or a composite may be done between the polymerization and spinning processes.[64]

1.8.4 Anisotropic fiber spinning

High strength fibers made from anisotropic polymers are more difficult to synthesize because of the technical process required to form an anisotropic solution from the solid polymer. Aromatic polymers such as polyimides and heterocyclics, for example, are characterized by extended chain conformation and are known to form anisotropic solutions or melts that have liquid crystal behavior at the correct solution temperature and composition. During the fiber formation process, the liquid crystal domain in the polymer melt will undergo orientation as a result of the influence from the shear and elongation flow. When cooled, these anisotropic polymers also exhibit phase transition, forming highly crystalline solids. Fiber spinning of anisotropic polymers will therefore result in highly crystalline and oriented fibers with high strength and modulus. Anisotropic polymers are classified into two types: lyotropic, in which solutions respond to different solvent types and concentrations in a varying manner, and thermotropic polymers, in which melts respond to temperature changes by behaving like liquid crystals. In a molten or solution state, anisotropic polymers display mesomorphic behavior similar to low molecular weight liquids, but differ in having have higher molecular weights.[65]

1.8.5 Thermotropic liquid-liquid crystal polymer spinning

Fibers with very high strength and modulus can be fabricated from polymers that have a molecular structure in which the chains are packed in small cross-sectional areas with strong bonds and low elongation. However, some of these aromatic polymers have melting points that are higher than their decomposition temperatures due to the rigidity of their molecules. It is therefore impossible to process them in thermotropic liquid crystal form.

It has been shown that this can be overcome by a slow introduction of flexible alkyl groups into the main chain, by introducing substituents into the individual aromatic ring in the main chain, by co-polymerization of more than one rigid molecule, or by the introduction of non-molecular structures.

Combinations of these techniques have been shown to provide a means of creating thermotropic LCPs that can be injection-molded or melt-spun. The chemical structures of thermotropic LCP fibers are varied and based on the original polymer material characteristics and conditions. The choice of synthesis process is therefore the key to achieving the desired end product characteristics and qualities. The current challenge, however, in the spinning of thermotropic LCPs is to improve cost effectiveness through performance process optimization.

1.8.6 Gel spinning

Hiroshi *et al*. have defined the gel spinning process as a method of achieving high strength fibers through an intermediate gel-like state. In gel spinning, the most important feature of the polymer is the degree of polymerization. Polymers with an average molecular weight above 600 000 g/mol are effectively processed by this technique. Although gel spinning is a relatively long-standing process, in its current adaptation, polymer of an extremely high molecular weight is dissolved in a solvent at low concentrations of about 1–2 percentage of polymer by weight, making a highly viscous solution. The solution is then dry- or wet-spun to a fiber that retains most of the solvent and is actually a gel of polymer and solvent.[66,67] The gel spun fiber is further drawn with the removal of the solvent to produce a very highly oriented and ordered structure with high strength and modulus.

1.8.7 Spinning of ultra-fine fibers and optical fibers

Any fiber that is less than 0.7 denier is referred to as ultra-fine fiber. These fibers can be processed by significantly reducing the polymer output at the spinneret while drawing it with a large draw ratio. Currently, ultra-thin continuous filaments may be produced by various methods including direct spinning, conjugate spinning and multi-layer type spinning. Ultra-fine fibers can be produced by methods that include melt blowing, electrospinning, flash spinning, polymer-blend spinning, and centrifugal spinning. Softness, flexibility, smoothness, fine textile structures, micro-pockets in fibers, quick stress relief, low resistance to bending and many other properties characterize ultra-fine fibers. These qualities are definitive in determining combinatorial processing techniques.[68–70]

An optical fiber is composed of a core made from a light transmitting material which is transparent and has a very low refractive index. Depending on the application of such fibers, the choice of the spinning method is based on the polymer material used.[71]

1.9 Post-fiber formation treatments

The reasons for post-fiber formation treatments are many and varied. Fiber treatment may involve drawing, twisting, texturing, coating, further thermal treatment, chemical, or combinatorial processes. Growing environmental concerns may require fibers to be treated to minimize toxic emissions. Fibers for some applications may require reinforcement, which can be achieved by chemical or thermal treatments. The need to prolong the lifetime of fibers for certain applications will also call for post formation treatments. Fibers designed for biological implants applications, for example, should be treated to minimize side effect reactions with the body, and its lifetime should be such that it can remain functional during the life of the person or animal. Other processes can be determined and influenced by aesthetic modification for desired qualities.

1.10 Current trends

The consumer market-driven demand for improved products has led to a growth in production techniques for a variety of materials. There is an increase in the applications of polymeric fibers, the limited capabilities of naturally occurring fibers having caused a growth in research into man-made fibers which can be engineered for specific applications. The reliability of polymeric fibers is influencing applications in several areas, including the biomedical, aviation, and automobile industries. The need for materials with nanocomposite structures and high performance standards has driven research in both laboratory and industry. Another area that has attracted attention in the past decade and remains of interest is that of submicron and nanofibers. Several polymers and processing techniques continue to be investigated.

1.11 Conclusion

The demand for man-made polymers and polymeric fibers is growing due to the flexibility of processing, which allows a material with specific mechanical, electrical, optical, and chemical features to be tailored to fit a specific application. This has led to an increase in research to find more source polymers. However, the growth in man-made polymers has raised environmental and health issues. Research and developmental activity has increased in the development of biopolymers to meet the current and future demand for sustainability. There is also a need to develop processing equipment for the production of fibers in the nanometer range. The future of polymer production appears to be interesting and commercially sustainable.

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