The Mole

... FOR ANYONE INSPIRED TO DIG DEEPER INTO CHEMISTRY

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Stamping down on soggy shoes

The British nano-coating company P2i is putting an end to wet feet. Josh Howgego and Nina Notman find out how to stay dry.

It's not hard to see why a British company should be leading the way with new waterproofing technology: we are, of course, world-renowned for our wet weather! The technology sold by Oxfordshire-based P2i was originally designed to improve the chemical protection of soldiers' clothes, but since then this innovative chemical coating has been developed for use in more familiar locations.

How it works

The degree to which water is attracted to or repelled from a surface is determined, at the most fundamental level, by the intermolecular forces between the two phases. There is a general rule in chemistry that 'like interacts with like'. Since water is highly polar it 'likes' to dissolve charged ions such as Na^+ and Cl^-. It doesn't like to interact with non-polar things, which is why oil spills float on the ocean, rather than mixing into it.

The same principles are used by coatings chemists. When they find a material that water doesn't like to interact with, there's a good chance it'll make a decent repellent. Of course, whether one material interacts with another is not really about whether they 'like' each other. It's more accurate to think about how the overall energy of the system changes when contact happens. To make an interaction more favourable, the energy of the system must decrease overall ($\Delta G < 0$) when the two materials come into contact with each other. If the energy increases overall ($\Delta G > 0$), they will be mutually repelled.

In this issue

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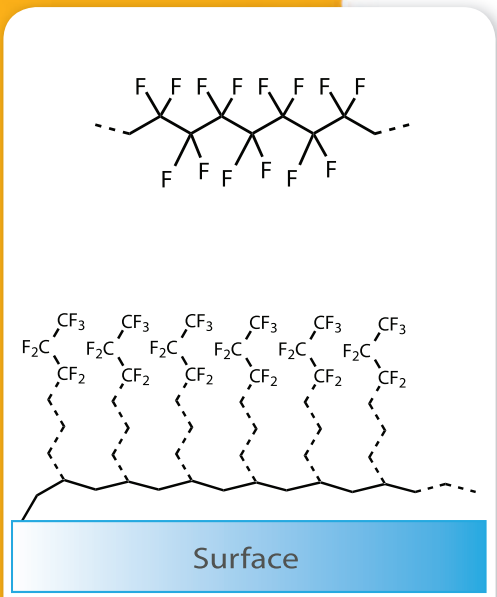


Fig 1: For a standard PTFE coating (top) incoming water droplets 'see' CF_2 units, whereas with P2i's coating (bottom) the molecules 'see' a terminal CF_3 group

P2i understand this chemistry pretty well. Delwyn Evans, a senior principal chemist at P2i, explains their coating is a lot like polytetrafluoroethylene (PTFE) – the non-stick material which coats saucepans in kitchens up and down the country – but with an important difference. 'PTFE is the benchmark material for having a low surface energy' says Evans. 'All PTFE consists of is polymeric chains of CF_2 groups. (*fig 1*) What we have with the polymer that we grow, is that on the upper surface of the coating are CF_3 groups. The chains are orientated so they are perpendicular to the surface, rather than aligned flat with the surface, as with other coatings.'

PTFE is a common material which has well known applications as a water repellent coating. As well as a saucepan coating (Du Pont's Teflon®), it is used as a waterproof membrane barrier in shoes and outdoor clothing.

Looking at the chemical differences between normal PTFE and P2i's chemicals, it may come as no surprise that the latter is more effective. 'The change going from CF_2 to CF_3 groups is sufficient to reduce the surface energy [of P2i's coatings] to about a third of that of regular PTFE' says Evans. 'Because you have reduced the surface energy that much, the water will tend to bead up and just roll off it. Basically, the water interacts much less with the surface, so it interacts with itself more.'

Soggy shoes: a thing of the past

One of the most obvious applications for the new technology is outdoor footwear, and sure enough, P2i have quickly stormed into the market. The launch of the technology was with trainer brand Hi-Tec at first, explains Evans, but since then other household names like Teva, K-Swiss and Timberland have started using the coating on their shoes too.

Unlike traditional water repellent coatings, P2i's technology (which, when applied to shoes, is branded *ion-mask*™) actually forms a covalent bond between the coating and the shoe substrate. Most coatings are held to their substrate simply by weak intermolecular forces, and so are inherently weaker and less durable than *ion-mask*™.

'Most other water resistant coatings are just physically dried on,' says Evans.

The P2i process

The process starts by putting the shoes into a vacuum chamber and evacuating all the air. Radio frequency plasma in the chamber is then used to knock electrons out from the surface material of the shoe


Water beads roll off shoes coated with *ion-mask*™

creating radicals; that is, unpaired electrons. 'Once you've got the free radicals [on the surface], we turn the power off and introduce the fluorocarbon-based monomer,' says Evans. 'This starts attaching to all the free radical sites that were generated in the first stage.'

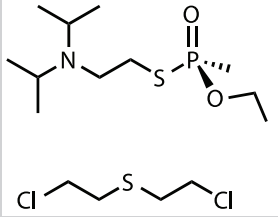
Now there is a nanoscale film of polymer on the shoe surface. To propagate the reaction, and begin to build up the comb-like strands of polymer perpendicular to the shoe surface, more short bursts of plasma are used to create further radicals in the film and keep the polymerisation process going (*fig 2*). The process is quick – it takes between 10 and 30 minutes to finish. Treated shoes are good news for long distance runners as their shoes will not absorb water and gain any weight in wet weather.

Evans says one of the biggest challenges for P2i has been taking this laboratory process and working out how it can be applied during a shoe manufacturer's production line. It has been the combination of science with engineering that has given the step change that allows its application to high throughput manufacturing.

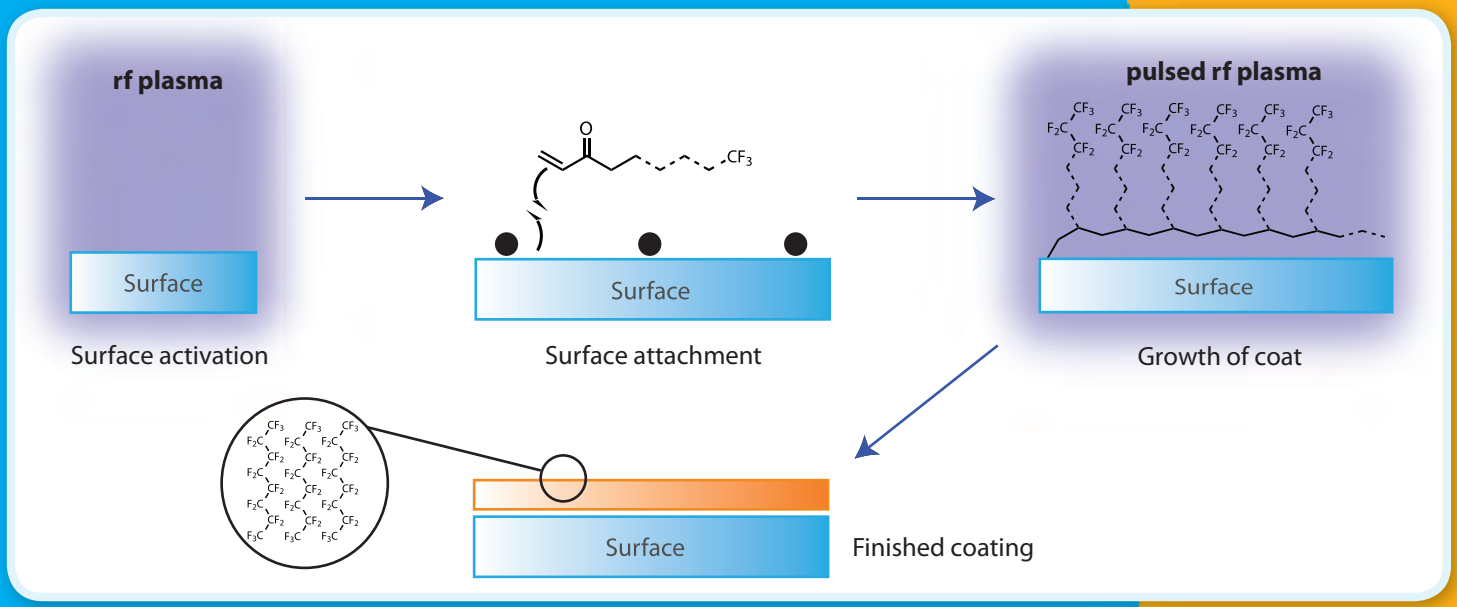
'There is a facility out in China where the shoes from different brands can go, be processed and then come back out,' says Evans. 'However, for other customers we do try to fit it into their production line. That's one of the tricky bits for the business. It is relatively easy to do on a university bench scale, but the trick has been how you can deliver that type of performance at the speed that the customers want it.'

'The big technology step we've been able to do over the last few years is in taking the business from the small

Did you know?



The P2i coating started out as a project for the Ministry of Defence to develop coatings that would repel poison gases like VX gas (*O*-ethyl *S*-[2-(diisopropylamino)ethyl] methylphosphonothioate) and mustard gas (*bis*(2-chloroethyl) sulfide).



research level up to an industrialised process. We are one of the few companies doing this who have been able to industrialise on a really large scale.'

Water-resistant electronics

It's not just shoes and clothes that P2i can apply its coating to. There are a host of consumer products that would benefit from water repellency. One of the most annoying things in modern life has to be dropping a mobile phone or camera in a puddle, but with P2i, that might be a forgotten frustration.

P2i are also active in the electronic devices market, where they call their technology Aridion™. The main challenge in working with different substrates (phone casings, as opposed to shoe fabric) is working out how to generate the radicals on the various surfaces.

'Each product has its own particular challenge and characteristics with activation and how they behave in vacuum. So what you'll get out of a leather shoe – because leather retains a large amount of water – would be different to what you'd get off a hard plastic.'

'For each of the customers, we optimise the process for individual products and then ideally provide them with a machine. They just load it up, press the button and that's it; everything is automated.'

Despite these challenges, P2i has seen significant success in recent years. 'We were on over half the world's hearing aids that were manufactured last year,' says Evans. Aridion™ works particularly well for hearing aids – unlike solvent or water based coatings, the Aridion™ treatment is carried out on the fully assembled device, giving a superior water-repellent coating.

Environmental impact

Another attractive feature of P2i's technology is its low environmental impact. 'We use very small amounts of chemicals, because the layer we grow is on the nanoscale [10^{-9} m] rather than on the micron [10^{-6} m] scale,' says Evans. That's possible, of course, because the coating is so much more effective than its competitors.

And in terms of the process, fewer chemicals are used. The fluorocarbon-based monomer can be vaporised directly due to the very high vacuum in the deposition chamber. That means that unlike many of P2i's competitor coatings, which are applied by dipping the shoe material into a coating solution, P2i's process uses no solvent at all. There is also no need to waste time waiting for the shoe to dry off. Overall, P2i's technology is simple but highly effective. The sky seems to be the limit for this technology; wherever water is an unwanted and inconvenient companion, P2i can foresee a potential market.

Fig 2: The P2i process

Find out more

Go to P2i's website at: **www.p2i.com** to see videos and find out lots more information about the technology and processes.

Loading devices into the vacuum chamber