Institution: University of Birmingham

Unit of Assessment: : UoA 12 - Aeronautical, Mechanical, Chemical and Manufacturing Engineering (Chemical Engineering submission)

Title of case study: Enabling the commercial development of market-leading microcapsule-based products by Procter & Gamble using a novel mechanical analysis technology.

1. Summary of the impact

The impact presented in this case study is the commercialisation of 15 products with perfume microcapsules by Procter and Gamble (P&G), made possible using capsule mechanical strength data provided by Prof Zhibing Zhang's research group at Birmingham. Use of microcapsules gives improved freshness performance, and thus commercial advantage, compared with traditional formulations; they have been incorporated in P&G's four major billion-dollar brands – Downy, Febreze, Lenor and Tide. This has significantly improved their competitiveness enabling P&G to retain their leading position in the USA and Western Europe. A novel micromanipulation technique developed at the University of Birmingham has been used extensively to obtain mechanical properties data for the micro-particles, including microcapsules prepared in Birmingham and provided by companies, which is related to their formulation and processing conditions and end-use performance. In addition, the knowledge generated has helped 15 other companies to commercialise new functional products containing micro-particles.

2. Underpinning research

Micro-particles have found ever increasing applications in functional products over a wide range of industrial sectors including chemical, agrochemical, food and feed, pharmaceutical and medical, human care and household care. Mechanical characterisation of single micro-particles is essential to detect the variation between individual micro-particles, and predict their behaviour during manufacturing and their performance in end-use applications.

However, it had not been possible to measure the mechanical properties of single micro-particles due to technical difficulties until a novel micromanipulation technique was developed at Birmingham. The micromanipulation technique is based on compression of single particles between two parallel surfaces and measurement of the force imposed versus displacement of the particles. Following the early work on micromanipulation studies of the mechanical properties of biological materials (1991-1994), the technique was applied to measure the mechanical properties of single starch granules and skin cells for Unilever (1995-1996) and herbicide agglomerates for Zeneca Agrochemicals (1996-1997).

The technique was adapted to measure the bursting strength of single microcapsules in collaboration with Mr Richard Saunders, Argo Wiggins Research and Development Ltd. UK[3.1] in 1998 which forms the basis of methodologies used in this impact case study. From 10.1998 to 10.2000, a research project on "Micromanipulation studies of microcapsule strength" funded by EPSRC was undertaken by Prof. Z. Zhang, employing a research fellow Dr Guangzhi Sun. Microcapsules made of a shell of melamine formaldehyde, urea formaldehyde or gelatin and a core of oil were prepared and their rupture force, deformation at rupture in relation to their size, shell thickness and preparation conditions have been characterised, resulting in two academic journal papers[3.2,3.3] and 3 conference publications. This laid the foundation for all subsequent work performed in Prof Zhang's group on microparticles which led to the collaboration with a number of international companies. For example, the micromanipulation technique has been used to measure various micro-particles provided by international companies, including microcapsules from Bayer, Germany (2001); drug granules from Merck Sharp and Dohme, UK (2002); vitamin granules from Roche, Switzerland (2002); microcapsules as artificial organs from Bavarian Nordic, Germany (2001-2005); flavour microcapsules from Rhodia, France (2003-2005), chromatography media in microspheres from MILLIPORE Bioprocessing Ltd (2006) and microcapsules from P&G, and thus led to the development of novel products containing microcapsules.

Single micro-particles can be compressed and held to detect their visco-elastic behaviour,

compressed and released to determine their elastic limit and plastic behaviour, and compressed to rupture to evaluate their rupture strength. Moreover, the force versus displacement data can be modelled either analytically or by using finite element analysis (FEA) to determine their intrinsic mechanical property parameters. For compression of elastic microspheres, the Hertz model or Tatara model has been used by Professors Z. Zhang and M. Adams (2003-2006) to fit experimental data corresponding to small or large deformations to determine the elastic modulus of the materials. For visco-elastic micro-spheres with small deformation, an extended Hertz model was developed by Professors M. Adams and Z. Zhang (2003-2006) to account for the time-dependent behaviour. For visco-elastic microspheres such as calcium alginate with large deformations, finite element analysis was applied Professors Z. Zhang and C. R. Thomas (1997-2010) to determine their visco-elastic property parameters including the instantaneous elastic modulus, the equilibrium elastic modulus and relaxation times.

For spherical microcapsules with a liquid core and solid shell such as melamine formaldehyde (MF) microcapsules with perfume, the micromanipulation measurements demonstrate that the MF microcapsules were mainly elastic at small deformations, elastic-perfectly plastic at moderate deformations, and plastic with strain hardening at large deformations leading to rupture. The work was undertaken by Prof. Z. Zhang from 2006-2010. Moreover, finite element analysis[3.4, 3.5, 3.6] has been used by Prof. Z. Zhang to determine the elastic modulus, shell thickness, yield stress, strain hardening modulus, strain and stress at rupture of the microcapsule shell materials made from different formulations and at different processing conditions (2009-2011).

Different types of microcapsules to encapsulate various active ingredients were prepared using in-situ polymerisation, interfacial polymerisation, coacervation, gelation etc, and the mechanical properties of the formed microcapsules and their other properties including encapsulation efficiency, release rate of the core materials, storage stability in liquid environment and their adhesion on fabric surface were characterised to determine appropriate formulation and processing conditions for industrial applications. The works have been supervised by Prof. Z. Zhang and carried out by several research fellows: Dr R. Mercadé-Prieto (2009-2011), Dr B. V. Nguyen (1997-2010), C. Boswell (1996-1997), Dr G. Sun (1999-2011), Dr L. Zhao (2003-2004), Dr T. Liu (2005-2008), Dr Y. Ren (2006-2009) and PhD students: W. Chan (1997-2000), E.S. Chan (1998-2001), S. Yap (2002-2005), D. Law (2005-2008), B. Huckle (2006-2009), J. Xue (2006-2010), A. Fernandez (2005-2012), Y. Long (2006-2009), R. Allen (2009-2012), X. Pan (2008-2012) and Y. He (2009-2012). The last 4 PhD students have been jointly supervised with Prof. J. A. Preece, School of Chemistry.

3. References to the research Outputs 3.4, 3.5 and 3.6 best represent quality of the research.

3.1 Zhang, Z., Saunders, R. and Thomas, C. R. (1999) Mechanical strength of single microcapsules determined by a novel micromanipulation technique *J. Microencapsulation* 16: 117-124. DOI: 10.1080/026520499289365.

3.2 Sun, G. and Zhang, Z. (2001) Mechanical properties of melamine-formaldehyde microcapsules. *J. Microencapsulation*. 18:593-602. ISSN: 0265-2048.

3.3 Sun, G. and Zhang, Z. (2002) Mechanical strength of microcapsules made of different wall materials. *International Journal of Pharmaceutics*. 242: 307 - 311. DOI: 10.1016/S0378-5173(02)00193-X.

3.4 Mercadé-Prieto, R., Nguyen, B. V., Allen, R., York, D., Preece, J. A., Goodwin, T. E. and Zhang Z. (2011) Determination of the elastic properties of compressed microcapsules using finite element modelling. *Chemical Engineering Science*. 66**:** 2042-2049. DOI: 10.1016/j.ces.2011.01.015.

3.5 Mercadé-Prieto, R., Allen, R., York, D., Preece, J. A., Goodwin, T. E. and Zhang Z. (2011) Compression of elastic -perfectly plastic microcapsules using micromanipulation and finite element modelling: Determination of the yield stress. *Chemical Engineering Science.* 66: 1835–1843. DOI: 10.1016/j.ces.2011.01.018.

3.6 Mercadé-Prieto, R., Allen, R., York, D., Preece, J. A., Goodwin, T. E. and Zhang Z. (2012) Failure of elastic-plastic core-shell microcapsules under compression. *AIChEJ* 58**:** 2674-2681, DOI: 10.1002/aic.12804.

4. Details of the impact

"The contributions made by Birmingham have enabled us to develop superior products with perfume microcapsules, significantly improved our competitiveness and secured our leading position in the market of North America and Western Europe."

[redacted] *Research Fellow P&G*[5.1]*.*

Use of the micromanipulation technique has enabled characterisation of fracture strength, and thus performance, of a range of microcapsules which have been used in commercial products. However the thrust of this case study is the incorporation of perfume microcapsules into a range of fabric enhancer products sold by P&G (see Smets letter of support[5.1]). Prof Zhang's research has enabled the design of capsules with the correct properties for the task; both in terms of obtaining reliable measurements of fracture data using micromanipulation but also in training the supplier (a contract manufacturer) on how to manufacture capsules with the right properties and in development of a QA method to ensure consistent quality (see letter of support from Prof. David York, FREng [5.2]).

"The result of all this work was that the company (P&G) was able to incorporate consumer noticeable perfume capsules into a range of the company's large billion dollar bands across the globe. I have no doubt that this would not have been achieved without the ground-breaking work of Professor Zhang and his researchers."

[redacted] *former Research Fellow P&G, now at University of Leeds*[5.2]

Perfume microcapsules have now entered most fabric enhancer products sold by P&G in North America and Western Europe. As explained above, data obtained at Birmingham on the mechanical strength of the microcapsules and other performance attributes including mechanical stability in detergent powders, storage stability in liquid detergents, degree of deposition on fabric surfaces and scent benefit at end-use have been used to optimise the formulation and processing conditions[5.1, 5.2].

Since 2008, this has enabled P&G to commercialise 15 new Laundry products with functional microcapsules in Western Europe (including Bold, Dash 2 in1, Dash with Febreze Freshness and Dash with Touch of Lenor) and the USA (Tide Sports, Tide with Febreze Freshness and Tide with a Touch of Downy). The launch of these new products has secured P&G's dominant position in these markets as No. 1 supplier of sensory products; Downy, Febreze, Lenor and Tide are all major Billion Dollar brands for P&G[5.1].

P&G made the strategic decision to develop a large number of new functional products with microcapsules in 2003, this decision involved Professor Zhibing Zhang who was invited to join a consortium with nine experts in encapsulation and characterisation from different countries as consultants to the company. It was at this stage that the potential of the micromanipulation technique was first highlighted within P&G. Perfume was first considered to be encapsulated, which would be incorporated into sensory detergent products for fabric care. The microcapsules for such applications should have desirable mechanical, structural and surface properties. In particular, they should be strong enough to survive a number of processing steps required to manufacture final products, including mixing, pumping, and extrusion, but should be weak enough to be ruptured by mechanical forces generated by rubbing and friction on fabric surfaces to release perfume. In addition, the microcapsules should be stable in detergents during storage and in laundry processes, and be able to deposit on fabric surfaces. To meet these criteria requires appropriate formulation and processing of perfume microcapsules. The performances of sensory detergent products with perfume microcapsules are normally determined by consumer tests, which are time-consuming and expensive.

Using the Birmingham micromanipulation technique, the mechanical strength of microcapsules as a function of their formulation and processing conditions can be characterised, and appropriate

candidates selected for incorporation into products. Not only has this approach reduced the time and cost of product development (and thus environmental impact), the novel measurements developed have enabled microcapsules to be used in products for the first time (see David York letter of support[5.2])

Given the critical importance of the micromanipulation data in the development of these products, it is perhaps unsurprising that Professor Zhibing Zhang's group has had 12 research projects, fully funded or co-funded by P&G since 2001. In addition, he served as a consultant to P&G and Appleton Paper Inc. USA (now named as Encapsys) in 2006-2008, and took a secondment for 3 months in P&G in 2007, funded by the Royal Academy of Engineering. ZZ has provided advice on improving various aspects of microcapsule formulation, processing and characterisation (See letter of support from Prof. David York, FREng[5.2]). For example, during the secondment, he did an analysis of mechanical damage to perfume microcapsules when they were mixed with dry detergent granules. Based on this analysis, P&G developed a new process of agglomeration of microcapsules to protect them in 2008, which has significantly reduced their damage.

Particularly since 2008, Prof Zhang has provided scientific services to analyse the mechanical strength of more than a hundred of perfume microcapsule samples using the above mentioned micromanipulation technique, which were prepared by the companies using different formulation and processing conditions. Moreover, the impact generated from the above research on P&G's development of new products with perfume microcapsules helped to establish a strategic and long-term partnership between P&G and University of Birmingham in 2010, and contributed significantly as a case study within the School's successful application for a Queen's Anniversary Prize in 2011. A number of patents have been filed based upon the Birmingham fracture strength data.[5.3-5.6]

The micromanipulation technique has also been used to characterise other microparticles supplied and exploited by other international companies during the REF period of 2008-2013. Characterisation of the compression behaviour of chromatographic microparticles produced by Tosoh Bioscience has enabled the company to understand better how to pack and operate industrial scale chromatography columns (See letter of support from Dr E. Müller[5.7]).

Other microcapsules characterised include perfume microcapsules from ICI, UK (2008) and National Starch, USA (2008-2010); perfume microcapsules from Firmenich SA Corporate R&D, Switzerland (2008-2010), perfume microcapsules from Unilever, UK, the Netherlands and China (2001-), perfume microcapsules from Givaudan Schweiz AG, Switzerland and UK (2007-) microspheres from Micropore Technologies Ltd., UK (2011) and perfume microcapsules from International Flavors and Fragrances, USA (2012). The data generated has also helped these companies develop commercial products containing these micro-particles.

5. Sources to corroborate the impact (indicative maximum of 10 references)

5.1 Corroborating statement from Research Fellow, P&G Brussels Innovation Centre; Leader of encapsulation projects for liquid detergents.

5.2 Corroborating statement from Professor, Institute of Particle Science and Engineering & former Research Fellow, P&G Newcastle Technical Centre and Leader of encapsulation projects for detergent powders.

5.3 Patent: Perfume Systems, US Patent Application 20100287710

5.4 Patent: Benefit agent containing delivery particle, EP 2349551 A1 (text from WO2010053940A1)

5.5 Patent: Shampoo Compositions with Increased Deposition of Polyacrylate Microcapsules. US 20120276210 A1

5.6 Patent: Conditioner Compositions with Increased Deposition of Polyacrylate Microcapsules. Patent application number: 20120282309

5.7 Corroborating statement from Technical Director, Tosoh Biosep Gmbh, Germany