## SPEAKER ABSTRACTS

## A Biomedical Engineering Project from Lab to Spin-off to Market

#### Dr Andrew Lynn Orthomimetics

#### Background

Orthomimetics (OM) was founded in March 2005 on the basis of research conducted collaboratively between the University of Cambridge and the Massachusetts Institute of Technology (MIT). The biomaterials technology that underlies Orthomimetics' technology platform was the culmination of 30 years of research into the repair of bone and soft tissues by world-leading scientists from both institutions.

#### The technology and identification of need

Orthomimetics specialises in the design and manufacture of regenerative medical implants and minimally invasive delivery systems for the treatment of sports injuries, trauma and other conditions that affect knees, ankles and other articular joints.

Degenerative joint disease or arthritis caused by trauma or sports injuries is the leading cause of limitations to daily living and second only to heart disease in work disability. Data suggests the incidence of arthritis will increase by 40% by the year 2030 due to shifting demographics and growing levels of obesity. This represents a significant cause of disability and pain to patients and a huge cost burden to health service providers.

Orthomimetics' implants support the separate yet simultaneous repair of soft skeletal tissues (such as articular cartilage, meniscus, ligament and tendon) and the bone to which these tissues are anchored. All of these implants are based on natural biomaterials and have also been engineered to work in combination with emerging cell- and biologics-based products. By treating damage to joints at an early stage, Orthomimetics' products hold the potential to reduce the risk of osteoarthritis and delay the need for total joint replacement.

#### **Company Development**

Having secured £5.6m in Series A funding in Dec 06, the company recruited an experienced executive team and well respected scientific and medical advisory boards. Since 2007 Orthomimetics has raised a further £2.3m in non dilutive grant funding, enabling the company to achieve commercial scale GMP manufacturing capabilities and CE Mark approval for the first product, Chondromimetic ,a resorbable implant for the repair of articular cartilage and bone which is currently being trialled in Europe.

Orthomimetics maintains strong links with the University of Cambridge through collaborative research projects in the research and development of its product pipeline.

## Regenerative medicine: A role in cartilage repair.

Dr Aileen Crawford,

Centre for Biomaterials & Tissue Engineering University of Sheffield, School of Clinical Dentistry,

Articular cartilage covers the ends of articulating bones in synovial joints such as the knee. This cartilage functions as a biological 'shock absorber' to decrease mechanical loading on the bones and is essential for smooth, painless movement of the skeleton. These important functions of the cartilage are entirely dependent on its structural integrity. However, articular cartilage has a very limited self-repair capability. Therefore, cartilage injuries caused through trauma (e.g. sports injuries) or degeneration due to mechanical overloading (through joint misalignment, instability or morbid obesity) may lead to significant lesions which do not heal spontaneously and lead to progressive erosion of the cartilage, pain and osteoarthritis. Ultimately the disability and pain are such that replacement of the joint by a prosthesis is necessary. Currently, no joint prosthesis has the same mechanical or biophysical properties or durability of the native cartilage tissue.

Developing regenerative medicine approaches and tissue engineering offer real potential to provide cartilage and bone grafts to replace or regenerate the defective cartilage to prevent or delay further tissue degeneration which would necessitate joint replacement. Currently these approaches are based on implanting cartilage-forming cells (alone or in combination with a biomaterial support or scaffold) into the cartilage lesions to initiate repair. Emerging technologies are aimed at introducing suitable biomaterials into the cartilage lesions which stimulate repair mechanisms *in vivo*. The aim of all these approaches is to regenerate articular cartilage which will restore full tissue function.

## Smart Polymers for Smart Garments: Next generation polymer applications for sports & defence clothing

Cath Rogan Smart Garment People Ltd

Some of the most exciting areas of clothing development are being driven by nanotechnology and wearable electronics, many of them made possible by brand new polymer formulations and applications. These disruptive technologies are being used to create *smart garments*, capable of sensing and reacting to changes in their environment and interacting with wearers.

Smart Garment People specialise in locating the most innovative new and emerging textile/garment technologies and working with end users (Military, Police, Sports, Medical) and garment suppliers, to develop new clothing applications.

This presentation will outline the major development trends in these specialist markets, some key growth opportunities for new polymer applications and also what options are available for the commercialisation of new ideas from polymer scientists.

### Making products without tools: how a profound change in manufacturing is being applied to sports footwear

Dr. Neil Hopkinson Rapid Manufacturing Research Group, Loughborough University

Today's mainstream polymer manufacturing processes all require tooling of some sort in order to create products for the end use. A new breed of tool-less, effectively 3D printing, manufacturing processes called Rapid Prototyping has appeared over the last ~20 years. Increasingly these processes are being used to manufacture end use products, leading to the term Rapid (or Additive) Manufacturing. The processes require no tooling which has profound impacts on manufacturing by enabling hitherto impossible geometries and by making manufacturing in western economies more attractive than with traditional processes. This talk will describe how Additive/Rapid Manufacturing of polymers has grown with a particular emphasis on sports footwear.

## **Combating Climate Change in the Snowsports Industry**

Jonathan Philby School of Engineering, Design and Technology University of Bradford

Skiing and snowboarding are often accused by the green lobby of damaging the environment and promoting air travel. However, both are growth activities and have a "cool" image. Also, they are not easy to learn and the skills need regular practise to be maintained. Most people cannot afford to make multiple trips abroad to do this. There are many artificial skiing surfaces available some better than others. This presentation offers one alternative. Furthermore, it is a polymer based system and was conceived, designed and is made in Yorkshire, whilst being exported around the world.

"Snowflex", by Briton Engineering Developments, presented by their academic partner The University of Bradford.

## **Engineering in Sport: Gaining an Advantage**

Professor Peter Styring Department of Chemical & Process Engineering, University of Sheffield

Sport has always been driven by technology, some more than others. Recent advances in swim wear have led to accusations of 'technological doping'. So is the use of engineering in sport seeking to gain an advantage? The answer has to be a resounding yes! So what makes one technology acceptable yet another is regarded as cheating? Wildfire is a self-waxing ski system that increases performance using non-toxic fluids and a skier induced pumping action to reduce friction between the ski base and the snow or plastic slope. In this talk we will discuss the evolution of the Wildfire system, looking at the performance enhancement and its position within the regulations that govern the sport: where engineering meets politics. We will also consider some ways forward for novel ski design.

## Composite Material Substitution in Formula 1 - Implications for industry

Mark Preston

Advanced Materials for Speed and Safety, Formtech Composites Ltd.

Formula 1 (F1) arguably leads the way in the development of composites structures because of the inherent nature of the sport. The rapid pace of development in F1 means that the series could be considered to be a prototyping competition with some parts on the car going through 20 iterations per season. High loads, harsh environments, complex components and short design cycles mean that processes for the design, manufacture and testing of composite structures have come a long way. Composite material substitution has gone further than many other industries and therefore provides an interesting insight into future developments.

Perhaps one of the most important structures in the car is the driver safety cell, or monocoque. First pioneered in the early 80's with McLaren, these structures have developed to a point where it is not possible to make a competitive structure out of any other material. This presentation will discuss the substitution of composite materials in F1 and how this may effect the development of other industries such as aerospace and automotive.

### DEVELOPING THE NEXT GENERATION OF POLYETHYLENE BASED SINGLE POLYMER COMPOSITES

P.J.Hine#, A.P.Unwin\* and I.M.Ward<sup>#</sup> # School of Physics and Astronomy, University of Leeds, Leeds, LS2 9JT, UK \* - School of Engineering, University of Bradford, Bradford, BD7 1DP, UK

p.j.hine@leeds.ac.uk, i.m.ward@leeds.ac.uk

Self-reinforced single polymer composites, where both the reinforcing fibre and matrix are both polymeric and usually the same polymer, offer new opportunities to manufacturers. They can help to confront increasing costs arising from emerging environmental constraints which focus on issues such as recyclability and the greater emphasis on the reduction in material and energy consumption during the life cycle of a product. The technical challenge is to extend the considerable advantages in respect of mechanical properties that can be achieved in small cross section, such as highly oriented fibres, to a composite sheet with all the associated material issues of matrix type, fibre properties, compatability between fibre and matrix and arrangement of the reinforcement (e.g. weave style) Of equal importance is the choice of material type depending on the end use application, and in particular can it be thermoformed. In this paper we present some recent work where we have investigated these issues for self reinforced polyethylene composites.

## POSTERS

#### 1. Cold Flow Additives for Diesel Fuels Stephanie Camerlynck, Infineum

- 2. Crystallization of hydrogenated polybutadiene: the control of structural morphology by shear flow Masayuki Okura, Department of Chemistry, University of Sheffield
- **3.** Designing a pressure sensitive adhesive based on Polyurethane technology (Sticky Shoes)

Lewis Williams, Department of Chemistry, University of Sheffield

- **4. Development of ionic liquids for catalytic reactions and polymerisation** Barry Dean, Department of Chemistry, University of Durham
- 5. Die swell and melt fracture of glass-bead filled monodisperse polyisoprene composite Dietmar Auhl, School of Physics and Astronomy, University of Leeds
- 6. Effect of Solvents on the Ultrasonic Degradation of Polystyrene and Poly(DLlactide)

Joyce Wong, Department of Chemistry, University of Sheffield

- 7. Electron Microscopy at Durham IRC Helen Riggs, Department of Chemistry, University of Durham
- **8. Extensional Flow Properties of PEO/SiO2 Dispersions** Siling Su, Department of Chemistry, University of Sheffield
- **9. Film-Casting Properties of Polyethylenes with Different Branching Structure:** Suneel Kunamaneni, School of Physics and Astronomy, University of Leeds
- **10. Kinetic Studies on the Polymerisation of Functionalised Norbornenes** Lynn Donlon, Polymer IRC, University of Durham,
- **11. Novel Interlayers for Self-Healable Sandwich Structures** Peter Bailey, Composite Systems Innovation Centre, Kroto Research Institute, University of Sheffield

#### 12. Polydispersity in Block Copolymers

Christine Fernyhough, Department of Chemistry, University of Sheffield

#### 13. Polymer Technologies for Water Purification

Sarah Kettlewell, Department of Chemistry, University of Sheffield

#### 14. Real-Time Monitoring of Injection Moulding for Part Mass Determination

Mohammad Umar, IRC in Polymer Science & Engineering, University of Bradford

15. Synthesis and Characterization of Multi End-functionalised Polymer Additives for the Modification of Surface Properties

Norazilawati Muhamad Sarih, Department of Chemistry, University of Durham

16. Synthesis of end-functionalised polymers via the use of functionalised RAFT chain transfer agents William Department of Chemistery University of Durham

William Bergius, Department of Chemistry, University of Durham

- 17. Synthesis of well-defined highly branched polymers dendrimacs and hypermacs Solomon Kimani, Department of Chemistry, University of Durham
- **18. The Effect of Polydispersity on the Self Assembly of Diblock Copolymers** Chris Howell, Department of Chemistry, University of Sheffield

#### 19. The Hot Compaction of Oriented Fibres : From Invention to Commercialisation Peter Hine, School of Physics and Astronomy, University of Leeds

**20.** Thermoreversible gelation of methylcellulose and hydroxypropyl methylcellulose in aqueous solution Hao Yu, Department of Chemistry, University of Sheffield

## **POSTER ABSTRACTS**

## **Cold Flow Additives for Diesel Fuels**

Stephanie Camerlynck

#### Infineum UK Limited, P.O. Box 1 Milton Hill, Abingdon, Oxfordshire OX13 6BB England stephanie.camerlynck@infineum.com

When middle distillate fuels are cooled to temperatures below their cloud points, wax crystals form within the fuel. Without the addition of cold flow additives, these are typically flat rhombic shaped crystals that can cause problems:

- At temperatures close to the cloud point, fuel system filters in both vehicle and static installations rapidly become blocked.
- At only slightly lower temperatures an interlocking wax crystal structure forms which totally prevents flow within the fuel system (the pour point is reached).

Addition of cold flow additives modifies the shape of the wax crystals which form. This:

- Reduces the tendency to block fuel filters.
- Extends the temperature range over which a vehicle will operate.
- Significantly lowers the fuel pour point.

Infineum has a wide range of additives which have been developed to provide extended cold flow performance across the spectrum of middle distillate fuels.

## Crystallization of hydrogenated polybutadiene: The control of structural morphology by shear flow

Masayuki Okura, Oleksandr O. Mykhaylyk, Pierre Chambon, J. Patrick A. Fairclough, Anthony J. Ryan Department of Chemistry, University of Sheffield

The shear-induced crystallization behaviour of linear hydrogenated polybutadiene (h-PBD) has been studied by X-ray scattering and polarized light imaging. A tri-modal h-PBD blend composed of short ( $M_w = 15$  kDa, matrix) and long chains ( $M_w = 1.0$  MDa and 1.7 MDa) was prepared from near mono-disperse polymers to obtain the relationship between molecular weight distribution and the formation of shish-kebab crystals. The critical parameters of flow responsible for the formation of the crystals were measured. It was found that the tri-modal blend has two sets of critical parameters corresponding to the orientation of 1.0 MDa and 1.7 MDa chains respectively.

## Designing a pressure sensitive adhesive based on polyurethane technology (Sticky Shoes)

#### L.K. Williams, A.J. Ryan Department of Chemistry, University of Sheffield

The aim of the research was to attach an upper-less shoe to the foot using a pressure sensitive adhesive. It was necessary to create an adhesive capable of secure adhesion to the foot but which could also be easily removed after use i.e. the shear and tensile properties were optimised for this purpose. The polyurethane-based adhesive was synthesised from polyether polyols and a methyl diphenyl diisocyanate (MDI) based prepolymer. Polymer cohesion, and thus the adhesive properties, was controlled via the cross-link density. The final product was free of metal catalysts, plasticisers and other potentially harmful materials; the other major advantage was that the adhesive could be cold cured. A series of prototypes were fabricated, and industry standard tests were used to characterise the adhesive's tensile strength, elongation and tack. Tests for peel strength and duromer hardness were also performed and indicated that the adhesive was fit for use in the desired application.

## Development of ionic liquids for catalytic reactions and polymerisation

Barry Dean, Ezat Khosravi Department of Chemistry, University of Durham

Ionic Liquids are defined as compounds consisting of anions and cations (i.e. salts), which melt at or below 100°C. Ionic liquids show a lot of promise as green solvents that could replace volatile organic solvents in a range of reactions. Ionic Liquids have been referred to as "Designer Solvents" as a wide variety of properties, such as solubility, density and viscosity, can be adjusted by simply making changes to the structure of either the anion, cation or both. Ionic liquids have also been shown to improve reaction yields, rates and selectivity.

This work reports the synthesis and characterization of several families of novel protic ionic liquids based on the diallylalkylammonium cation. The work attempts to understand the effect of changing the alkyl substituent on the cation and varying the counter anion on the physical and electrochemical properties measured. The diallylalkylammonium salts reported in this paper yielded viscosities as low as 2061cPs and water contents ranging from less than 0.18wt%. The salts were also thermally stable up to 272°C, had T<sub>g</sub>'s as low as -95°C and electrochemical stabilities of up to 4.1V. The work also demonstrates the relationship between the counter anion and the viscosity of the diallylalkylammonium salts.

## Die swell and melt fracture of glass-bead filled monodisperse polyisoprene composite

M. Tassieri, D. Auhl, P. J. Hine Polymer IRC, University of Leeds

In order to understand the complex flow behaviour of polymer composites a study on the non-linear flow behaviour of a pure monodisperse polyisoprene (PI) melt and on samples filled with micrometer-sized spherical particles (glass beads) has been carried out. The pure matrix and the composites with a volume fraction of 1% and 5% glass beads have been investigated by rotational and capillary rheometry regarding the effect of filler concentration on the linear and non-linear flow behaviour, die swell, and melt fracture. The conclusions are that the melt fracture and surface instabilities are reduced with increasing glass-bead concentration while the zero-shear viscosity increases slightly with glass-bead concentration.

# Effect of Solvents on the Ultrasonic Degradation of Polystyrene and Poly(DL-lactide)

Joyce Wong Department of Chemistry, University of Sheffield

High intensity ultrasonic waves are generally employed in the areas of cleaning, plastic welding, machining, etc. In addition to these conventional applications, numerous studies have suggested a new possibility as a useful way to induce mechano-chemical degradation in polymeric materials. It was observed that if polymer solution is subjected to irradiation of high intensity ultrasonic waves, main-chain scission of polymer chains occurs and consequently the molecular weight is decreased.

Ultrasound has been used for degradation of a wide range of polymers. Most of the effects caused by ultrasound are due to the growth and rapid collapse of micro bubbles as the wave propagates through the solution. Due to the relative motinon of the polymer segments and solvents, stresses are produced in the polymer chain causing scission.

## **Electron Microscopy at Durham IRC.**

Helen Riggs MSc MRSC Department of Chemistry, University of Durham

The IRC at Durham has a Philips/FEI XL30 TMP Environmental<sup>®</sup> Scanning Electron Microscope (ESEM), producing micrographs by back-scattered or secondary electron detection.

The ESEM can be used in the same way as any conventional high-vacuum microscope to image dry, electrically-conducting samples.

However, the microscope is also capable of working with up to ~15 Torr of pressure in the sample chamber – the so-called "environmental" mode - whilst at the same time maintaining the gun column at high vacuum. In addition, a Peltier cooling stage or a  $1500^{\circ}$ C furnace can be used inside the chamber.

This not only enables dry, non-conducting samples to be imaged without electricallycoating them, but also allows wet, greasy or out-gassing samples to be viewed, and *insitu* experiments to be followed.

#### **Extensional Flow Properties of PEO/SiO2 Dispersions**

Siling Su Department of Chemistry, University of Sheffield

Colloidal dispersions, such as polymer-particle dispersions, are widely used in the industrial and technological fields, including paints, cosmetics, food, etc. The extensional flow properties of these colloidal dispersions are critical to product performance. In this study, the extensional properties of poly (ethylene oxide)/silica dispersions with different silica concentrations (0, 1, 5, 10 wt%) were investigated. The results showed that both shear viscosity and apparent transient extensional viscosity of 2.5 wt% PEO are increased with the increasing silica contents. The apparent transient extensional viscosity and Trouton ratio are dramatically increased at a critical Hencky strain, indicating the strain hardening behaviour. The strain hardening behaviour is depressed by the adding of silica particles, especially at higher silica contents."

#### Film-Casting Properties of Polyethylenes with Different Branching Structure

D. Auhl, S. Kunamaneni, J. Embery, T.C.B. McLeish Polymer IRC, University of Leeds, Leeds, United Kingdom T. Malmgren, J.W. Mays, Department of Chemistry, University of Tennessee, Knoxville, TN, United States C.D. McGrady, C.W. Seay, D.G. Baird, Department of Chemical Engineering, Virginia Tech, Blacksburg, United States

We investigated the influence of branching structure on the cast-film processing, i.e. the neck-in profile and final cast-film dimensions, for a series of metallocene catalysed PE as well as tubular reactor PE with various branching levels. For this study a lab extruder has been employed due to the small sample quantities available. The materials and flow conditions have been chosen specifically in order to match for various polyethylenes with different molecular structures at the die exit. Non-linear visco-elastic properties in shear and uniaxial elongation have been determined from constant strain-rate tests and fitted with a multi-mode Pom-Pom model, the parameters of which are discussed with respect to the molecular analysis of the branching structure. The experimental results for the film-casting behaviour as a function of long-chain branching content and draw ratio will be further compared to model predictions using recent theoretical approaches together with the Pom-Pom constitutive equation.

#### Kinetic Studies on the Polymerisation of Functionalised Norbornenes

Lynn Donlon,<sup>a, b</sup> Philip W. Dyer,<sup>a\*</sup> Ezat Khosravi,<sup>a, b\*</sup> and Andrew Bell<sup>c</sup>

<sup>a</sup>Durham University, South Road, Durham, DH1 3LE, UK. <sup>b</sup>Polymer IRC, Durham University, South Road, Durham, DH1 3LE, UK. <sup>c</sup>Promerus LLC, 9921 Brecksville Road, Brecksville, OH 44141, USA.

The metal-catalysed vinyl addition polymerisation of functionalised norbornene (NB) derivatives is an area of considerable interest. The resultant polymers exhibit properties such as high T<sub>g</sub>, excellent thermal stability, and superior etch resistance, attributes that make them ideal candidates for use in deep UV photolithography, a technique employed in the preparation of surface features on microchips.<sup>1</sup> The desired substituted NB monomers are prepared *via* Diels-Alder reactions that typically afford approximately an 80:20 mixture of *endo* and *exo* isomers, respectively, which are generally extremely hard to separate. Previous work has established that *endo*-substituted norbornenes are polymerised much more slowly than their *exo* counterparts.<sup>2, 3, 4</sup> As a result, reactions in which a mixture of isomers is polymerised afford *pseudo*-co-polymers, something that significantly affects the physical properties of the final materials.

In order to probe how the substitution pattern of functionalised NB monomers impacts on the relative rates of *exo* versus *endo* isomer polymerisation, a detailed analysis of the polymerisation kinetics of a series of pure *exo* NB monomers is compared with that of mixtures of *endo-* and *exo-* substituted norbornenes.

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#### **Novel Interlayers For Self-Healable Sandwich Structures**

P B S Bailey, S A Hayes, A D Lafferty

Composite Systems Innovation Centre, Kroto Research Institute, University of Sheffield, Broad Lane, Sheffield, S3 7HQ <u>p.bailey@sheffield.ac.uk</u>

Sandwich composites are already an essential part of structural design, with ever expanding interest, particularly in the transport sector. While they offer great benefits, the fact remains that sandwich composites are highly susceptible to impact damage, but difficult to repair. Standard repair schemes require, as a minimum, the replacement of an entire section of front face and core. It is argued that such a degree of time and expense is not always warranted or even possible for minor damage in many applications. This research seeks to offer an alternative solution by building in the ability to conduct a simple, noninvasive repair.

Novel interlayer materials are demonstrated which can fill the void left by core crushing and reinstate adhesion between skin and core. Following impact damage, the repairing function is activated by moderate heating of the affected area to a point above service temperature, causing local volume expansion and flow of the interlayer material. The interlayer material can be processed at low to moderate temperature and easily incorporated (for example laid up as a part-cured sheet, or sprayed *in situ*) as the structure is assembled, replacing any other adhesive used between core and skin.

#### **Polydispersity in Block Copolymers**

C. M. Fernyhough, C. Howell, and J. P. A. Fairclough Department of Chemistry, University of Sheffield, Brook Hill, Sheffield. S3 7HF

For many years, the polymer chemist has been striving to make "perfect polymers" whereby properties such as molecular mass, composition and architecture are controlled and the polydispersity minimised. Originally, anionic polymerization was the favoured method for the controlled synthesis of block copolymers and it led to a fundamental understanding of structure-property relationships e.g. morphological behaviour in the solid state and in selective solvents. However, the stringent conditions required and the limited number of monomers that can be used for this technique are major drawbacks. Given the ascendency of controlled radical techniques whereby reasonable control can be exerted over mass and composition but with broader molecular weight distributions and greater compositional heterogeneity, how does this affect the polymer properties? In conjunction with Vince Ladmiral, Sebastien Perrier, Wilasinee Sriprom and Chiara Neto at the University of Sydney, a study has been made looking at the morphology and long-range order of acrylate and methacrylate copolymers synthesised via controlled radical techniques and comparing them with those made via classical anionic polymerisation.

#### **Polymer Technologies for Water Purification**

Sarah Kettlewell, Prof .A. J. Ryan & Dr J.P. A. Fairclough, Department of Chemistry, University of Sheffield

Close to half the population of the developing world are suffering from waterborne diseases associated with inadequate provision of water and sanitation. 2.5 million people die annually from water related diseases most of whom are children under 5. The project is working towards developing a point of use water purification unit for short term use and emergency and disaster relief. Current technology for personalised water purification is largely based around military applications, where cost is less of an issue. One clear opportunity is to use second use goods, such as old drinks bottles. The project aims to use recycled produces and very low cost materials to produce a personalised, reusable water purification system operating by forward osmosis. Temperature responsive polymers will be used to generate internal pressures and remove microbes such as the rotavirus (the main viral cause of diarrhoeal disease) via size exclusion.

#### **Real-Time Monitoring of Injection Moulding for Part Mass** Determination

M. Umar<sup>1</sup>, L Muvaney-Johnson<sup>1</sup>, R G Speight<sup>2</sup>, P Brincat<sup>2</sup>, P D Coates<sup>1</sup>
1) IRC in Polymer Science and Engineering, University of Bradford, UK
2) Autodesk Australia Pty Ltd, Moldflow

A methodology is presented for determining moulded part mass from a combination of continuous process measurement and known polymer material pressure-specific volume-temperature (pvT) characteristics. The methodology determines the mass of melt that has been delivered to the mould cavity through the swept volume of the injection screw, but taking into account melt compressibility. The screw position is continually monitored by a computerized system along with the melt pressure and temperature. Results show a good correlation between the predicted and measured specimen mass over a range of processing conditions.

#### Synthesis and Characterization of Multi End-Functionalized Polymer Additives for the Modification of Surface Properties

Norazilawati Muhamad Sarih, Lian R. Hutchings, Richard L. Thompson IRC in Polymer Science and Technology, Department of Chemistry, Durham University, Durham DH1 3LE, UK.

There are many occasions when it is desirable to have specific properties at the surface of a polymer which differ from the bulk, for example, hydrophobicity, wettability, biocompability or chemical resistant, while retaining the advantages characteristics of bulk polymers.

The use of functionalised polymer additives carrying multiple fluoroalkyl groups at one chain end have been investigated as surface modifying additives. A range of such polymers with different molecular weights have been prepared by living anionic polymerization. It has been discovered that these additives undergo rapid adsorption to a surface or interface and significantly modify surface properties. We have systematically studied the effect of additive molecular weight, concentration and annealing conditions on the surface properties of thin films containing these additives. We describe the synthesis and characterization of a range of polymer additives made from polystyrene, polyisoprene and hydrogenated polyisoprene with 1 to 3 fluoroalkyl groups and with molecular weights in the range of  $5000 - 50000 \text{ gmol}^{-1}$ .

#### Synthesis of end-functionalised polymers via the use of functionalised RAFT chain transfer agents

William Bergius Department of Chemistry, University of Durham

An ongoing challenge in polymer science is the preparation of materials with specific surface properties that differ from the bulk, for example, hydrophobicity, wettability, adhesion or biocompatibility, whilst retaining the advantageous mechanical properties of the bulk polymer. We have explored the use of multi-end functionalised polymer additives which undergo rapid spontaneous adsorption to a surface or interface as an efficient method of modifying surface properties. Radical addition-fragmentation transfer (RAFT) polymerisation is an extremely versatile controlled radical polymerisation (CRP) technique. The main advantages of RAFT over other CRP techniques such as ATRP and even NMP is that a far wider range of monomers can be polymerised, more functionalities are tolerated, as well as a broad range of solvents including water, a wide range of temperatures are appropriate (20-150°C), and it is suitable for use in several different types of process (bulk, suspension, emulsion etc). Our work is focussed on the polymerisation of a monomer containing a functional group that would make it incompatible with most other controlled methods of polymerisation. RAFT chain transfer agents containing aryl-ether moieties bearing up to three C8F17 groups have been used to produce various well-defined, low molecular weight, endfunctionalised polymer additives that can be used in modest quantities (<5%) to render the surfaces of their corresponding bulk polymers hydrophobic.

### Synthesis Of Well-Defined Highly Branched Polymers - Dendrimacs And Hypermacs

KIMANI S. M.\*, DODDS, J. M. AND HUTCHINGS L. R. IRC in Polymer Science and Technology, Department of Chemistry, University of Durham, Durham DH1 3LE, United Kingdom. Email: s.m.kimani@durham.ac.uk

Synthesis of "model" branched polymers with predicable molecular weights, narrow molecular weight distribution and well defined architecture such as star branched polymers and H-shaped polymers have contributed much to the understanding of the correlation between the molecular structure and physical properties of polymeric materials. To advance these studies, various strategies are being developed to synthesis more complex architectures like dendritically branched polymers, in which it is possible to control all the molecular parameters.

In this work we describe a versatile approach for synthesis of DendriMacs and HyperMacs. These materials are essentially long-chain branched analogues of classical dendrimers and hyperbranched polymers. The building blocks for DendriMacs and HyperMacs, AB<sub>2</sub> macromonomers are synthesised by living anionic polymerisation and are therefore well-defined in terms of molecular weight and molecular weight distribution. Synthesis of DendriMacs follows an iterative convergent approach that involves chain end modification, coupling reaction (e.g. Williamsons, chlorosilane and click reactions) and purification steps to build-up well-defined structures. This ensures that the number and location of each branch point can be predetermined, controlled and characterised. HyperMacs are on the other hand made via a one-pot coupling reaction in a relatively shorter time but leading to products with a distribution of molecular weights and architecture. These methodologies work well with a wide range of polymer types and also offer a facile route to making copolymeric DendriMacs and Hyperblocks. Since the synthesised polymers have well-defined and closely controlled parameters between branch points they can be used as models in understanding the influence that branching has on rheology and process properties of polymers.

#### The Effect of Polydispersity on the Self Assembly of Diblock Copolymers

<u>C. Howell</u>, C.M. Fernyhough, J.P.A. Fairclough, V. Ladmiral, S. Perrier, T. Beardsley, M. Matsen Department of Chemistry, University of Sheffield, Sheffield, S3 7HF School of Chemistry, University of Sydney, Australia, Dept. of Physics, University of Reading, UK

Block copolymers have been of particular interest due to their ability to undergo microphase separation. In general, block copolymers are produced with a low polydispersity index as they have been made primarily through anionic polymerisation, which is a demanding and laborious technique. As a result, they have not been commercially exploited due to the relatively high cost of manufacture. The recent development of controlled radical techniques such as ATRP and RAFT while lacking the control finesse of anionic produced polymers opens up the possibility that production of block copolymers will become economically viable in the future. ATRP and RAFT produced polymers have higher PDIs than their Anionic counterparts and in particular it important to note how this change in polydispersity will alter the microphase separation and resultant structure of block copolymers.



An increase in the Polydispersity Index (PDI) in one block would initially increase domain spacing of the more polydisperse block. Longer chains increase the domain size, while smaller chains will pack better at domain interfaces. What is not so fully understood is the effect upon the segregation lengths, subsequent stability of morphologies and order to disorder temperature (ODT) in regard to fluctuations in temperature and volume fraction. Radical Addition Fragmentation Chain Transfer (RAFT) polymerisation has produced PS-b-PHMA with a slight increase in the polydispersity. SAXS studies of current samples has only confirmed either a lack of range order or disorder. In itself this has shown that RAFT can facilitate the preparation of block copolymers with varying PDI and near-symmetric molecular weight distributions and thus potentially provide a route toward the targeted synthesis of microstructures with particular topological characteristics.



An OOT transition in a compositionally symmetric PS-PHMA copolymer would indicate that the predictions of the effect of block-selective polydispersity on the microstructure formation process are robust with respect to the shape of distributions but that the relative abundance of small and large chains can alter the stabilisation of morphologies.

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## The Hot Compaction of Oriented Fibres: From Invention to Commercialisation

Dr Peter Hine and Professor Ian Ward, Polymer IRC, University of Leeds

Composites are 'engineered' materials formed from two components, a reinforcement phase and a matrix phase. The wide variety of choices that is available for these two components, in terms of mechanical properties, reinforcement shape and orientation, gives enormous potential for tailoring performance, which has made them a popular choice for designers and engineers, particularly for aerospace and aeronautical applications. Polymer composites are a class of composite materials where at least one of the components is a polymer. At the high performance end the reinforcing fibre, usually continuous carbon filaments, has a very high stiffness and strength and the role of the polymeric matrix while primarily a binder, can also be important in controlling aspects such as fracture toughness, fatigue and high temperature performance. At the other end of the performance scale, chopped glass fibres are frequently used to improve the properties of injection moulded thermoplastics, increasing stiffness, strength, temperature performance and impact toughness compared to a pure polymer. These injection moulded short fibre components are used regularly in the automotive industry (clutch pedals, gear wheels, housings etc) where a polymer is preferred (lightweight, corrosion resistance) but enhanced performance is required.

The development of high stiffness and high strength polymeric fibres, such as Kevlar and Dyneema for ballistic applications, has seen parallel research into making all polymer based composites. The advantage of these polymer fibres is that they often have high specific stiffness and strength and so result in a composite with similar attributes. Composite materials from these fibres also show high impact strength, leading to these all polymer composites being used in applications that require lightweight and high toughness. A natural extension of these 'all polymer composites', is to have both phases of the composite made from the same polymer, generally termed self reinforced, or single, polymer composites.. The resulting composites show the combination of lightweight, good mechanical properties and exceptional impact performance described above. In addition, as identical polymers are used for the two phases the single polymer composite materials can be recycled, a process which is much easier than when using conventional glass or carbon fibre polymer matrix composites described earlier. A further advantage is that the single polymer composites can be thermoformed into a range of component shapes. As such these materials can be considered as forming a bridge between pure polymers and traditional glass fibre reinforced polymers, having the density, thermoformability and recyclability of polymers combined with mechanical properties that are competitive with chopped glass reinforced composites.

Single, or self reinforced' polymer composites are a new emerging class of composite materials that show a unique combination of properties, bringing together lightweight and outstanding impact performance with recyclability. This collection of properties has seen a number of applications recently appear in the market place, including shinguards for Nike (BPS Contour) and the Samsonite Black Label X'Lite suitcase range. In this poster we will describe how these materials are made, by the Leeds process of Hot Compaction, and their distinctive portfolio of mechanical properties. Some examples of typical parts will also be available.

## Thermoreversible gelation of methylcellulose and hydroxypropyl methylcellulose in aqueous solution

Hao Yu, Oscar Kelly, Patrick Fairclough, Anthony J. Ryan, Department of Chemistry, University of Sheffield

Methyl Cellulose (MC) and Hydroxypropyl methylcellulose (HPMC) are produced commercially in a heterogeneous manner. This results in what is commonly believed to be a blocky structure that undergoes self assembly in aqueous solution at moderately elevated temperatures. Rheology indicates that a network structure is formed on heating. The nature of the interactions that form the physical network junction points is still under debate.

As the system forms the physical network, the optical properties change from a clear solution to a cloudy gelation, in extreme cases separating into polymer and water rich phases. This phase separation can be seen on the nanoscale by SAXS, showing that there is no dominant size scale in this range, similarly SALS also shows no dominant size scale. However optical microscopy reveals textures that would seem to indicate a spinodal structure. Rheology and SAXS indicate that the network evolves over time, rheology and scattering studies show that at temperatures 20-30K below the typically quoted gel point the network is already forming. This would suggest that gel structure is kinetically limited, as in most studies to date a constant heating rate has been employed, resulting in the gel structure being pinned at the gel temperature.