Just 3 nanometres thick and weighing a mere 5 g/m², non-woven, electrospun membranes are setting new standards in lightweight protection.

Next-generation membranes

Not a film, but a fabric. Lighter and finer than conventional extruded films, non-woven membranes, made using a manufacturing technique called electrospinning, may be the next big thing in protective outdoor apparel. Their open pore structure means they "breathe" but also block out rain, functioning much like the PTFE or PU films used in many laminated hard shells.

In the electrospinning process, a polymer is mixed with a solvent, to make it liquid, and pushed through a nozzle or syringe into an electrical field where the yarns are whipped or spun and fall on a moving carrier in a scrambled and tangled array of nano-filaments. The yarns measure in the order of a hundred nanometres and form a non-woven fabric. "This non-woven manufacturing method has been used in industrial applications for fifteen or so years, mostly for filtration purposes but also for waterproof-breathable membranes," says Bruno Mougin, a project manager at the textile research cluster Techterra, based in Lyon, France. Electrospinning is not a new technology. Its development goes back to the early 20th



Millet's ski touring collection features Polartec NeoShell and is designed for "fast forward athletes seeking durable protection and comfort."

D. Ravanel

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century and owes much to a German textile engineer, Anton Formhals, who believed it could be a method to produce synthetic fibres and filed some 22 patents in the 1930s and 1940s.

The first electrospun membrane to be used in performance sportswear was Polartec's PowerShield Pro, a three-layer soft shell fabric, launched in the fall of 2010. Its performances were considered ideal for soft shells (5,000 mm waterproofness and 2 cfm air permeability), but not offering the protection needed for hard shells. One year later, Polartec introduced NeoShell, its first waterproof-breathable hard shell fabric, based on an improved version of the nonwoven the company calls a "discontinuous polyurethane membrane", with a 10,000 mm water column for waterproofness and 0.5 cfm for air permeability (0 cfm, or total windproofness being the standard for hard shells). The small amount of air that passes through the fabric makes the garment much more comfortable, and that was the point Polartec wanted to make with its new generation membrane.

The membrane used in the NeoShell range is "predominately made of polyurethane," says Polartec CEO Gary Smith, while indicating that the manufacturing process does readily allow combinations of multiple materials in different layers: "we're only just scratching the surface." Though he declined to specify what other polymer might be present, it is implied there might be a measure of non-hydrophobic polymer to round out the membrane's overall performance. The non-woven membrane used by Polartec is manufactured by Finetex, a Korean company that holds the patent for what it calls Technoweb Pro nanofibre technology and licenses the product exclusively to the fleece manufacturer. Based in Seoul and founded in 2004, Finetex has been working on electrospinning since the 1990s and is one of the few companies producing the material on an industrial scale.

There are two important innovations in NeoShell, says Mr Smith at Polartec: "the membrane itself, which is only 3 nanometres thick, the bulk of which is air, and has high mechanical stretch; and the lamination process, which was as difficult to develop as the membrane." A key complication was finding the right type of glue and reduce the amount used to avoid a plastic feel, ultimately leading the company to produce its own resin. Gary Smith insists that the membrane and adhesive are of equal importance: "the process technology is as important as the materials used."

There are many labs working on electrospinning, and several companies making machines in Europe, such as Czech Republic-based El Marco, but South Korean companies have made much progress and are considered leaders in the field, says Prof. Paul Kiekens, director of the Textile Department at the University of Ghent, which is currently installing a semi-industrial electrospinning machine developed by the institution.

A 3D nanoweb

Korean company Bristex, the maker of Sealon tapes, has been working on electrospinning for the past two to three years. The firm has patented the concept as an Electro-Nano Membrane and currently sells it to Korean companies only. "It is essentially a nano-sized version of an interlining," says Bristex managing director Keun-Hun Chang, who mentions that Korean telephone maker Samsung uses these



Rossignol's Phantom freeride outfit is made in Polartec NeoShell, which the company claims to be the most breathable fabric in the waterproof-breathable hard shell category.

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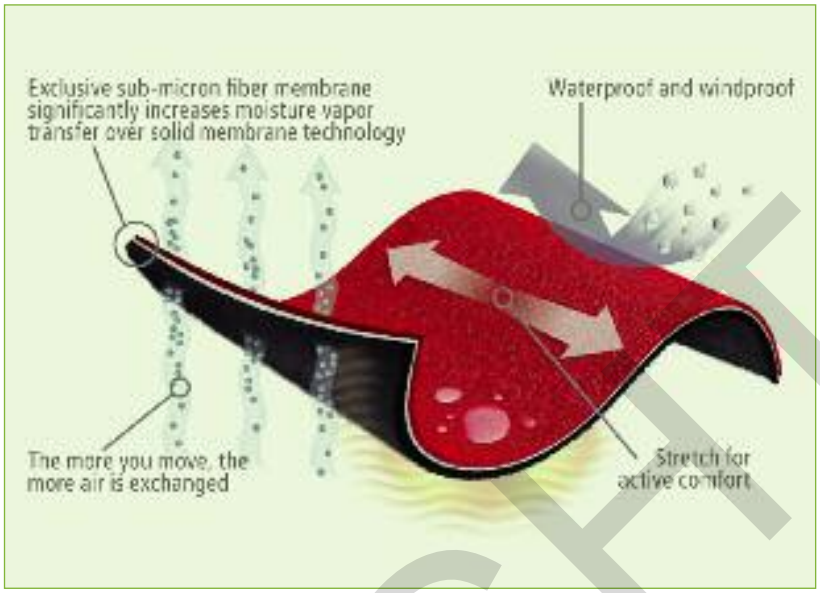
fabrics to protect devices from humidity and shield out sound. "Our technology is known as a top-to-down or melt electrospinning technique in which the chips are melted and nano-sized fibres pushed through nozzles, subjected to high voltage and air that spins and scrambles them as they fall on a slow moving carrier." The speed of the carrier determines the thickness of the non-woven.

The resulting non-woven web is made of fibres measuring between 5 and 500 nanometres in a 3D open-pore structure with an average of 25 billion microscopic pores per centimetre. Alone, it weighs 7 g/m^2 but the company says it can go down to 5 g/m^2. The polymer used in the Electro-Nano Membrane is PVDF (polyvinylidene difluoride), a fluoropolymer part of the Teflon family, which means it is hydrophobic, as opposed to polyurethane (PU), the dominant polymer used by Finetex, which is hydrophilic. "PVDF has a lower elongation point than PU," says KH Chang. "We are currently working on a PU version, too."

Once laminated, Bristex's membrane is said to offer an initial waterproof barrier of 5,000 mm, which levels off at 3,000 mm after washing. Maintaining durable waterproofness was one of the big hurdles the company faced in developing the product, says Mr Chang. Water vapour permeability is 9,000 to 10,000 using the CaCl, or so-called "dynamic" breathability test, and 30,000 to 40,000 g/m^2/24 hours when applying the "static" breathability, or potassium-acetate procedure. Air permeability is said to be 1 cfm. "High air permeability improves wearer comfort," notes Mr Chang. "Also, in very cold climates, our nanospun material won't freeze, as opposed to a PU membrane which absorbs humidity and may therefore ice over." Because of its high level of breathability, Bristex is developing this product for hard shells for high aerobic activities, such as trail running and mountaineering. It is also understandably best suited for lamination on lightweight fabrics, weighing less than 100 g/m^2. Bristex currently offers several fabric combinations in 109, 112 and 132 g/m^2.

Three-layer laminates first

Compared to conventional porous or nonporous films, the non-woven structure of electrospun fabrics means they generally have low mechanical resistance. This is why they are only available in three-layer laminates, sandwiched between two fabrics to protect the fragile non-woven. Both Polartec and Bristex are working on developing 2.5 layer laminates. But it is "difficult to make a 2 layer laminate with an electrospun membrane," concedes Gary Smith, at Polartec. The company is expanding its current range of some twenty NeoShell references to address the ski and cycling apparel markets. "We're also developing lighter weight references for sports such as running and trail running," says Eric Yung, Polartec's European sales manager. He anticipates that 2 and 2.5 layer laminates could be market-ready for summer 2015.



The "submicron" membrane, a term the Polartec favours over "nano", used in NeoShell fabrics is not only highly breathable, but stretchable as well.

Polartec

Prof. Paul Kiekens' team of researchers has been working on electrospinning for the past ten years and is installing its own machine built by the lab. "Our machine is quite flexible, we have tested many different types of materials, and all the usual textile polymers such as polyester, polyamide, polypropylene, etc.," says Prof Kiekens, who sees great potential in the technology: "The nanoweb has an enormous surface area, it is easy to add other components or active ingredients during the manufacturing process, and these will have higher efficiency due to the material's high surface area." The inherent fragility of non-woven materials will be solved in time, he says, by 2020 or 2025. The real difficulty lies in identifying "the optimal resin, in the right concentrations" to laminate the fine membrane. This he believes will be worked out by the end of the decade.

A remaining hurdle for electrospun membranes is addressing the risk factor of working with nanomaterials. "Once stabilised in the non-woven, the nanofibres do not pose a problem," says Prof Kiekens. "But you cannot exclude the element of risk during the manufacturing process because this is when the fibres can be volatile. There are concerns, which the European Union considers real, conducting numerous studies." Proper measures must be taken during production to ensure worker safety. Meanwhile, the next generation membrane is just beginning its career in performance sportswear, where it has the potential to define new standards in lightness, comfort and protection.

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