Institution: Loughborough University

Unit of Assessment: B12 Aeronautical, Mechanical, Chemical and Manufacturing Engineering

Title of case study: Unprecedentedly high modulus, high tensile strength light weight tapes and films for demanding applications

1. Summary of the impact (indicative maximum 100 words)

The development of disentangled, ultrahigh molecular weight polyethylene at Loughborough University since January 2007 has provided an environmental friendly route to the manufacture of high modulus, high tensile strength tapes with applications ranging from body armour to helmets, ropes and cables. Commercialisation is being undertaken by the Japanese company Teijin, in the Netherlands, under the brand name Endumax®. The new business, started in 2011, now employs >80 staff and predicts annual sales of >€15M from 2014 with an increase of ~10% over the first five years. Competitors such as Du Pont (Tensylon®) and DSM (Dyneema BT10®) have also initiated development of products using the new process route.

2. Underpinning research (indicative maximum 500 words)

Polyolefins constitute more than 80% of the polymers produced by industry. By tailoring the molecular characteristics it is possible to change their physical and mechanical properties, e.g. by varying the chain length of a simple linear polyethylene it is possible to make use of the same class of polymer as either a commodity or an engineering plastic. The latter is used for highly demanding applications such as security (body armour or vehicle protection due to its light weight and high tensile breaking strength); healthcare (prostheses due to its biocompatibility); energy (in the form of biaxial drawn films and composites) and water filtration (membranes by changing the functionalities).

Although desirable physical properties such as abrasion resistance and high impact strength increase with increasing molar mass, the processing of these materials via conventional routes becomes very challenging due to the material's very high melt viscosity. Attempts have been made to process this material at the border between the solid and melt states, but the results have been poor. To circumvent the difficulties in the processability of Ultra High Molecular Weight Polyethylene (UHMWP) for the production of high modulus and high strength fibres, a solution based spinning route is commonly adopted. In this process, 5 wt% of the polymer is dissolved in 95 wt% of a suitable solvent in order to reduce the entanglements between very long molecular chains that are responsible for the very high melt viscosity **[3.1-3.5]**. This solution-processing route demands solvent recovery, thus making the whole process economically, technologically and environmentally unattractive. The process developed in Loughborough University does not involve any solvent and the properties of several products are unprecedented **[3.5].**

Research at Loughborough University by Rastogi and his team since January 2007 has adopted a strategic chain of knowledge approach, where the combination of chemistry, physics, rheology and processing led to the development of disentangled polyethylene directly from the synthesis **[3.5, 3.6]**.

The new synthetic route allows a product to be obtained that shows better mechanical properties compared to commercially available rivals, with the additional advantage that it can be processed without making use of solvent(s), yielding fibres with unprecedentedly high values of modulus and strength **[3.5]**. The ease in sintering and the exceptional mechanical and wear properties shown by the polymer can be applied in a variety of applications, such as the development of lighter bullet-proof vests, improved knee and hip prostheses, and thin films for batteries.

Combined with the technological developments, the synthesised polymers have opened new questions in polymer science, thus giving Loughborough a leading position. For example, when

melting the 'disentangled' crystals a metastable melt state is obtained, which slowly evolves to the thermodynamically stable state **[3.1, 3.2, 3.4]**. The research has found that the transient state of the metastable melt shows a strong time dependence on molecular weight and distribution. Rheological aspects of the metastable melt state in the linear and the nonlinear viscoelastic region remain unexplored and existing theories based on the thermodynamically stable melt state cannot be applied. Our research is currently addressing these new and challenging aspects of polymer science **[3.1-3.4]**.

Key researchers involved in this activity at Loughborough University are Sanjay Rastogi (Professor, Polymer Technology Sep 2006 to present), Sara Ronca (Lecturer, Polymer Chemistry Oct 2008 to present), Giuseppe Forte (Technician, Ethylene Polymerisation Lab Oct 2008 to present), Anurag Pandey (PhD student 2008 -2012), A. Ailianou (PhD student CalTech visiting Loughborough 2011-2012). Teijin staff include: Johan Bos (Scientist), Joris van der Eeem (Scientist).

3. References to the research (indicative maximum of six references)

3.1. S Rastogi, D Lippits, G Peters, R Graf, Y Yefeng, H Spiess, Heterogeneity in polymer melts from melting of polymer crystals; Nature Materials 2005, 4, 635. DOI:10.1038/nmat1437

3.2. D.R. Lippits, S. Rastogi, G.W.H. Hoehne, Melting Kinetics in Polymers; Physical Review Letters, 2006, 96, 218303. DOI:10.1103/PhysRevLett.96.218303

3.3. S. Talebi, R. Duchateau, S. Rastogi, J. Kaschta, G. W. M. Peters and P. J. Lemstra, Molar Mass and Molecular Weight Distribution Determination Of UHMWPE Synthesized Using a Living Homogeneous Catalyst; Macromolecules, 2010, 43, 2780. DOI: 10.1021/ma902297b

3.4. A. Pandey, A. Toda, S. Rastogi, Influence of Amorphous Component on Melting of Semicrystalline Polymers; Macromolecules, 2011, 44, 8042. DOI: 10.1021/ma201797k (the work has received an Austrian award of Euro 5000)

3.5. S. Rastogi, Y. Yao, S. Ronca, J. Bos, J. van der Eem, Unprecedented High-Modulus High-Strength Tapes and Films of Ultrahigh Molecular Weight Polyethylene via Solvent-Free Route; Macromolecules, 2011, 44,5558. DOI: 10.1021/ma200667m

3.6. S. Ronca, G. Forte, A. Ailianou, J.A. Kornfield, S. Rastogi, Direct Route to Colloidal UHMWPE by Including LLDPE in Solution during Homogeneous Polymerization of Ethylene ACS Macro Lett., 2012, 1, 1116. DOI: 10.1021/mz300369x (selected for the American Chemical Society journal cover)

The quality of the research undertaken is indicated by the recognition that it has achieved, see the list below, and the continuous nature of the funding received by Loughborough University (£3.2M since 2006), see the table below.

- **2011** Dutch Polymer Institute Innovation Award (http://www.polymers.nl/News/News_archive/DPI_Annual_Meeting_2)
- **2011** Teijin Global Technology Expert Award
- **2012** Paul Schlack Austrian foundation award of Euro 5000 for PhD thesis of one of our student on the subject (http://www.polymers.nl/News/News_archive/Paul_Schlack_Award_for_Dr._Anurag_Pandey)
- **2012** Cover page for an American Chemical Society journal (http://pubs.acs.org/toc/amlccd/1/9)

Funding agency	fEC	Start date	End date
1. Dutch Polymer Institute (MPJ11)	£302,453	01-Mar-2007	28-Feb-2011
2. Dutch Polymer Institute (MPJ10792)	£228,929	01-Mar-2007	24-Nov-2009
3. Teijin Twaron, NL (MPJ11168)	£312,328	15-Jul-2007	14-Jul-2009
4. Teijin Twaron, NL(MPJ11168)	£450,000	15-Jul- 2009	01-Nov-2011
5. Teijin Twaron, NL(MPJ11168;	£150,000	01-Nov- 2010	01-Nov-2011

extension)			
6. Dutch Polymer Institute (MPJ11170)	£269,900	01-Sep-2009	31-Aug-2012
7. Teijin Twaron, NL (MPJ10783)	£50,103	15-Jan-2007	14-Jul-2007
8. Dutch Polymer Institute (MPJ10793)	£269,900	1st Aug 2008	31-Jul-2011
9. Teijin Twaron, NL (Rastogi's secondment agreement)	£150,000 (approx.)	1st Aug 2008	1-Nov-2012
10. Teijin Aramid NL (MPJ11168; extension)	£253,274	1-Dec-2012	30-Nov-2014
11. Dutch Polymer Institute (MPJ13341)	£715,194	1-Apr-2012	1-Mar-2016

Prof Sanjay Rastogi was the PI for all of the grants listed above.

4. Details of the impact (indicative maximum 750 words)

Loughborough University's research, as cited in s2 and s3, has helped in the establishment of a new business, involving ~80 employees, in producing products out of Ultra High Molecular Weight Polyethylene in an environmentally friendly, solvent-free new process. The engineering polymer – with potential uses including body armour, prosthetic limbs and hip and knee joints – can be used to make tapes and films of unprecedented tensile modulus and strength. Weight for weight, it is 11 times stronger than steel.

The technological process researched at Loughborough is under commercialisation by the research sponsor, Teijin Aramid B.V. located at Arnhem, Netherlands. The activity began in 2007 with the first contract between Loughborough University and Teijin Aramid. Since then, the contract has been renewed without any break. The total amount raised from Teijin is ~£1.37M and the company considers the lab located in the Materials Department at Loughborough as one of its satellite laboratories and hence provides its running costs. This research activity has been further complemented by more than another ~£1.79M in funding from the Dutch Polymer Institute. In total, Teijin Aramid has invested more than €20M in bringing the product from the lab scale to the market.

The official announcement of the start-up of production lines located at Emmen in the Netherlands was made in 2011 **[5.1]** and Oct 2011 saw the product launch under the commercial name Endumax® **[5.2]**. The second step to make more advanced products having higher tensile strength and tensile modulus is being realised during 2013. Endumax® is currently commercialised in the form of tapes that have high strength and stiffness. The two main applications are for ballistic and robotics/force transmission **[5.3]**. For the production of ballistic articles, the tapes offer a significant advantage over yarns in terms of weight and the amount of chemicals needed. Moreover, plates made from Endumax® retain the original form and performance levels, even when exposed to high temperatures and moisture **[5.4]**. For robotics, the Endumax® tape proved to be ideal for use in the Darwing®, a dynamic arm support for people with severely limited arm function. The Darwing was developed by Focal Meditech, in close cooperation with the Teijin Endumax® team, and was presented at RehaCare International 2011 **[5.5]**.

Beside the technological advantages that the polymer offers, the process has opened new frontiers in polymer science, such as the presence of a unique metastable melt state where well-established rheological theories cannot be applied. Loughborough's research has ushered in a new product sector of engineering polymers. Competitors including Du Pont (Tensylon®) **[5.6]** and DSM (Dyneema BT10®) **[5.7]** have also initiated development of products using the new process route. DuPont estimates the total industry opportunity at more than $1 billion **[5.5]**.

The research has resulted in more than twelve patents plus many external collaborations as a result of interest generated within the scientific community. Collaborators include Julia Kornfield (Professor, Caltech), Gerrit Peters (Professor, Eindhoven University), Yao Yefeng (Professor, East China Normal University), Ashish Lele (Senior Scientist, National Chemical Lab), Hans W. Spiess (Director, Max Planck Institute), Michel DuPont (General Manager, Polyethylene Business, Teijin Aramid), Akihiko Toda (Professor, Hiroshima University).

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

The following sources can be made available at request:

5.1. http://www.teijinaramid.com/2011/10/new-teijin-plant-in-emmen-makes-world%E2%80%99s-strongest-tape-endumax%C2%AE/
5.2. Letter from the Research and Development Director, Teijin Aramid, Netherlands.
5.3. www.teijinendumax.com
5.4. http://www.teijinendumax.com/applications/applications/ballistics-protection-products/
5.5. http://www.teijinendumax.com/applications/applications/force-transmission-products/
5.6. http://www.dupont.com/products-and-services/personal-protective-equipment/vehicle-armor/products/dupont-tensylon.html
5.7. http://www.dyneema.com/emea/explore-dyneema/formats-and-applications/dyneema-tape/bt10.aspx