ZEUS®

TECHNICAL NEWSLETTER

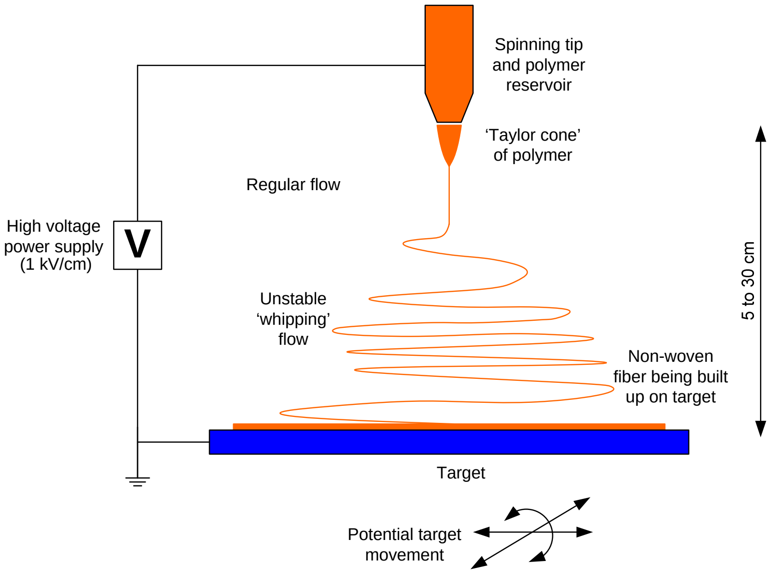
Electrospinning – Fibers at the Nano-scale

Introduction

Electrospinning uses an electrical charge to draw fine fibers from a liquid and shares characteristics with the better known processes of electrospraying and solution spinning of fibers. The process was first discovered by Lord Rayleigh (the Nobel Prize winning British physicist who is perhaps more famous for his discovery of argon in 1895) as part of his investigations into electrospraying in the late 1800s.The first patents for electrospinning were granted in 1902 to J. F. Cooley and W. J. Morton, but major commercialization did not occur until after the advances by Anton Formhals (1934) in the area of fabric yarns and by C. L. Norton (1936) in the area of electrospinning from a melt rather than from a solution. The main theoretical basis for electrospinning was developed by Sir Geoffrey Ingram Taylor between 1964 and 1969 when he created the model for the area known as the Taylor cone at tip of the polymer reservoir. Electrospinning remained a small market until the early 1990's when the rising interest in nanotechnology reawakened interest in the technology. Electrospinning is therefore not a new technique, simply one that has recently come of age and is capable of producing new products with remarkable properties.

Production

Electrospinning can be carried out either with a polymer solution or with a polymer melt. In either case, the basic system of this process is relatively straightforward. This is shown diagrammatically below:



Basic system for electrospinning

A typical system is made up of a strongly charged polymer solution or melt that is fed through a small opening such as a needle or a pipette. The charged material is strongly attracted toward the earthed target by the potential difference between the two. As the potential difference is increased, the material forms a unique shape known as the Taylor cone. As the potential difference is further increased, the electrical attraction becomes greater, the surface tension, and a jet of liquid is ejected from the Taylor cone. The rapid movement of the jet of material causes evaporation of the solvent (if a solution is used) or solidification of the melt (if a melt is used) to produce a very thin fiber. As the fiber is attracted toward the target, it decreases in diameter and the flow becomes unstable, creating a “whipping” mechanism that further significantly reduces the diameter. The final fiber, with a diameter of as low as 10 nm, builds up on the target to form a non-woven fabric.

Much of the research and commercial development to date has been in solution electrospinning, but electrospinning from a polymer melt is also being actively investigated. As a general rule, the fibers produced by electrospinning from the melt are much thicker (due to the higher viscosity of the melt and the lack of a solvent to evaporate), but the process has significant advantages in that no volatile solvent is required and the melt process can produce much higher volumes of material. At present, electrospinning from the melt is little used commercially, but the advantages are clear and progress continues to be made in this area.

A simple electrospinning system can be easily created on a desktop with a metering pump attached to the plunger of a syringe (to give a constant flow of material), a high voltage source (up to 30 kV), and a simple earthed target screen.

In commercial production, the process parameters are varied to create a wide range of designed fiber geometries. Some of the possibilities are:

1. Increasing the flow rate of the fluid or melt will increase the diameter of the fiber produced, but excessive flow can result in the formation of beads of liquid and inconsistent fiber diameter.
2. Increasing the distance between the polymer reservoir and the target will decrease the diameter of the fiber produced, but increasing the distance too much can result in breaking of the fiber during the whipping flow.
3. Increasing the potential difference (kV) will decrease the diameter of the fiber produced, but excessive increases can lead to fiber breakage.
4. Increasing the concentration of the polymer solution (when solution processing) will increase the diameter of the fiber produced, but can also lead to bead formation.
5. Decreasing the surface tension of the polymer solution (when solution processing) will increase the diameter of the fiber produced.
6. Increasing the melt temperature (when melt processing) will decrease the diameter of the fiber produced.

7. Changing the basic polymer characteristics such as molecular weight or molecular structure (particularly the actual structure of the polymer, i.e. linear, branched) will affect the diameter of the fiber produced when either solution or melt processing.

Electrospinning at the basic level is straightforward, but the design and production of a highly controlled product requires the control of a wide range of process parameters.

Variations

Electrospinning was primarily developed to produce simple non-woven fabrics from either a solution or a melt, but electrospinning is no longer restricted to simple mats.

> Shell/core Structures- Just as it is possible to co-extrude polymers, it is possible to co-electrospin polymers and other materials. This technique uses a co-electrospinning device similar to a conventional co-extruder. In this case the shell can be an electrospun polymer and the "core" can be either a solid material (e.g. another polymer) or a solution of a biological material (e.g. a drug solution) that is drawn into the shell as it is spun.
>
> Micro-tubes- Micro-tubes are a variation of co-electrospinning. Co-electrospinning is carried out with a volatile core that evaporates to leave an electrospun micro-tube of dimensions that could not possibly be achieved by conventional extrusion of a tube.
>
> Oriented Fabrics - A stationary target leads to a random non-woven fabric being built up, but moving the target in the horizontal plane will produce a non-woven fabric with directional properties. The fiber will still be laid down in a largely chaotic manner, but the movement of the target will create a preference for fiber orientation. The orientation will never be as distinct as that created by traditional woven fabrics, but will create a fabric with enhanced directional properties.
>
> It is also possible to improve orientation by techniques such as using a rotating wheel as a target or using multiple targets to produce fabrics with a high degree of orientation, but again, the orientation achieved is not as high as that achieved in conventional woven fabrics.
>
> 3-D Structures- Most of the early work on electrospinning concentrated on the production of flat 2-D fabrics, but investigations into the production of 3-D structures are now active throughout the world. The technique generally involves rotating a tubular target plate around the axis to create a tube, which can not only be tubular but also conical and have open or closed ends. More complex structures (branched tubes, connectors etc.) can be created by more complex rotation of a shaped target in at least 2 axes and simultaneous manipulation of the applied voltage.

Properties

Due to the very small size of electrospun fibers, it is very difficult to measure the mechanical properties of the fibers with any degree of accuracy. Some research indicates that the Young's Modulus of electrospun fibers and tubes increases as the fiber diameter is decreased. This is because mechanical properties do not always scale directly (e.g. thin fibers of glass are much stronger than large plates of glass due to the reduced probability large flaws in the glass being present). Similar effects are thought to be present in electrospun fibers and increased mechanical strength is useful in the production of high strength composite reinforcements.

Electrospun fabrics are very light weight and efficient, but their low mass means that they often need support from other materials, such as paper or other more conventional fabrics to be used effectively. This is particularly true for filter applications where the electrospun fabrics need to be pleated, folded, and treated to fit into the filter housing.

Materials

Electrospinning can be carried out with a wide variety of polymers solutions and melts. Typical materials used are:

Solution	Melt
Polyethylene oxide (PEO)	Polypropylene (PP)
Polvinylidene fluoride (PVDF)	Polyethylene (PE)
Polyamide (PA6)	Polyethylene terephthalate (PET)
Polyacrylonitrile (PAN)	Polyethylene oxide (PEO)
Polystyrene (PS)	Polyester
Acrylics	
Polyurethanes	
Polycaprolactone (PCL)	

This is a wide range of materials and researchers are constantly attempting to electrospin new materials. Further development of electrospinning form the melt will undoubtedly greatly increase the number of polymers that can be processed by electrospinning.

Applications

The initial applications of electrospinning were in the production of simple non-woven fabrics, but actual and potential applications are appearing rapidly as part of the nanotechnology “boom.” Some of the current applications for electrospinning are:

Filters

One of the benefits of electrospun fibers is they have a very large surface area to volume ratio as a result of simple scaling (surface area varies in proportion to D^2 whereas volume and mass vary in proportion to D^3). This means that electrospun fabrics have a very high surface area/mass and are ideal for use as light weight, but very effective filtration media. In fact, one of the first high volume applications of electrospun was in gas mask filters.

These same properties are now being used in other filtration applications where sub-micron particles need to be removed or where controlled biological interactions are required. Electrospun filters are already in use as HEPA (High Efficiency Particle Accumulation) filters in vacuum cleaners and in many military applications.

Filtration applications are being developed not only for gaseous media, but also for aqueous media where electrospun fabrics are being investigated as filter media for water purification and the removal of metals, such as cadmium from water supplies as part of land remediation or water purification.

Protective clothing

In addition to the use of electrospun fibers for gas masks, electrospun fibers and fabrics are being developed for the manufacture of protective clothing. The electrospinning process can be used to create fibers that incorporate anti-bacterial agents or compounds, such as oximes that break down nerve gases, insecticides, pesticides and other toxic compounds. The result is protective clothing that does not simply isolate the wearer from the hazard, but actively works to neutralize the potential threat.

Tissue engineering - biomedical scaffolds

Electrospinning can be used to produce porous 3-D structures or scaffolds from bioabsorbable polymers (*see the previous Zeus Polymer Minute on bioabsorbable polymers – 'Disappearing Act- Science of Bioabsorbables'*). In this case the structure can be used to support the healing process by providing a multitude of sites for cell and tissue growth and at the same time break down naturally in the body.

The bioabsorbable nature of the scaffold means that it breaks down gradually as the cells grow and eventually disappears completely, leaving only healthy tissue. Scaffolds manufactured from bioabsorbable electrospun fibers do not require later surgical removal and break down naturally in the body to by-products that are disposed of by the standard metabolic pathways.

These new scaffolds have many advantages over traditional methods:

- They are easy to use and are readily available.
- They are relatively low cost compared to cell-seeded scaffolds.
- They can have biological or therapeutic agents incorporated into the fibers (or scaffold) to Improve response.
- They are manufactured entirely from synthetic materials and therefore there are no concerns with contamination (animal or human) of the scaffold.
- They completely and naturally disappear in the body.
- They can be made much smaller than possible with competing technologies.
- A 3-D scaffold can be produced for applications in complex blood vessel reconstruction.

Bio-medical scaffolds are an incredibly versatile technology, but are still at an early stage in their development. Work continues around the world to extend the range of applications to areas, such as the regeneration of bone, nerves, muscles and potentially even complete organs. You may not hear electrospinning mentioned specifically when you read about miraculous advances, but it is proving to be one of the fundamental 'enabling technologies' for medical science.

Drug delivery

Drugs can be incorporated into the electrospun fiber by creating a core/shell structure with a drug solution as the core. This produces a drug delivery system where the delivery rate is controlled by the rate of migration of the drug through the wall of the electrospun fiber. The overall delivery rate can then be increased or decreased by changing the wall thickness of the electrospun fiber.

High strength composite reinforcements

Electrospun fibers are being investigated as long nanofiber reinforcements for composites. While it is difficult to achieve full orientation of electrospun fibers, the polymer chains in the fibers themselves can achieve a reasonably high degree of orientation due to some cold drawing during the whipping mode. A major concern is that the amount of material required is larger than the solution electrospinning process can realistically provide. Successful commercialization of melt electrospinning will further open up the possibilities in this area.

Future Applications

The current applications for electrospun products are only the start. The amount of work being carried out in the area has increased dramatically in the past 15 years and some of the potential applications being investigated are:

1. Combining electrodes and electrolytes into fibers to create fabrics that are also batteries (i.e. “wearable power”).
2. Using electrospun genetically engineered collagen to produce complete membranes for wound dressings and medical implants.
3. Using tailored electrospinning to give fabrics a color without the need for dyes (i.e. dyeless coloring).
4. Fabrics that are breathable, waterproof, lightweight and much cheaper than current technologies.
5. Fabrics that are not only waterproof, but which also repel oil and water.
6. Solar sails and mirrors for space applications.

Summary

Electrospinning is an old technology that has changed into one of the newest polymer processing technologies. It is a vibrant and rapidly developing part of the nanotechnology revolution where the sub-micron properties of materials and assemblies are being developed and exploited as fast as applications can be identified. The nanotechnology revolution is alive, well and living at a plastics processing site near you.

How Zeus Can Help

Capitalizing on more than 40 years of polymer experience, Zeus is able to develop fabrics with complex shapes from solutions, pastes, and bioabsorbables. The result is a broad range of fiber and fabric properties that are able to meet some of the most challenging demands. Zeus is capable of electrospinning PTFE with a lower basis weight than extruded PTFE, thus resulting in very thin structures. Zeus’ evolving list of electrospun materials includes, PTFE, nylons, bioabsorbables, and other thermoplastic materials. Electrospun materials are also available in sheet and 3- dimensional structures.

With a technical inside and outside sales force backed up with engineering and polymer experts, Zeus is prepared to assist in material selection and can provide product samples for evaluation. A dedicated R&D department staffed with PHD polymer chemists and supported by a world-class analytical lab allows Zeus an unparalleled position in polymer development and customization.

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The *Zeus Polymer Minute*

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