Cost-Effective Method Developed to Fabricate Polymer Membranes for Chemical Separations

The Idaho National Laboratory (INL) has developed a membrane fabrication method using a rapid evaporative spray process (RESP) that deposits atomized droplets of a polymer onto a surface. Compared with membranes made using conventional approaches such as knife- or spin-casting, RESP membranes require less processing time and offer improved separation performance and the ability to control the membrane's shape. For example, RESP membranes are 40–70 times more selective than conventional membranes, can be fabricated in seconds rather than minutes or hours, and can be fabricated in complex shapes relatively easily.

In 2004, the U.S. market for membranes used in separations applications was around $2.5 billion. It has recently been reported that this market is rising at an annual rate of 6–7%. The major markets that use membranes for separation include water purification and the dairy, food, beverage, chemical, and pharmaceutical industries. Additional applications include the production of hydrocarbon fuels, gas separation, and medicine. Emerging markets for membranes include fuel cells, batteries, and pollution control. The INL's fabrication process addresses a primary concern of industry, namely, the ability to produce high-performance membranes inexpensively.

The transport properties of membranes depend on their microstructure, or "fabric," as well as the physical and chemical properties of the polymer and the operating conditions. The microstructure, in turn, is dictated by the fabrication method. INL's approach produces unique, asymmetric membrane microstructures that perform well in many solubility-driven separations. In one example, membranes

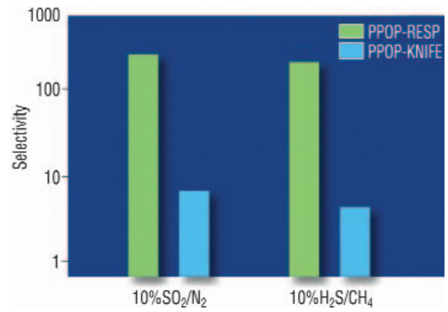

Figure 1. Comparison of the selectivity of poly[bis(phenoxy)phosphazene] (PPOP) membranes prepared by the rapid evaporative spray process (RESP) and by conventional knife-casting.

of poly [bis(phenoxy)phosphazene] (PPOP) were fabricated by RESP and by the conventional method, evaporative knife-casting. PPOP is an inorganic polymeric material with exceptional stability in the adverse thermal and chemical environments frequently encountered in industrial separations.

Gas chromatography was used to evaluate the selectivity (i.e., the permeability ratio of the components) of RESP and knife-cast PPOP membranes for several acid–gas mixtures (10% SO_2/90%N_2, 10%H_2S/90%CH_4, 10%CO_2/90%CH_4). At 80°C, RESP membranes had four times the selectivity of knife-cast membranes when separating SO_2 from nitrogen. At 130°C, the difference improved to about 42 times. RESP membranes had twice the selectivity of similar knife-cast membranes when separating H_2S from methane at 80°C and had 67 times the selectivity at 130°C, as shown in Figure 1. The separation of CO_2/CH_4 mixtures was also improved with the use of RESP membranes.

According to INL, technical advantages of the RESP process over other membrane fabrication processes include the following:

- membranes with complex shapes, which are difficult or impossible to manufacture by conventional approaches can be produced in a straightforward manner;
- semipermeable membranes for separating a wide variety of materials can be produced;
- little or no solvent is emitted;
- thin and delicate films or membranes can be applied onto strength-providing supports, including mesh, porous, and nonporous supports;
- an improved method for controlling thickness is provided; and
- asymmetrical membranes with improved selectivity can be fabricated.

The economic advantages include savings in production time and costs by eliminating unit operations, greater flexibility, and improved performance.

Opportunities

The Idaho National Laboratory has several patents for the RESP process that can be licensed exclusively or nonexclusively for membrane production. Interested parties are invited to contact the INL for additional details about the technology, partnering, licensing, or for further development and commercialization of this technology.

Source: Technical: Kevin M. McHugh, 2525 N. Freemont Avenue, MS-2050, Idaho Falls, ID 83415 USA; tel. 208-525-5713, fax 208-525-5877, or e-mail Kevin.McHugh@inl.gov. Commercialization: Jason C. Stolworthy, 2525 N. Freemont Avenue, MS-3805, Idaho Falls, ID 83415 USA; tel. 208-526-5976, fax 208-526-0876, or e-mail Jason.Stolworthy@inl.gov.

Technology Advances provides up-to-date reports of materials developments that show potential to bridge the gap between research innovation and application of advanced materials technologies. If you encounter or are involved with materials research that shows potential for commercialization and would like to present these developments, contact Renée G. Ford, Renford Communications, renford@comcast.net.

https://doi.org/10.1557/mrs2006.115 Published online by Cambridge University Press

Electrospun Nanofibers Tailored to Meet End-Use Applications

Uniformly laid, paper-thin weblike structures or membranes made from nanoscale-diameter fibers (20–200 nm) are particularly suitable for a broad range of potential applications in areas such as filtration, electronics, insulation, biomedicine, energy storage, textiles, cosmetics, and aerospace. A high-throughput electrospinning manufacturing process that produces nanofibers from organic polymeric materials such as nylon and polyester (shown in Figure 1) has been developed by eSpin Technologies. In addition, activated-carbon nanofibers and high-temperature alumina (Al_2O_3) nanofibers can be manufactured using eSpin's process. In contrast to other available carbon nanomaterials, eSpin's carbon nanofibers do not need additional purification prior to their use.

Nanofibers have a broad range of market opportunities in both traditional and emerging industries. The near-term market is projected to be $20 million and is expected to grow as nanotechnology-based products find markets.

eSpin's nanofibers are manufactured in the form of self-supporting weblike structures to serve as laminates with materials such as textiles, nonwovens, films, and paper, and also as short, high-aspect-ratio (length-to-diameter >1000) whiskers. The membranes or webs fabricated from these nano-diameter fibers have unique characteristics such as high surface area (50 m^2/g), high porosity (92%), and relatively small pore size (1–3 µm). In addition, based on the polymer properties and web characteristics, the product can have high moisture transport rates of vapor, high liquid absorbency, and the ability to possess large numbers of chemical functional groups so that the material's properties can be tailored (e.g., hydrophobic, hydrophilic, antimicrobial, and antistatic). The number of functional groups that can be attached to the surface of the nanofiber depends on the relative size of the molecules, the type of functional group, and the surface area of the nanofibers. The whiskers are manufactured in dry form or as a colloidal suspension in various fluids to meet end-use applications (e.g., cosmetics).

In eSpin's electrospinning process, an electrical charge is concentrated on the dielectric liquid (polymer/solvent) surface at the tip of a capillary. With sufficient voltage (7–10 kV), the liquid is attracted to a grounded target, forming a jet at the capillary tip. As the jet diameter is reduced in size due to jet acceleration under the electrical force, the jet elongates and goes through a whipping action, fracturing into many fine jets as a result of surface instabilities. These fine jets dry to form polymeric nanofibers. Individual nanofibers are typically 1/100th of the diameter of fibers commonly used in textile processes (20 µm).

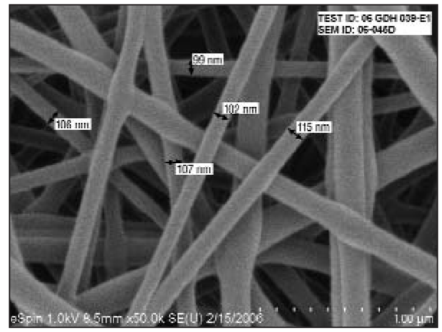

Figure 1. Scanning electron photomicrograph of electropsun nylon nanofibers developed by eSpin Technologies.

The company is also commercializing activated-carbon nanofibers. These are produced from acrylic copolymers (e.g., polyacrylonitrile) and have high surface area (1800 m^2/g). Micropore and mesopore sizes can be tailored to meet the properties required for various applications.

Opportunities

The developer, eSpin Technologies, is seeking partners that can assist technically and financially to broaden the market penetration for its nanofiber technology.

Source: Jayesh Doshi, president, eSpin Technologies Inc., 7151 Discovery Dr., Chattanooga, TN 37416 USA; tel. 423-267-6266, fax 423-267-6265, and e-mail jdoshi@espintechnologies.com.

https://doi.org/10.1557/mrs2006.115 Published online by Cambridge University Press

Boron Carbide Reaches Full Theoretical Density for Complex-Shaped Ballistic Armor

Boron carbide (B_4C) is the material of choice for U.S. military personal armor because of its combination of high hardness (Knoop: 2800) and low density (2.52 g/cm^3). However, it does not sinter well without sintering aids, which can degrade its ballistic properties. Currently, B_4C small-arms-protective inserts (SAPIs) are hot-pressed to ~98% relative density, which produces acceptable ballistic properties; the ballistic stopping power of a ceramic increases substantially with decreasing porosity. Hot-pressed parts, however, are shape-restricted to plates or simple curves. Researchers at the Georgia Institute of Technology have developed methods to circumvent mechanisms of particle coarsening that have impeded sintering. As a result, B_4C can now be pressureless-sintered without additives to ~96.5% relative density, with hardness values comparable to those of the hot-pressed material (see Figure 1). Pure B_4C can now be sintered to closed porosity and then exposed to hot isostatic pressing (i.e., hydrostatic squeezing using high-temperature, high-pressure argon gas) bringing it to its full theoretical density (zero porosity), with hardness values considerably higher than those of the hot-pressed material. This technology is being commercialized by Verco Materials, a Georgia-Tech-incubated company.

Military applications are the initial focus, specifically, body armor and lightweight ballistic protection for land, sea, and air vehicles. The military market is growing rapidly, with more than a half-billion dollars' worth of ceramic armor orders pending in the 2006 fiscal year.

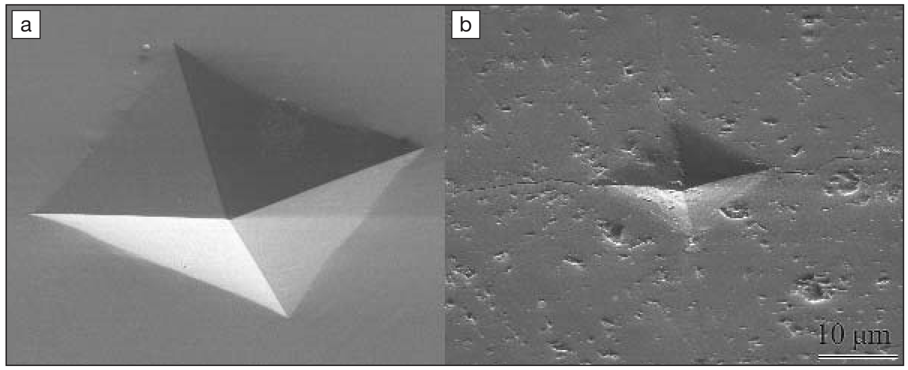

Figure 1. (a) Indentation made in stainless steel by a Vickers indenter; and (b) indentation made with the same indenter and load into B_4C. The comparatively small indentation mark in B_4C is an indication of its hardness.

Considering equipment costs, labor, throughput, manufacturing expendables, and safety issues, this new technology is expected to have cost and quality advantages over current methods. The ability to produce complex-shaped components will open new military and commercial markets. Increased protection will become feasible and available for body extremities and helmet liners. Dual-use lightweight B_4C aircraft components will protect crew, avionics, and engines as opposed to being a parasitic armor on existing structures. Because pressureless sintering enables cost-effective net-shape forming, opportunities are being explored in engine applications owing to the material's exceptional wear resistance and specific stiffness (elastic modulus per unit density). The material's high wear resistance is being exploited as a nozzle for cutting systems using a high-velocity aqueous suspension of abrasive ceramic particles, and for wear-resistant powder-based paint nozzles. Further applications are anticipated in tool and die design, mining equipment, and for bearings. Bearings alone are a $27 million market with 5.7% annual growth expected through 2007.

Boron carbide is typically coated with a thin layer of amorphous or partially crystalline boron oxide (B_2O_3). This oxide contributes to particle coarsening during heat treatment by either evaporation/condensation or liquid-phase conduit mechanisms. It also delays the onset of sintering until the oxide is removed through volatilization. At temperatures above 2000°C, B_4C forms an appreciable boron-rich vapor pressure, which also contributes to particle coarsening. Both mechanisms of particle coarsening decrease the solid–vapor surface area, which drives sintering. By heating rapidly through the temperature range in which B_4C-vapor-based coarsening occurs, and by removing the B_2O_3 at temperatures well below the onset of sintering (either by H_2 or vacuum treatment), coarsening can be largely attenuated. A sintering temperature and time optimization study has demonstrated the importance of heat-treating only to completion of sintering, since extended times led to abnormal grain growth, increase in pore size, and decrease in overall relative density. Additional refinements to the green body (pre-sintered) and adjustments in the furnace atmosphere to eliminate residual graphite in the fired body have led to further improvements.

Opportunities

Verco Materials has developed a family of pressing, casting, and injection-molding technologies for fabricating a wide variety of prototype complex-shaped, theoretically dense components for various military and commercial applications. The company is interested in developing prototype components for wear-resistant and armor applications, and also in discussing partnering opportunities for specific markets.

Source: Technical: Robert Speyer, School of Materials Science and Engineering, Georgia Institute of Technology; tel. 404-894-6075 or e-mail robert.speyer@mse.gatech.edu. Commercialization: Elizabeth Judson, Verco Materials, 75 Fifth Street NW, Suite 470, Atlanta, GA 30308-0390 USA; tel. 770-891-2212 or e-mail beth.judson@vercomaterials.com.

https://doi.org/10.1557/mrs2006.115 Published online by Cambridge University Press