

NONCONFIDENTIAL TECHNOLOGY BRIEF

Cellulose Nanofiber Technologies

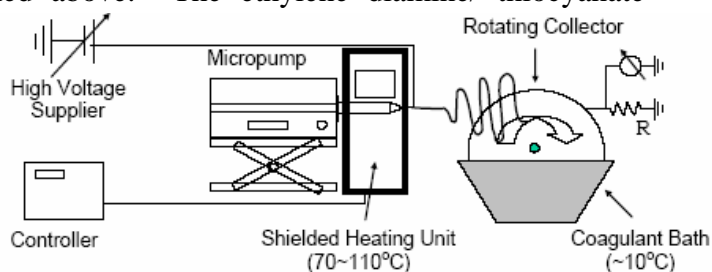
(D-3385, 3439, 3791, 3858)

Cellulose Electrospinning Overview:

Although cellulose is biodegradable and an abundant natural polymer, processing of cellulose into nanofibers had been limited due to its lack of solubility in common solvents and its inability to melt. Existing methods using cellulose derivatives (i.e. cellulose acetate) resulted in non-uniform and bulky mesh fibers with low mechanical properties. In response, Prof. Y.L. Joo and D.S. Kim at Cornell University have designed a unique system to directly produce cellulose nanofibers via a modified electrospinning setup, which incorporates new and improved solvents (3385), a shielded heating unit (3439), and a coagulant bath (3858). Also, Professor Frey and her research team have designed a method for attaching a polyamide layer to a cellulosic substrate for increased filtration efficiency when applied to air filter media (3791).

• Solvents for Dissolving Cellulose (3385)

Commercially used NH_4SCN and hydrazine (N_2H_4) have shown that the solvents were too volatile for electrospinning and extremely toxic. In response, Cornell researchers formulated nontoxic solvents capable of *directly* dissolving cellulose without degradation or derivatization. The salts containing Li, Na, K, SCN (thiocyanate), and I, based on ethylene diamine ($\text{C}_2\text{H}_8\text{N}_2$) were most recently discovered as being suitable (containing sufficient polarity and volatility for electrospinning) and less toxic. The researchers observed that potassium thiocyanate (KSCN) and potassium iodide (KI) are especially preferable to other binary salts mentioned above. The ethylene diamine/ thiocyanate containing solvents manifested positive results for making flow solutions for regular nanofibers and gel solutions for 3-Dimensional nanofiber mats. The solutions require that $\text{C}_2\text{H}_8\text{N}_2$ be mixed with the cellulose first, addition of KSCN second, followed by multiple freezing/thawing cycle (up to 3), for complete dissolution.

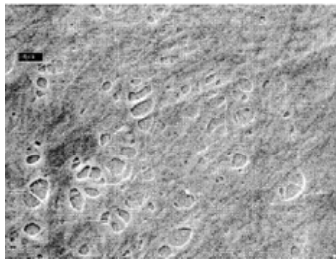


• Melt electrospinning via shielded heating unit (3439)

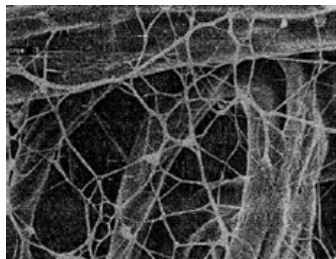
The best cellulose nanofibers are obtained from elevated temperature electrospinning. N-methylmorpholine oxide (NMMO)/water remains the best known solvent for cellulose, and is more frequently used than another well known solvent, LiCl/DMAc, as it is environment friendly and easier to prepare. When using NMMO/water, the electrospinning process is significantly improved by the addition of a shielded heating unit that provides both thermal and electrical insulation to prevent premature solidification of the nanofibers and induction of relaxation of molecular orientation, producing strong and uniform nanofibers. The shielded heating unit is used for both elevated temperature and melt electrospinning. By modifying existing facilities, in which conventional fiber processes for many polymers are based on melt spinning, mass production of improved and environmental friendly nanofibers is possible. The technology is applicable to previously non-dissolvable polymers such as PE, PP, PET, PBT, thus expanding the types of nanofibers available for usage and application in filtration.

- **Cellulose Electrospinning via Direct Dissolution and Coagulation (3858)**

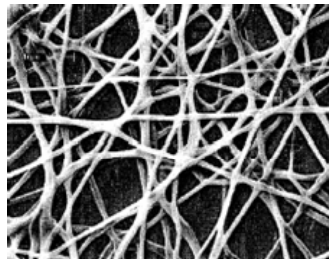
In this improvement to existing processing equipment, when cellulose is completely dissolved in NMMO/water solvent, or in any of the solvents identified above, and electrospun within the heating chamber regulating the solution temperature, the nanofibers are collected on a rotating collector. *After* the fibers are collected, the collector partially immerses the new fiber into a cold-water coagulant bath for complete eradication of solvent residual. The results are dry, uniform, stable, and smaller nanofibers (200-500 nm).



Electrospun fibers without rotating chamber or coagulation



Electrospun fibers without coagulation



Electrospun fibers with a rotating collector and coagulation

- **Electrospun Cellulosic Fibers Applied to Air Filter Media (3791)**

The thread-count of electrospun fiber applied to a filter is the most important factor affecting filtration efficiency. Thread count refers to the number of fibers crisscrossing a given area of a nanofiber mat. The larger the diameter of the nanofibers in the nanofiber mat, the shorter the length of fiber that can be electrospun from a given amount of material and the lower the thread count (there is simply less fiber available), resulting in decreased filtration efficiency. Cornell researchers have discovered that the thread count of the nanofiber mat deposited on the air filter media can be increased and higher filtration efficiency achieved without sacrificing air flow or increasing back pressure. They have also discovered how to achieve good adhesion between the air filter media and the applied nanofiber mat.

The composites can be prepared via softening and swelling of polyamide fibers and cellulosic fibers with solvent which causes inseparable bonding between the two layers. This adhesion between the air filter media fibers and the cellulosic fibers is desirable for good durability of the air filter media. Another way is via solution electrospinning of polyamide fiber onto a moving web of cellulosic fiber substrate layers followed by evaporation of residual solvent. The benefit obtained by the addition of the polyamide layer is increased efficiency without a large increase in pressure drop.

Competitive Advantage:

The new technology avoids lengthy and complex steps, does not require side reactions or extra purification steps. Using the new solvents, dissolution occurs at room temperature, does not require antioxidants to avoid side reactions, prevents degradation of cellulose, and is less harmful.

The use of Cornell's novel electrospinning set up results in production of finer nanofibers with larger surface area, uniformity, and crystallinity for enhanced degradability. These nanofibers can be oxidized with $\text{HNO}_3/\text{H}_3\text{PO}_4$ and NaNO_2 for better use in nontoxic biomedical applications and usage.

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Patents and Publications: U.S. Patent Application Nos. 10/965,813, 10/834,041, 11/748,958, 11/637,745, and PCT/US2006/048458

C.W. Kim, M.W. Frey, M. Marquez and Y.L. Joo, "Preparation of Submicron-Scale Electrospun Cellulose Fibers via Direct Dissolution," *Journal of Polymer Science: Part B: Polymer Physics*, 43, 1673-1683 (2005).

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