Institution: Durham University

Unit of Assessment: 8

Title of case study: Super-repellent surfaces by plasmachemical functionalization

1. Summary of the impact

Super-repellent surfaces created by plasmachemical techniques invented at Durham University have been exploited by P2i as the Ion-mask™ and Adiron™ brands and used to protect the surfaces of millions of products worldwide including: 3 million pairs of footwear (Timberland, Hi-Tec); 8 million mobile phones (Nokia, Motorola, Alcatel); 60% of the world's hearing aids (HLT, GN Resound); 55,000 feet of filter media (Porvair); and 100 million pipette tips (Eppendorf). This has earned P2i industry awards including the 2011 and 2012 International Business Award for "Most Innovative Company in Europe" and the "Global Business Excellence Award" 2012. The combined turnover of P2i since 2008 was *ca.* £20M, it received external investment of £31.75M and has created 115 new jobs. A DU IP-holding spin-out company, Surface Innovations, was purchased by P2i in 2010, and further applications of DU plasmachemical functionalization were commercialized by Dow Corning Plasma Solutions Ltd and exploited in-period.

2. Underpinning research

Research focused on understanding and controlling chemical reaction pathways at plasma-solid interfaces was led by Professor Jas Pal Badyal (Durham staff, 1989–present).

Surface engineering and modification techniques are being used in all sectors of the materials, engineering, electronics and health-care industries to provide devices with specific functional properties such as waterproofing, antifouling and corrosion-resistance properties. This industry has an estimated value of $50 billion per annum and new technologies to enhance surface properties of all types of materials are highly valued.

The plasma state was discovered in 1879 by the English scientist William Crookes and, despite being used for technological applications such as lighting for over 100 years, very little progress had previously been made in relation to achieving high chemical reaction pathway selectivities within this 4th state of matter. Durham research has, however, developed methods to use plasmachemical techniques to selectively functionalise the surfaces of a wide range of different materials. Two particular areas of research which underpin the impact described in Section 4 are:

(a) Synthon theory for plasmachemical surface functionalization: this theory allows rational prediction of the surface functionalization of polymers by electrical gas discharges. It uses a synthon approach to correlate the reactivity of chemical groups located at a polymer substrate surface with the impinging plasma species. In this way, desired functionalities can be incorporated into a surface by the judicious choice of electrical discharge and polymer substrate. Structure-behaviour relationships were developed which explain the interfacial plasma-solid chemical reaction pathways [1,2].

(b) Structurally well-defined functional nanofilms: Most established surface treatment methods are substrate-specific and cannot be easily adapted to different materials or geometries (making them no more than an academic curiosity in many cases). Durham research showed that plasmachemical deposition offers the potential to address this limitation by exploiting the inherent substrate activation by the electrical discharge prior to the onset of film growth. This allows substrate-independent surface functionalization. Furthermore, this approach is single-step, solventless, operates at ambient temperature, and requires very low energy input. Two methods utilized by Durham have been shown to achieve extremely high chemical selectivity at the plasma-solid interface during functional nanolayer deposition:

- *Pulsed Plasmachemical Deposition (PPD):* By pulsing the electrical discharge on ms-μs timescales, two distinct reaction regimes can be constructed: firstly activation of precursor molecules by UV irradiation, ion, or electron collisions during the plasma duty cycle on-period (typically μs), and then conventional chemistry (e.g. cyclisation or polymerisation) proceeding in the absence of any damaging plasma species during a much longer off-period (typically ms). This has been shown to lead to extremely high levels of surface functionality [3,4].
- *Atomised Spray Plasma Deposition (ASPD)**:*** Structurally well-defined functional nanofilms can also be obtained by the nebulisation of precursor molecules into an electrical discharge. Mechanistically, this proceeds by highly excited metastable atoms possessing sufficient energies to activate precursor molecules (Penning type reactions) which initiate conventional

chemical reaction pathways during the impact of the supersonically expanding atomised liquid droplets onto the substrate surface [5]. It has also been shown that well-defined nanocomposite films can be created by utilizing nanoparticle slurries [6].

3. References to the research

[1] J. Hopkins and J. P. S. Badyal, “Nonequilibrium Glow Discharge Fluorination of Polymer Surfaces”, *J. Phys. Chem.*, 1995, **99**, 4261-4264. **DOI**: 10.1021/j100012a056 **[60 citations]**

[2] I. S. Woodward, W. C. E. Schofield, V. Roucoules and J. P. S. Badyal, “Super-Hydrophobic Surfaces Produced by Plasma Fluorination of Polybutadiene Films”, *Langmuir*, 2003,**19**, 3432-3438. **DOI**: 10.1021/la020427e **[203]**

[3] M. E. Ryan, A. M. Hynes and J. P. S. Badyal, “Pulsed Plasma Polymerization of Maleic Anhydride”, *Chem. Mater.,* 1996, **8**, 37-42. **DOI**: 10.1021/cm9503691 **[135]**

[4] S. R. Coulson, I. S. Woodward, S. A. Brewer, C. Willis and J. P. S. Badyal, “Ultra-Low Surface Energy Plasma Polymer Films”, *Chem. Mater.,* 2000, **12**, 2031-2038. **DOI**: 10.1021/cm000193p **[141]**

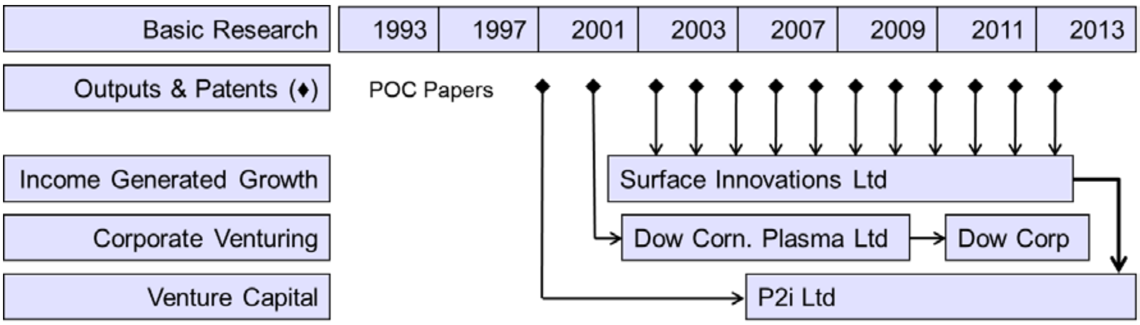
[5] L. J. Ward, W. C. E. Schofield, A. J. Goodwin, P. J. Merlin and J. P. S. Badyal, “Atmospheric Pressure Plasma Deposition of Structurally Well-Defined Polyacrylic Acid Films”, *Chem. Mater.*, 2003, **15**, 1466-1469. **DOI**: 10.1021/cm020289e **[82]**

[6] L. J. Ward and J. P. S. Badyal, “Method and Apparatus for Forming a Coating on a Substrate”, *Patent* WO 2006/092614, 8 September 2006.

The quality of this research is evidenced by several major awards to Badyal including: the Harrison Prize of the Royal Society of Chemistry; the Burch Prize of the British Vacuum Council; and the International Association of Advanced Materials Medal for “Outstanding and Notable Contribution in the Field of Nanomaterials and Nanotechnology”. He has given 13 plenary/keynote and 12 invited lectures at overseas international conferences since 2008 (in countries including Australia, Austria, Belgium, Canada, Czech Republic, Denmark, France, Germany, Greece, India, Italy, Luxembourg, Mexico, Netherlands, New Zealand, Poland, Portugal, and USA). The surface science described in this study was funded by a variety of research grants from several sources including EPSRC, British Gas, EU, Mupor Ltd, DERA and Dow Corning.

4. Details of the impact

The Durham research described in Section 2 has been transferred to industry through three different business models (income generated growth, corporate venturing, and venture capital). The transfer methods are summarized in the flow chart below and an example of impact generated through each method is given in the following sections.



(a) Income Generated Growth (Surface Innovations Ltd, Durham, UK): Atomized-Spray Plasma Deposition (ASPD) described in [6] is capable of producing a wide variety of thin, high quality, functional coatings, at throughputs attractive to a large number of markets. The approach allows lost-cost substrates to exhibit the surface properties and performance of far more expensive materials**.** To exploit this technology Badyal and Dr Luke Ward (a former PhD student) founded the IP-ownership company Surface Innovations Ltd. in 2001 [Im1]. Durham University agreed to assign non-industrially sponsored intellectual property developed within the Badyal group to the company in return for an equity stake. 14 core patent families were filed during the period 2001–2010 on surface functionalization for applications including: filtration; antifogging; bioarrays; antibacterial; antifouling; high dielectric constant; super-repellency; fog harvesting; and rewritability. The company was funded by loans and income generated from prototype development amounting to £824K for industrial partners including: Siemens (Germany); Arcelor (Belgium); Procter & Gamble (USA); Sauflon (UK); Federal Moghul (Luxembourg); Dow Corning (USA); IRD Fuel Cells

(Denmark); Kimberly-Clark (USA); Gillette (USA); Calgon (USA); Porvair (UK); and SMB Microfluidic Devices (Denmark). The company had 5 employees when it was bought out by P2i Ltd in July 2010 [Im2] for *ca* £737K (P2i 2010 Annual report [Im8]). The Department's share of the income has been used to fund undergraduate research internships in Durham and abroad to highlight entrepreneurship opportunities and benefits to our students. Badyal has utilized proceeds to help alleviate extreme child poverty in India and Africa.

(b) Corporate Venturing (Dow Corning Plasma Ltd, Cork, Ireland): The atomised spray plasmachemical deposition (ASPD) technique developed in Durham [5] was patented in collaboration with Dow Corning and a start-up company [Im3,Im4] was set up in Ireland with an initial investment of €3.3 million made by Dow Corning Corporation (USA). Its managing director was Dr Alan Hynes (a former Badyal PhD student). Large scale (up to 2.8 m width roll-to-roll) industrial manufacturing machines were built based upon the Durham ASPD equipment design and sold for significant sums. The company employed 28 people, and in 2008 the business became fully integrated into Dow Corning Corporation. Current licensees of the ASPD technology include Invexus (USA) which is supplying to the >£2 billion global market for antibacterial surfaces.

(c) Venture Capital (P2i Ltd, Abingdon, UK): In 1996 Badyal was approached by the UK MoD concerning the dehydration of British soldiers in the desert during the 1990 conflict with Iraq. In particular, the military wanted to reduce the number of layers of clothing that soldiers had to wear in the battle field. Badyal proposed the utilization of pulsed plasmachemical deposition (PPD) which led to the funding of a PhD student (Stephen Coulson). The idea was successful, a patent for treating fabric was filed (GB Pat Appl. 9712338.4, 1997) and the research published [4,Im5,Im6]. Upon completion of his PhD, Stephen Coulson moved to the MoD and in 2004 helped found P2i Ltd (UK Company 04814350), where he has remained as Chief Technology Officer (CTO). P2i has raised £40 million investment from Swarraton Partners, NAXOS Capital Partners, Porton Capital Limited, Unilever Ventures, OMBU Group, and the Rainbow Seed Fund, including £31.75M since 2008. The company headquarters are in Abingdon, and it currently has offices in Savannah (USA), Oregon (USA), Singapore, and an applications centre in China. In 2010, having undergone very rapid growth, P2i purchased Surface Innovations from DU and Badyal in order to broaden its portfolio of functional nanocoatings [Im2,8].

P2i has built its business by developing and commercialising the Durham plasma deposited liquid repellent nanocoatings described in [4]. It has commercialised treatments as the Ion Mask™ brand for footwear, clothing and accessories, and as Aridion™ for electronics applications [Im7]. These ultra-low surface energy nanocoatings impart numerous benefits to consumer products. For footwear and filtration media, treated products no longer absorb liquids but instead remain dry, clean and lightweight. For complex three dimensional products such as smartphones, and computer tablets, the low surface energy prevents liquids from being drawn into the device by means of capillary action.

Figure: Some examples of product applications using Durham-derived plasma nanocoatings.

Over 150 commercial plasma coatings units based on the Durham design have been manufactured by P2i and installed with customers in Argentina, Australia, Brazil, China, Germany, India, Indonesia, Singapore, Spain, Thailand, UK, and the USA for the surface treatment of products in the electronics, lifestyle, life sciences, filtration, energy, military, and institutional sectors. Examples of the use of Ion Mask™ and Aridion™ technologies are given in the figure above and the table below. This is sourced from Case Studies described in P2i open literature [Im8] in July 2013, and is not a comprehensive list of applications.

Application	Examples: Brand (models)	Notes
Phones	Alcatel (ONE TOUCH 997 and 992D); Plantronics (Headsets Voyager legend, Backbeat GO); Motorola (RAZR and Moto X smartphones and Xyboard tablet)	8 million units >£4M retail
Hearing Aids	Hearing Lab Technology (HLT) – GN Resound 60% of the world's hearing aids	6 million units >£3M retail
Footwear	Hi-Tec (V-Lite Mach 4, V-Lite Infinity, Sierra Lite); Teva (Links Mtb, Mush Frio Lace, Fuse-ion, Reforge-Ionmask); K-Swiss (Kwicky Blade Light, California); Timberland (Tall Zip Boot, Desert Boot, City 6IN Boot, Formentor Boot); Scott (Eride Icerunner); Van Dal (suede shoe range); Mizuno (Weathers golf); MAGNUM (Sidewinder Combat Desert Boot, Elite Force Boot); Nike; Adidas	3 million pairs of shoes >£2M retail
Clothing	Kangol Headwear (Tropic Jacquard 507, Zig Duke, Pole Stripe); Trekmates (Mountain Lite Mitt); Global Armour (G Tech Vest)	Potential market of >£1 billion
Filtration and Energy	Porvair (filtration and separation equipment) Crowcon (gas detection equipment, STAY-CLIR) Eppendorf (Pipette tips)	55,000 ft of filter media 100 million pipette tips

P2i company turnover has grown rapidly since 2008 (see table), exceeding £8.8M in 2011–12 with 93% of revenues generated in geographic markets outside of the UK, leading to the creation of >100 new jobs and the establishment of wholly owned subsidiaries in China, Hong Kong, USA and Singapore. P2i currently own a portfolio of over 60 patent families to protect their core businesses.

	2008	2009	2010	2011	2012	Totals*
VC raised (£M)	2.0	6.1	5.5	11.4	6.75	31.75
Turnover(£M)	0.862	1.035	3.180	6.021	8.886	19.984
Employees	15	27	48	90	115	115

* Company report for January – July 2013 unavailable at time of writing

P2i is widely recognized as being the world leader in plasmachemical deposited functional nanocoatings and has won numerous awards including: International Business Award for "Most Innovative Company in Europe", 2011 and 2012; "Footwear Innovation" category at the 2009 Company Clothing Awards, London, 2009; "Borderless Business" category, Management Today, 2011; "Best of Show" award, American Academy of Audiology, 2011; Global Business Excellence Award 2012; and 27th fasted growing UK technology company in the 2012 Sunday Times Tech Track 100 league table. The Durham research has featured extensively in the media, including: the Sunday Times newspaper; the national BBC Evening TV News; BBC Radio 4 Today Programme; Channel 5's Gadget Show; and the Discovery Channel.

5. Sources to corroborate the impact

[Im1] Surface innovations: www.surface-innovations.com and annual reports filed with Companies House 2008–2013.
[Im2] P2i acquisition of Surface Innovations: P2i Press Release, 13 July, 2010.
[Im3] Dow coatings: Dow Corning Plasma Solutions Application Note, 2005.
[Im4] Dow coatings: Chem. Eng. News, October 16, 2006, 84 (42), 18-20.
[Im5] Fabric coating: DSTL Annual Report and Accounts, 2004/2005, p17.
[Im6] Fabric coating: Sunday Times main section, 11th October 1998.
[Im7] P2i brands: Financial Times, March 4, 2012.
[Im8] P2i awards: www.p2i.com, P2i Media Information Pack and Annual reports filed with Companies House 2008–2013.