Chapter 1

Introduction

1.1. Preface of Nanofibers

It is essential in the beginning of this book to firstly define what a nanofiber is. To do so, we split the term into two parts, namely "nano" and "fiber". As the latter term is more common, we begin by considering the latter from various professional viewpoints. Botanists identify this term with elongated, thick-walled cells that give strength and support to plant tissue. Anatomists understand "fibers" as any of the filaments constituting the extracelullar matrix of connective tissue, or any of various elongated cells or threadlike structures, especially muscle fiber or nerve fiber. The textile industry views fibers as natural or synthetic filament, such as cotton or nylon, capable of being spun into yarn, or simply as material made of such filaments. Physiologists and biochemists use the term "fiber" to refer to coarse, indigestible plant matter, consisting primarily of polysaccharides such as cellulose, that when eaten stimulates intestinal peristalsis. Historically, the term "fiber", or "fibre" in British English, comes from Latin "fibra". In this book we define a "fiber" from a geometrical standpoint – a slender, elongated, threadlike object or structure.

The term "nano" is historically interesting. Like many prefixes used in conjunction with Système International d'unités (SI units), "nano" comes from a language other than English (see Table 1.1). Originating from the Greek word "nannas" for "uncle", the Greek word "nanos" or "nannos" refer to "little old man" or "dwarf". Before the term nanotechnology was coined and became popular, the prefixes "nanno-" or "nano-" were used in equal frequency, although not always technically correct. For example the term nannoplanktons or nanoplanktons have been used, and has since been socially accepted, for describing very small planktons measuring 2 to 20 micrometers – a technical error which should be more correctly termed as microplanktons.

Table 1.1. Modern definition of "nano" and other prefixes.

Prefixes	Meaning	Original language
Yokto	10^{-24}	Latin
Femto	10^{-15}	Danish Norwegian
Pico	10^{-12}	Spanish
Nano	10^{-9}	Greek (dwarf)
Micro	10^{-6}	Greek (small)
Hecto	10^{+2}	French Greek (hundred)
Giga	10^{+9}	Greek (giant)
Yotta	10^{+24}	Latin

With the modern definition, we use "nano" to technically refer to physical quantities within the scale of a billionth of the reference unit – hence nanometer, nanosecond, nanogram and nanofarad for describing a billionth of a meter (length), second (time), gram (weight) and farad (charge) respectively. At the point of writing, nanotechnology refers to the science and engineering concerning materials, structures and devices which at least one of the dimension is 100nm or less. This term also refers to a fabrication technology in which objects are designed and built by the specification and placement of individual atoms or molecules or where at least one dimension is on a scale of nanometers.

At this juncture, we wish to point out that whilst the academic community has somewhat agreed to the <100nm criterion as the benchmark for the nanotechnology classification, the commercial sector has allowed broader flexibility – such as 300nm or even up to 500nm – which some academics would classify as sub-microtechnology. The authors are of the opinion that both benchmarks have their own merits. Whilst the imposition of a strict guideline is essential for maintaining some form of standard, the loose definition would be beneficial for the industry – for which the product quality and dimension is ultimately determined by the consumers and not mere measurements. Having pointed out the merit of the loose definition, the importance of the strict definition becomes evident in the light of the loose definition – a strict standard inhibits the loose definition from getting out of hand.

Ever since the the term "nanotechnology" was coined by K. Eric Drexler in his book "Engines of Creation", the field of nanotechnology has been a hot topic both in the academia and the industry. Although the positional manipulation of xenon atoms on a nickel substrate in 1990 (to spell the logo of a very large computer company) was hailed by some as the "first unequivocal" nanofabrication experiment, it should be borne in mind that the growth of nanowires and nanorods by vapor-liquid-solid method was reported in the beginning of 1960s and the spontaneous growth of nanowires and nanorods was in the 1950s. The scientific know-how of gold nanoparticle synthesis was, in fact, performed by Faraday. Perhaps the first nanotechnologists can be attributed to medieval stained-glass makers who, by prescribing varying amount of gold particles, produced gold with colors other than gold color. Unbeknown to the medieval stained-glass makers, these tiny gold spheres, which absorbed and reflected sunlight in differing frequency, will forever be part of the history of size effects in nano-scale object.

1.2. Nanotechnology and Nanofibers

In this sub-chapter an attempt is made to classify nanofibers into one or more sub-category of nanotechnology.

To do so we briefly review some common sub-fields of nanotechnology itself. As far as "nanostructures" are concerned, one can view this as objects or structures whereby at least one of its dimensions is within nano-scale. A "nanoparticle" can be considered as a zero-dimensional nano-element, which is the simplest form of nanostructure. It follows that a "nanotube" or a nanorod" is a one-dimensional nano-element from which slightly more complex nanostructure can be constructed of. Following this train of thought, a "nanoplatelet" or a "nanodisk" is a two-dimensional element which, along with its one-dimensional counterpart, are useful in the construction of nanodevices.

The difference between a nanostructure and a nanodevice can be viewed upon as the analogy between a building and a machine (whether mechanical, electrical or both). It goes without saying that as far as nano-scale is concerned, one should not pigeon-hole these nano-elements – for an element that is considered a structure can at times be used as a significant part of a device. For example, the use of carbon nanotube as the tip of an Atomic Force Microscope (AFM) would have it classified as a nanostructure. The same nanotube, however, can be used as a single-molecule circuit, or as part of a miniaturized electronic component, thereby appearing as a nanodevice. Hence the function, along with the structure, is essential in classifiying which nanotechnology sub-area it belongs to.

Whilst nanostructures clearly define the solids' overall dimensions, the same cannot be said so for nanomaterials. In some instances a nanomaterial refers to a nano-sized material while in other instances a nanomaterial is a bulk material with nano-scaled structure. Nanocrystals appear to be a misnomer. It is understood that a crystal is highly structured and that the repetitive unit is indeed small enough. Hence a nanocrystal refers to the size of the entire crystal itself being nano-sized, but not of the repetitive unit.

Nanophotonics refers to the study, research, development and/or applications of nano-scale object that emit light and its corresponding light. These objects are normaly quantum gots. Whilst the emission of photon is largest for bulk (3-dimensional), followed by quantum well (2-dimensional) and finally quantum dot (0-dimensional), the ranking is reversed in terms of efficiency.

Although the term nanomagnetics is self expanatory, we wish to view it in terms of highly miniaturized magnetic data storage materials with very high memory. This can be attained by taking advantage of the electron spin for memory storage – hence the term "spin-electronics", which has since been more popularly and more conveniently known as "spintronics".

In nanobioengineering, the novel properties at nano-scale are taken advantage of for bioengineering applications. The many naturally occurring nanofibrous and nanoporous structure in the human body further adds to the impetus for research and development in this sub-area. Closely related to this is molecular functionalization whereby the surface of an object is modified by attaching certain molecules to enable desired functions to be carried out – such as for sensing and/or filtering chemicals based on molecular affinity.

With the rapid growth of nanotechnology, nanomechanics is no longer the narrow field it used to be. This field can be broadly categorized into the molecular mechanics and the continuum mechanics approaches – which view objects as consisting of discrete many-body system and continuous media respectively. Whilst the former inherently includes the size-effect, it is a requirement for the latter to factor in the influence of increasing surface-to-volume ratio, molecular reorientation and other novelties as the size shrinks.

As with many other fields, nanotechnology includes nanoprocessing – novel materials processing techniques by which nano-scale structures and devices are designed and constructed.

Depending upon the final size and shape, a nanostructure or nanodevice can be produced by the top-down or the bottom up approach. The former refers to the act of removal or cutting down a bulk to the desired size whilst the latter takes on the philosophy of using fundamental building blocks – such as atoms and molecules – to build up nanostructures in the same manner as one would towards lego sets. It is obvious that the top-down and the botton-up nanoprocessing methodologies are suitable for the larger and to smaller ends respectively in the spectrum of nano-scale construction. The effort of nanopatterning – or patterning at the nano-scale – would hence fall into nanoprocessing.

So where does all these descriptions point nanofibers to? It is obvious that nanofibers would geometrically fall into the category of 1-dimensional nano-scale elements that includes nanotubes and nanorods. However, the flexible nature of nanofibers would align it along with other highly flexible nano-elements such as globular molecules (assumed as 0-dimensional soft matter), as well as solid and liquid films of nano-thickness (2-dimensional). A nanofiber is a nanomaterial in view of its diameter, and can be considered a nanostructured material material if filled with nanoparticles to form composite nanofibers.

Where application to bioengineering is concerned, such as the use of nanofibrous network to tissue engineering scaffolds, these nanofibers play significant roles in nanobioengineering [Lim and Ramakrishna (2005)]. The study on the nanofiber mechanical properties as a result of manufacturing techniques, constituent materials, processing parameters and other factors would fall into the category of nanomechanics. Indeed, while the primary classification of nanofibers is that of nanostructure or nanomaterial, other aspects of nanofibers such as its characteristics, modeling, application and processing would enable nanofibers to penetrate into many subfields of nanotechnology. Finally the processing techniques of nanofibers are diverse, and include both the top-down and the bottom-up approaches as we shall see in the next sub-chapter.

1.3. Various Ways to Make Nanofibers

Polymeric nanofibers can be processed by a number of techniques such as Drawing, Template Synthesis, Phase Separation, Self-Assembly and Electrospinning, which are briefly reviewed in this section. A comparison of the various issues relating to these processing methods and some of the polymers that can be converted into nanofibers can be found in Tables 1.2 and 1.3, respectively.

Table 1.2(a). Comparison of processing techniques for obtaining nanofibers.

Process	Technological advances	Can the process be scaled?	Repeatability	Convenient to process?	Control on fiber dimensions
Drawing	Laboratory	X	√	√	X
Template Synthesis	Laboratory	X	√	√	√
Phase Separation	Laboratory	X	√	√	X
Self-Assembly	Laboratory	X	√	X	X
Electro-spinning	Laboratory (with potential for industrial processing	√	√	√	√

Table 1.2(b). Advantages and disadvantages of various processing techniques.

Process	Advantages	Disadvantages
Drawing	Minimum equipment requirement.	Discontinuous process
Template Synthesis	Fibers of different diameters can be easily achieved by using different templates.	
Phase Separation	Minimum equipment requirement. Process can directly fabricate a nanofiber matrix. Batch-to-batch consistency is achieved easily. Mechanical properties of the matrix can be tailored by adjusting polymer concentration.	Limited to specific polymers
Self-Assembly	Good for obtaining smaller nanofibers.	Complex process
Electrospinning	Cost effective. Long, continuous nanofibers can be produced	Jet instability

Table 1.3(a).   Effect of processing method, material and solvent on the nanofiber dimension.

Process	Material	Solvent	Fiber diameter	Fiber length
Drawing	Sodium Citrate	Chloroauric acid	2 nm to 100 nm	10 microns to mms
Template Synthesis	Polyacrylonitrile	Dimethylformamide	100 nm	10 microns
Phase Separation	PLLA PLLA-PCL blends	Tetrahydrofuran	50 nm to 500 nm	Porous structure or continuous network
Self-Assembly	PCEMA core - PS shell	Tetrahydrofuran	100 nm	20 microns
	PAA/γ- Fe_2O_3 core – PCEMA middle layer – PS corona	Tetrahydrofuran	100 nm	20 microns
	PS core - P4VP corona	Chloroform	25 nm – 28 nm	up to 1 micron
	Peptide-Amphiphile	Chloroform	7 to 8 nm	several microns

Table 1.3(b). Effect of processing method, material and solvent on the nanofiber dimension.

Process	Material	Solvent	Fiber diameter	Fiber length
Electro-spinning	Polyimides Polyamic acid Polyetherimide	Phenol m-cresol Methylene chloride	3 nm to 1000 nm	several cms to several meters
	Polyaramid Poly-gamma-benzyl-glutamate	Sulphuric acid Dimethylformamide		
	Poly (p-phenylene terephthalamide) Nylon 6-polyimide	Sulphuric acid Formic acid		
	Polyacrylonitrile Polyethylene-terephthalate Nylon	Dimethylformamide Trifluoroacetic acid Dichloromethane		
	Polyaniline	Sulphuric acid		
	DNA Polyhydroxybutyrate-valerate PLLA	Water Chloroform Chloroform or Mixed Methlyene chloride and Dimethylformamide		
	Poly (D,L-lactic acid)	Dimethylformamide		
	PEO	Water		
	PMMA	Toluene		
	PU	Dimethylformamide		

1.3.1. Drawing

Nanofibers have been fabricated with citrate molecules through the process of drawing [Ondarcuhu and Joachim (1998)]. A micropipette with a diameter of a few micrometers was dipped into the droplet near the contact line using a micromanipulator (see Fig. 1.1).

Milimetric
droplet

Micropipette
moves towards
contact line

Surface

Micropipette comes
into contact with
contact line

Withdrawal of
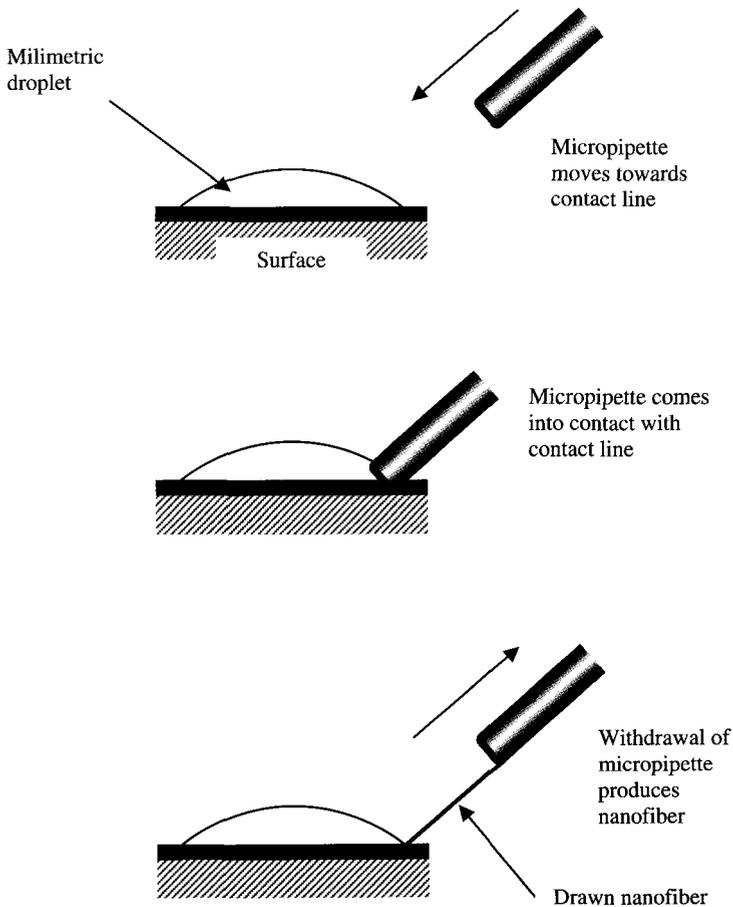micropipette
produces
nanofiber

Drawn nanofiber

Fig. 1.1. Obtaining nanofiber by drawing.

The micropipette was then withdrawn from the liquid and moved at a speed of approximately 1×10^{-4} ms^{-1}, resulting in a nanofiber being pulled. The pulled fiber was deposited on the surface by touching it with the end of the micropipette. The drawing of nanofibers was repeated several times on every droplet. The viscosity of the material at the edge of the droplet increased with evaporation. At the beginning of evaporation corresponding to part X of the curve in Fig. 1.2, the drawn fiber broke due to Rayleigh instability. During the second stage of evaporation corresponding to part Y of the curve, nanofibers were successfully drawn. In the final stage of evaporation of the droplet corresponding to part Z of the curve, the solution was concentrated at the edge of the droplet and broke in a cohesive manner. Thus, drawing a fiber requires a viscoelastic material that can undergo strong deformations while being cohesive enough to support the stresses developed during pulling. The drawing process can be considered as dry spinning at a molecular level.
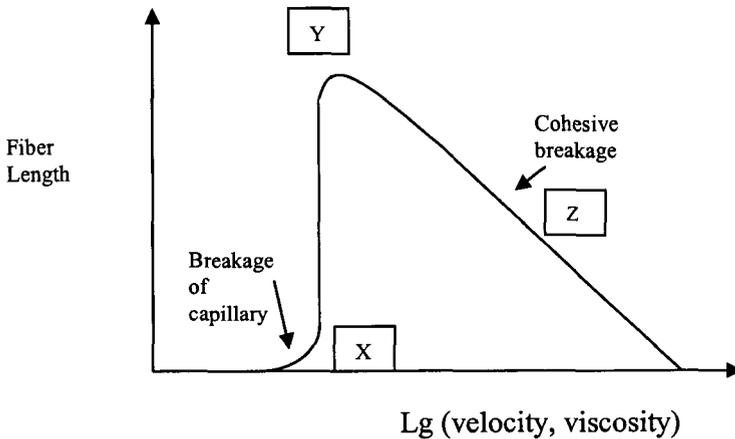

Fig. 1.2. Schematic representation of the length of the drawn nanofiber as a function of the drawing velocity and viscosity of the material (Adapted from [Ondarcuhu and Joachim (1998)]).

1.3.2. Template Synthesis

Template synthesis implies the use of a template or mold to obtain a desired material or structure (see Fig. 1.3).

Water

Polymer
solution

Aluminum
oxide
membrane

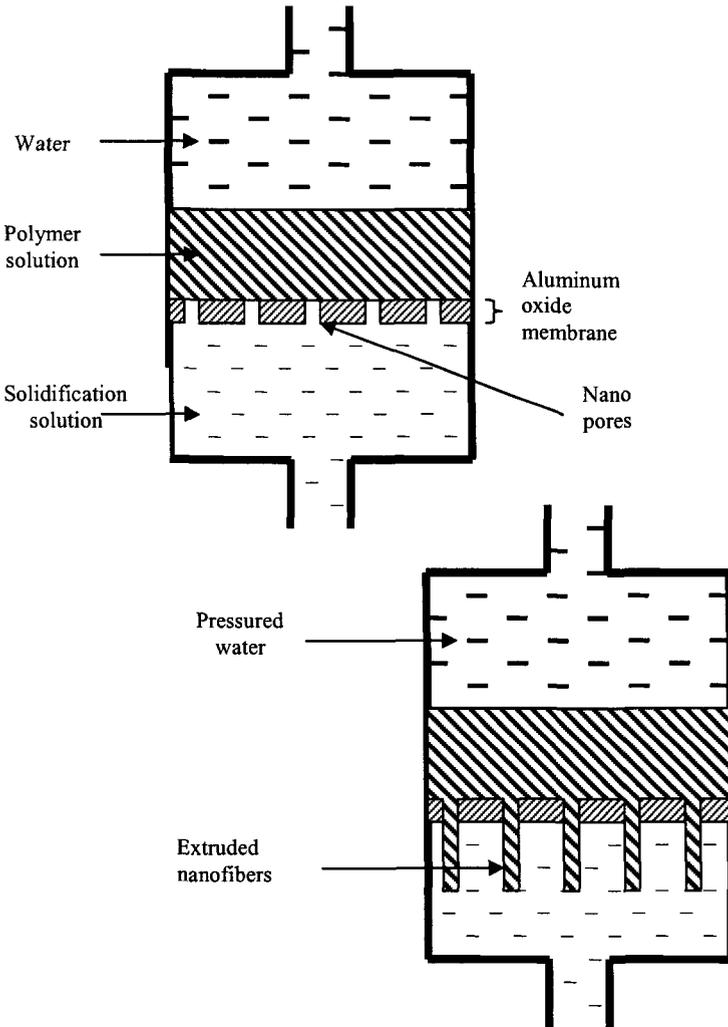Solidification
solution

Nano
pores

Pressured
water

Extruded
nanofibers

Fig. 1.3. Obtaining nanofibers by template synthesis.