Physical Aspects of Polymer Science 2024

(PAPS 2024)

9–11 September 2024
University of Edinburgh,
Edinburgh, UK

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Programme

Monday 9 September	
12:00	Registration and Lunch
	Session I Chair: Joao Cabral
13:45	Welcome from the Chair of the PPG Committee and Local Organisation **Nigel Clark**, University of Sheffield, UK
14:00	Invited: Exploring the physics, materials science, and biological implications of polyelectrolyte complexation **Matthew Tirrell, University of Chicago, USA**
14:35	Colloidal polymer binders in synthetic biofilms for wastewater treatment **Joseph Keddie**, University of Surrey, UK
14:50	Environmental effects on the spatio-temporal evolution of plasma-wrinkled PDMS thin films **Zain Ahmed**, Imperial College London, UK
15:05	Functional polymer surfaces that resist Bio-fouling **Andrew Parnell**, University of Sheffield, UK
15:20	Observation of molecular motions in crystalline polymer surfaces using the diffracted x-ray blinking method **Rena Inamasu**, The University of Tokyo, UK
15:35	Exploring the impact of clay additives on the performance of a water-based reversible adhesive **Adriana Sierra Romero**, Newcastle University, Uk
15:50	Tea Break
	Session II Chair: Valeria Arrighi
16:20	DPOLY/PPG Exchange Lecture: Beyond alignment: novel mechanisms for controlling block copolymer phase behavior using magnetic fields **Michelle Calabrese**, University of Minnesota, USA
16:55	Studying the structure of liquid crystal elastomers using small- and wide- angle x-ray scattering **Emily Cooper**, University of Leeds
17:10	Counterion-solvent properties: how they influence the structure and solubility of carboxymethylcellulose **Can Hou**, RWTH Aachen, Germany
17:25	Polymer Opals 20 years on; current and future directions for shear-nanoassembly in soft-matter media **Chris Finlayson**, Aberystwyth University, UK

17:40	Understanding liquid crystal elastomer behaviours polymerised with flow chemistry **Jiancong Xu**, University of Leeds, UK
18:00	Poster Session
19:00	Drinks Reception
20:00	End of Day 1
Tuesday 10 September	
08:00	Registration, Coffee and Pastries
	Session III Chair: Chris Finlayson
09:00	Invited: Active Polymers in Biology **Tanniemola Liverpool**, University of Bristol, UK
09:35	Influence of solvent type and counterion on the viscosity and conformation of polyelectrolytes in solution **Anish Gulati**, RWTH Aachen University, Germany
09:50	Hidden symmetry in polymer field theory and its implications for self-consistent field theory and field-theoretic simulation **Jaeup Kim**, UNIST, South Korea
10:05	Equilibrium and dynamical polymer networks for flow **Kristian Muller-Nedebock**, Stellenbosch University, South Africa
10:20	Polymer dynamics in active nematic turbulence **Zahra Valei,** The University of Edinburgh, UK
10:35	Wetting, adsorption, and desorption behaviour of single polymer chains: a closer look **Vasileios Koutsos**, The University of Edinburgh, UK
10:50	Coffee Break
	Session IV Chair: Ali Nedoma
11:25	Invited: Capturing the structural evolution and mechanics of protein assemblies during network formation **Lorna Dougan**, University of Leeds, UK
12:00	Breath Figure Assembly on Evaporating Polymer Solution Droplets in Levitation **Joao Cabral**, Imperial College London, UK
12:15	A biodegradable scaffold for bioelectronic applications **Mark Geoghegan**, Newcastle University, UK
12:30	The effects of substrate glass transition temperature and hydrophobic heterogeneities on the wetting dynamics of a model infant milk formula **Solomon Melides,** University of Surrey, UK
12:45	Characterization of water adhesion on hydrophobic electrospun polymer fibers **Gabriele Livi**, University of Edinburgh, UK

13:00	Hydrogels for solar-driven water purification **Rodney Priestley**, Princeton University, USA
13:15	New methodology for anisotropic nanoparticles characterization by Depolarized Light Scattering measurements: length and diameter determination of rod-like nanoparticles **Hanna Anop**, Cordouan Technologies, France
13:30	Group Photo and Lunch
	Session V Chair: Paola Carbone
14:40	Invited: Optimising the performance of biodegradable polymers: design of fillers and plasticisers to tune polymer crystallization **Karen Johnston**, University of Strathclyde, UK
15:15	A comparison of crosslinking methods for the formation of atomistic crosslinked structures **Kieran Harris**, University of Manchester, UK
15:30	A framework for a high throughput screening method for polymeric systems using molecular dynamics **Lois Smith**, University of Manchester, UK
15:45	Quantifying the free volume distribution in acrosslinked epoxy coatings through a combined PALS and molecular dynamics simulation study **Joe Orgill**, University of Sheffield, UK
16:00	Electrospun polymer nanofibres for enhanced through-thickness electrical conductivity of CFRP composites **Muhammad Waqas**, The University of Edinburgh, UK
16:15	Tea Break
	Session VI Chair: Nigel Clarke
16:45	Telephone cord blister formation in solvent swollen elastomer films **James Sharp**, University of Nottingham, UK
17:00	Auxetic liquid crystal elastomers: fundamentals, applications and future outlook **Thomas Raistrick**, University of Leeds, UK
17:15	Solvent uptake in epoxy resins used as anti-corrosive coatings **Francis Gurman**, The University of Sheffield, UK
17:30	Topological understanding of degradability of polymer networks with cleavable strands or crosslinks **Maciek Kopec**, University of Bath, UK
17:45	Comfort Break
18:00	Founders Prize: Development of quantitatively accurate simulations for block copolymer materials **Mark Matsen**, University of Waterloo, Canda
19:00	Conference Dinner
22:00	End of Day 2

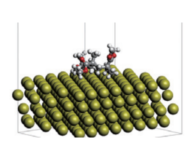
Wednesday 11 September	
08:00	Coffee and Pastries
	Session VII Chair: TBC
09:00	Invited: Entropic phase-separation in polymer grafted nanoparticle blends **Alamgir Karim**, University of Houston, USA
09:35	The effect of solvent quality on porous Poly(2,6-diphenyl-p-phenylene oxide) formation **Mihai-Andru Angheliu**, Imperial College London, UK
09:50	Relaxation dynamics in poly(methyl methacrylate)/poly(4-tert-butylstyrene) systems produced via thermal initiated random co-polymerization **Stavros X. Drakopoulos**, Princeton Materials Institute, Princeton University, USA
10:05	Testing the theory of Akcasu et al. for the time evolution of the scattering intensity during polymeric spinodal decomposition and dissolution using simulated scattering data **Matthew Jones**, Department of Physics and Astronomy, University of Sheffield, UK
10:20	Optically white porous polyethylene manufacture via thermally induced phase separation **Liva Donina**, Imperial College London, UK
10:35	Optimizing the performance of NMC622 Battery half-coin cells by using amphiphilic aqueous binders to modulate the percolation of carbon black **Chirag Patel**, University of Sheffield, UK
10:50	Coffee Break
	Session VIII Chair: Valeria Arrighi
11:20	Binder matters! Balancing viscosity with molecular weight in lithium-ion battery cathodes **Alisyn Nedoma**, University of Sheffield, UK
11:35	Reprogrammable 3d printed liquid crystal elastomer actuators **Meg Coleman**, University of Leeds, UK
11:50	Equilibrium and non-equilibrium behaviour in thin-film mixtures of polymers and small-molecule organic electronic materials **Anthony Higgins**, Swansea University, UK
12:05	The microstructure formation in multifunctional electrolytes using small angle neutron scattering **Natasha Shirshova,** Department of Engineering, Durham University, UK
12:20	Conductive Polymer Binders for Lithium-Ion Batteries **Laurence Middlemiss**, The University of Sheffield, UK
12:35	Multi-scale model of the conductivity of diblock copolymer system filled with conductive fillers **Alexander Chervanyov**, University of Münster, Germany

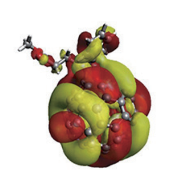
12:50	Closing Remarks
13:00	Lunch and removal of posters
14:00	Conference Closes and Depart

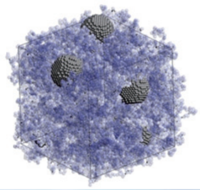
Posters

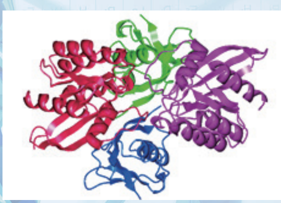
P1	Physical Properties of chitosan with varying degrees of deacetylation **Solomon Melides**, University of Surrey, UK
P2	Equilibrium and non-equilibrium behaviour in polymer/small-molecule mixtures for organic photovoltaic (opv) applications **Oliver Anyanor**, Swansea University, UK
P3	The role of internal strain in a nematic liquid crystal elastomer **Emily Cooper**, University of Leeds, UK
P4	Dissolution of wool yarns by 1-ethyl-3-methylimidazolium acetate studied with time-temperature superposition **Amjad Alghamdi**, University of Leeds, UK
P5	Investigating the influence of crosslinker concentrations on the phase templating of liquid crystal elastomers **Alanoud H. Al Suwaidan**, University of Leeds, UK
P6	Utilising microorganisms encapsulated within hydrogels for agricultural applications **Thomas Wallis**, University of Sheffield, UK
P7	Thermomechanical recycling of PET based textiles **Zara Standring**, Heriot-Watt University, UK
P8	Modelling polymer crystalline microstructure and gas barrier properties **Ville Remsu**, University of Strathclyde, UK
P9	Optimisation of frontal photopolymerisation for non-planar material assembly **Muhammad Ghifari Ridwan**, Imperial College London, UK
P10	Machine learning-enhanced metadata analysis for identifying polymer compositions **Sunny Chaudhary**, University of Southampton, UK
P11	Using coupled phase field models to understand microstructures induced by dual transition processes **Shing Wan**, University of Sheffield, UK
P12	Enhancing electrical properties of epoxy resins using bio-based modifiers **Orestis Vryonis**, University of Southampton, UK
P13	Hyperbranched polymer drug delivery vehicle **Andrews Pasick**, University of Sheffield
P14	Multiplexed microfluidic setup for analysing interaction of complex blend of triacylglycerols with surface active agents **Zain Ahmed**, Imperial College London, UK
P15	Nanophotonic taste buds for biomedical applications **Rebecca Setford**, University of Glasgow, UK
P16	Development of new sustainable adhesives promoting recycling using reversible conductive polyelectrolyte adhesion **Bassam Aljohani**, Newcastle University, UK

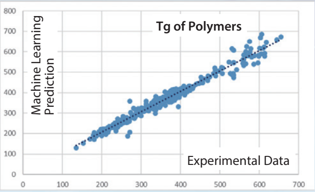
P17	Mechanical characterization of PDMS samples with varying prepolymer molar mass **Abdulraheem Alrefai**, Newcastle University, UK
P18	Unravelling capsule formation mechanisms in interfacially initiated PEGDA hydrogels **Joseph Keddie**, University of Surrey, UK
P19	Structure and rheology of semicrystalline dissociative polyurethanes **Thomas Jackson**, University of Sheffield, UK










Tg of Polymers
Machine Learning Prediction
Experimental Data
800
700
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700

Invited: Exploring the physics, materials science, and biological implications of polyelectrolyte complexation

Matthew Tirrell[1]
[1]University of Chicago, USA

The richness of liquid-liquid phase separation behavior in mixtures of oppositely charged polyelectrolytes has been greatly illuminated recently in the polymer physics literature. Precise determinations of phase diagrams, measurements of interfacial tension, scattering measurements of chain configurations, and increasingly insightful theory are all producing a clearer understanding of these phenomena. In parallel, physics is also being brought to bear on manifestations of these behaviors in biology. Diverse biological examples related to liquid-liquid phase separation of polyelectrolyte complexes include membraneless organelles, biological condensates that enhance transcription or protect from stress shock, and origin of life. This talk will spell out current understanding of the various contributions to the phase behavior, including the role of various entropic contributions, as well as the effects of charge density of the macromolecules. New results on stabilized droplets will be presented, which lend more credibility to coacervate droplets being a player in protocell development in the prebiotic world.

Colloidal polymer binders in synthetic biofilms for wastewater treatment

Joseph Keddie[1], Alexia Beale[1], Ezra Porter[1], Emily Brogden[2], Phil Chen[3], Suzanne Hingley-Wilson[1], Stefan Bon[2], and Bing Guo[1]
[1]University of Surrey, UK, [2]University of Warwick, UK [3]University of Newcastle, UK

A common biomimetic strategy to design the properties of polymeric coatings is to copy Nature, such as the texture of a lotus leaf. In our strategy, we directly use Nature to add functionality to polymer coatings. Specifically, we have successfully made synthetic biofilms, which confine non-growing, metabolically-active bacteria within a synthetic colloidal polymer (latex) film. We added halloysite nanoclay to build a network of pores to increase the permeability for mass transport. Our materials, called biocoatings, can be considered to be a type of living paint.

Conventionally, the film formation of biocoatings is achieved by drying a mixture of bacteria and colloidal polymers. However, this fabrication method decreases the viability of the encapsulated bacteria because of the osmotic stress induced by desiccation. To address this limitation, we developed a non-desiccating film formation process, which exploits two colloidal science phenomena: coagulation and wet coalescence. The latex binder is coagulated via the deposition of salt on a porous substrate before applying the wet colloidal film. A colloidal gel is created, and then the colloidal particles are coalesced in water under action of the polymer/water interfacial free energy. Coalescence occurs under immersion in heated water, thereby avoiding a

water meniscus. The method thus eliminates the Laplace pressure and associated cracking that is typically found in colloidal glassy films. The resulting materials have a continuous pore structure that can be tuned via the temperature and the duration of the water immersion.

Our biocoatings have applications in environmental remediation and in reducing carbon dioxide in the atmosphere. In one application, we are developing biocoatings as a synthetic replacement for natural biofilms in wastewater treatment. We add nitrifying bacteria to biocoatings to convert ammonium to nitrites and nitrates. Greater reactivity is achieved through optimisation of the microstructure. For the capture of carbonates and the generation of oxygen, we have employed desiccation-resistant cyanobacteria undergoing photosynthesis in biocoatings.

Environmental effects on the spatio-temporal evolution of plasma-wrinkled PDMS thin films

Zain Ahmed[1], and Joao Cabral[1]
[1]Imperial College London, UK

We investigate the surface plasma oxidation of polydimethylsiloxane (PDMS) elastomers and the impact of environmental conditions on the spatio-temporal evolution of the resulting wrinkling patterns. We employ a combination of small-angle light scattering (SALS), XPS, and optical and atomic force microscopy to examine the evolution of the crack density, and wrinkling profile following plasma exposure. Previous reports have rationalised the spontaneous isotropic wrinkling of PDMS supported thin films following plasma exposure in terms of a thermally-driven differential deformation of the elastomer normal to the direction of incident exposure. Our findings challenge this widely accepted mechanism and provide evidence that, while temperature plays a role, other environmental factors largely govern this process and can account for the considerable variability of results reported in the literature using this method. These findings open new possibilities for exceptional control of PDMS plasma functionalisation, in terms of tunable surface patterning, adhesion, and wettability.

Functional polymer surfaces that resist Bio-fouling

Andrew Parnell[1]
[1]University of Sheffield, UK

Tributyltin (TBT) was once a highly effective antifouling compound used to coat ships, preventing the accumulation of barnacles, diatoms, and other organisms that cause drag. However, it was banned in 2008 due to its severe environmental and ecological impact.

In this talk/poster, I will detail a biocide free antifouling coating that utilizes Perfluoropolyether (PFPE) copolymer incorporated into a Polydimethylsiloxane (PDMS) layer, focusing on the surface structural and chemical properties of this coating in water. Thin films of these materials were produced for neutron analysis, and challenges like autophobic dewetting were explored using SIMS analysis. Successful development of model systems enabled surface analysis using neutron reflectivity and atomic force microscopy, revealing that these coatings undergo strong surface reconstruction in water, forming an approximately 3 nm monolayer of PFPE copolymer that wets the PDMS-water interface. This monolayer renders the surface hydrophilic and alters its mechanical properties.

Bioadhesion studies using QCM, neutron reflectivity, and AFM showed a significant reduction in protein adsorption by at least 75% compared to PDMS controls. The foul resistance is attributed to strong hydrogen bonds between the surface and local water molecules, creating a hydration barrier to adhesion. Finally, the diffusion of the PFPE copolymer amphiphile was studied, with a diffusion coefficient of $3.6 \pm 0.2 \times 10^{-12}$ m^2/s, corroborated by ion milling XPS depth profiles, which showed strong surface enrichment of PFPE in the PDMS layers.

Observation of molecular motions in crystalline polymer surfaces using the diffracted x-ray blinking method

Rena Inamasu[1], Daisuke Sasaki[1], Kazuhiro Mio[2], and Yuji.C Sasaki[1,2]
[1]The University of Tokyo, Japan, [2]National Institute of Advanced Industrial Science and Technology, Japan

The surface of polymers exhibits unique functional properties such as repellency, adhesiveness, and antifouling. The demand for these properties is increasing due to the growing emphasis on recyclability and the need for alternative materials. Enhancing our understanding and control of polymer surfaces can significantly improve their functionality in fields such as biomedical devices, coatings, and electronics. Given the critical role of polymer surface studies in advancing technology and innovation across industries, it is imperative to elucidate the mechanisms behind these functional properties to develop more environmentally friendly products. However, accurately measuring polymer surface dynamics remains a significant challenge.

Our research focuses on diffracted X-ray blinking (DXB), a measurement method that calculates molecular motion from intensity changes in sequential diffracted images with short time resolution. We have applied grazing incidence (GI) to DXB to assess polymer surface motion. GI-DXB experiments were conducted at SPring-8, a synchrotron radiation facility in Japan, as well as with our laboratory X-ray source. Using this setup, we studied a crystalline and water-repellent polymer, poly{2-(perfluorooctyl)ethyl acrylate} (PC8FA), with a time resolution of 500 ms over 2000 frames. The results of GI-DXB revealed that the decay constant, indicating molecular mobility, was higher for the polymer surface compared to the bulk as measured by conventional DXB. Additionally, we conducted temperature-dependent DXB and GI-DXB measurements and examined the relationship between water repellency and surface mobility.

This research suggested the effectiveness of GI-DXB in measuring polymer surface mobility, highlighting its potential for elucidating the mechanisms of functional surface polymers through molecular mobility analysis. These insights will be useful for the development of high-performance functional polymers, paving the way for innovative and eco-friendly materials in various technological applications.

Exploring the impact of clay additives on the performance of a water-based reversible adhesive

Adriana Sierra Romero[1], Emmanuel Abotsi[1], Mark Geoghegan[1], and Katarina Novakovic[1]
[1]Newcastle University, UK

The development of a reversible water-based electrostatic adhesive consisting of a couple of oppositely charged polyelectrolyte emulsions has recently been reported.[1] Both formulations are based on poly(styrene-co-butyl acrylate) with either chitosan or poly(acrylic acid) as polycation and polyanion, respectively. These copolymer formulations possess good film forming properties and can be applied on a variety of substrates, from plastics to metals, including some low energy materials such as polypropylene. This adhesive system is stable in humid neutral conditions, but reversible in highly acidic or alkaline solutions. The individual formulations and the complementary system display a lap shear strength of up to 1 MPa, which is in the region between pressure sensitive and structural adhesives.

Although such materials promise to be scalable, their low viscosity limits their application. Hence, the incorporation of clays into these formulations was studied to identify their impact on the properties of the adhesive system. Hydrotalcite and montmorillonite clays were added the polycationic and polyanionic formulations, respectively, at different concentrations. Overall, it was found that their inclusion influences the viscosity, the mechanical performance, and the reversible behaviour of the adhesive. The advance of these new types of reversible adhesives is necessary to improve waste management processes and to ease the dismantling and recycling of products at their end-of-life within zero-waste industrial systems.

[1] A. Sierra-Romero, K. Novakovic and M. Geoghegan, Angew. Chem. Int. Ed., 2024, 63, e202310750.

DPOLY/PPG Exchange Lecture: Beyond alignment: novel mechanisms for controlling block copolymer phase behavior using magnetic fields

Michelle Calabrese[1]
[1]University of Minnesota, USA

Block polymers (BCPs) are attractive for developing novel materials due to their tunable properties and self-assembly via block chemistry, composition, and length. However, to harness the unique properties of BCPs in applications, their self-assembly and ordering on long length scales must be controlled. Unfortunately, practical methods for processing BCPs into materials with long-range order remain limited; for example, techniques like magnetic field alignment are typically infeasible because BCPs are weakly diamagnetic and respond minimally to magnetic fields. However, we discovered that magnetic fields can induce unexpected self-assembly and ordering in disordered BCP solutions via a new mechanism distinct from domain alignment. This process effectively converts a “non-magnetic” water-like fluid to a soft solid material using only a weak magnet. Here, the formation of stable ordered phases (cubic, cylinder, networks) causes up to a six order-of-magnitude increase in viscosity and modulus. Using a combination of magnetorheology, neutron and x-ray scattering, and vibrational spectroscopy, we demonstrate that magnetic fields likely facilitate these phase transitions by altering polymer-solvent interactions, hydrogen bonding, and polymer and solvent mobility – which in turn modify amphiphile packing. By identifying the molecular-scale mechanisms by which magnetic fields alter solvent structure and interactions with macromolecules in solutions, this work can be leveraged to improve chemical separations and to create polymeric new materials for applications in drug delivery, sensing, and catalyst templates.

Studying the structure of liquid crystal elastomers using small- and wide- angle x-ray scattering

Emily Cooper[1], Devesh Mistry[1], Peter Hine[1], and Helen Gleeson[1]
[1]University of Leeds, UK

The optimization of optical and physical properties is critical for material design, particularly for applications such as glass laminates, in which both good optical transparency and impact resistance are required [1]. Furthermore, understanding the temperature-dependence of the material properties is particularly important for real-world applications.

Liquid Crystal Elastomers (LCEs) are a form of material that has demonstrated good potential over a wide range of optical and mechanical applications. These types of materials are formed of loosely crosslinked liquid crystal polymers and the coupling of liquid crystalline and polymeric properties gives rise to highly ordered and birefringent soft materials.

Here, we will discuss the influence of molecular packing on a unique family of acrylate-based LCEs first developed by Mistry et al [2] which exhibit auxeticity (negative Poisson's ratio under strain). LCE properties such as refractive index and density are temperature-dependent [3,4] and have been previously investigated for LCEs of systematically varied liquid crystalline content [1]. We previously demonstrated the role of temperature-dependent density on optical properties; however, a change in density was not directly measured.

Small-Angle and Wide-Angle X-ray Scattering (SAXS and WAXS) are well understood techniques to provide information on the order and structure of a system. Using these techniques, we report that the internal spacing of LCEs are dependent on both the liquid crystalline content and phase (isotropic or nematic) of the network. Indeed, for an increase in liquid crystalline content, we see a reduction in internal spacing, signifying an increase in density.

[1] Cooper, E.J., et al. Macromolecules, 2024, 57 (5), 2030-2038.
[2] Mistry, D., et al. Nat. Commun. 2018, 9 (1), 5095.
[3] Broer, D. J., et al. Makromol. Chem. 1989, 190 (12), 3201–3215.
[4] Broer, D. J., et al. Macromolecules, 1993, 26 (6), 1244–1247.

Counterion-solvent properties: how they influence the structure and solubility of carboxymethylcellulose

Can Hou[1], Walter Richtering[1], and Carlos Lopez[2]
[1]RWTH Aachen University, Germany, [2]Pennsylvania State University, USA

Sodium carboxymethylcellulose (NaCMC) is among one of the most widely available and used polyelectrolytes, but its utility is limited by its insolubility in virtually all non-aqueous solvents. In contrast, TBACMC is soluble in several organic solvents such as ethanol and ethylene glycol. We set out to investigate how the solubility is influenced by varying the counterions with different sizes and functional groups, as well as how the structure in solution changes with different counterions and solvents.

Solubility phase mapping using the Hansen solubility parameters (HSP) was carried out for salts of CMC with different counterions. The results showed that the substitution of counterions did not change the solubility boundary, while increasing the size of the counterions slightly improved solubility. Moreover, small-angle X-ray scattering was carried to investigate how the structure changes with different counterions in different solvent conditions. It was discovered that the counterion species did not affect the conformation of the polyion, while changes in the solvent changed the stretch parameters for CMCs with organic counterions, in contrast with alkaline metal CMC, where the conformation is independent of solvent quality.

Polymer Opals 20 years on; current and future directions for shear-nanoassembly in soft-matter media

Chris Finlayson[1]
[1]Aberystwyth University, UK

This presentation reviews advances in the generation of photonics materials over large areas and volumes, using the paradigm of shear-induced ordering of composite polymer nanoparticles.

Structured materials at the order of the wavelength of light ("photonics") are central to many emerging technologies in optoelectronics, telecommunications, and sensing; however, the ability to assemble nanoparticles into bulk-scale periodic superstructures with fully controllable functionality remains challenging. By contrast, the work of the author and co-researchers over several years has demonstrated how synthetic opals (often referred to as "polymer opals"), based on permanently shear-assembled arrays of composite polymer microparticles, are a promising platform for next generation bulk-scale optical materials, flexible coatings, fibres, and sensors. These particles (diameters ca. 200-300 nm) are constructed of bulk-produced rigid polystyrene spheres, onto which a softer polyacrylate shell is grafted. The hard-core/soft-shell design of these particles produces quasi-solid "gum-like" media, with a viscoelastic ensemble response to applied shear, in marked contrast to the behaviour seen in colloidal and granular systems. The nature of the shear-assembly process has also been shown to greatly reduce the requirements for particle monodispersity in ordering as compared to (e.g. colloidal) crystalline assemblies. That monodispersity is not the limiting factor for ordering of particles, in this viscoelastic assembly, represents a significant breakthrough.

The further engineering of this shear-ordering using a controllable "roll-to-roll" process known as Bending Induced Oscillatory Shear (BIOS), together with the interchangeable nature of the base composite particles, opens potentially transformative possibilities for mass manufacture of nano-ordered materials, including advances in optical materials, photonics, and metamaterials/plasmonics.

Understanding liquid crystal elastomer behaviours polymerised with flow chemistry

Jiancong Xu[1], Nicholas Warren[1], Devesh Mistry, and Richard Mandle[1]
[1]University of Leeds, UK

Liquid crystals (LCs), feature high fluidity and orientational order, have been widely applied in LCD over the past century1. Combining LCs and elastomer networks, the position of LC mesogens are relatively fixed, resulting in liquid crystal elastomers (LCEs)2. The polar nature of LC mesogens allows them to rotate under external stimulus such as stress, heat, light, solvent, electric or magnetic fields, which brings the LCEs customizable deformation and impact dissipation properties. Acrylic-based LCEs have garnered significant attention due to their low costs and capability of deformations up to 700 times their original length3. However, despite these remarkable properties, the application of LCEs is still constrained by the difficulty in alignment for thick and large-scale bulk materials, necessitating further structure-property relationship understanding. Flow chemistry, as a novel synthesis tool, has been explored in many reactions4. A typical design of flow system is to infuse the reagents into a tubular reactor with milli-scale inner diameter at a constant flow rate. The large surface-to-volume reactor enables precise control over reaction conditions and produce uniform products, thus can program and adapt LCEs, which is critical for understanding LCEs behaviour.

[1] Mandle, R. J., Cowling, S. J. & Goodby, J. W. A nematic to nematic transformation exhibited by a rod-like liquid crystal. Physical Chemistry Chemical Physics 19, 11429 11435 (2017).
[2] Ware, T. H., McConney, M. E., Wie, J. J., Tondiglia, V. P. & White, T. J. Voxelated liquid crystal elastomers. Science 347, 982–984 (2015).
[3] Saed, M. O. et al. High strain actuation liquid crystal elastomers via modulation of mesophase structure. Soft Matter 13, 7537–7547 (2017).
[4] Zaquen, N. et al. Polymer Synthesis in Continuous Flow Reactors. Progress in Polymer Science 107, 101256 (2020).

Active polymers in biology

Tanniemola B Liverpool[1]
[1] School of Mathematics, University of Bristol, UK

I will start by discussing the long-standing problem of the emergence of forces in biology and attempts to link this to (active) biopolymers (proteins) that are involved in motility in biology.

Then I will give a (personal) summary of how far I think we have come in the programme of physical descriptions of these active polymers and suggest that developing synthetic analogues of these biopolymers might be a way for us to understand better what is going on in these types of systems. Then I will discuss a way to build synthetic active polymers from electrically driven active dipolar colloids, which spontaneously form travelling self-propelled strings at low packing fractions. I will compare explicit Brownian dynamics simulations with a theory based on an active Rouse model of flexible polymers. From measurements of the local bond vector correlation function, one finds an emergent apparent active stiffness, which is only possible because the system is out of equilibrium. One can show that the apparent stiffness is due the finite correlation time of the active driving (which depends on rotational diffusion). and it is possible to make a detailed comparisons of our theory/simulation to the experiments.

Influence of solvent type and counterion on the viscosity and conformation of polyelectrolytes in solution

Anish Gulati[1], and Carlos G. Lopez[2]
[1]RWTH Aachen University, Germany, [2]The Pennsylvania State University, USA

The behaviour of polyelectrolytes in solution has been predicted by the scaling theory[1] under varying conditions. According to the theoretical predictions, the solvent type has a significant influence on the conformation of polyelectrolytes. In agreement with these predictions, experimental and simulation reports provide evidence for a partial collapse of polyelectrolyte chains into a 'pearl-necklace' conformation under solvophobic conditions[2].

A similar collapse is also predicted under solvophilic conditions at low dielectric constants (ε) but no experimental studies have verified this phenomenon so far. In this work, we have found empirical evidence suggesting a collapse for polystyrene sulfonate (PSS) with tetra-butyl ammonium (TBA) counterions under solvophilic conditions. The small angle neutron scattering results reveal a transition in the scaling behaviour of the correlation length (ξ) with concentration, shifting from ξ ≈ c^(-1/2) to ξ ≈ c^(-1/3) as the dielectric constant of the solvent decreases below ε ≈ 25, which indicates a partial collapse of the PSS chains. This collapse is believed to stem from attractive forces originating between condensed counterions.[3]

Furthermore, we have conducted a rheological study for TBAPSS in different solvents. We observe an increase in the viscosity of these systems at higher concentrations which is sharper than the scaling theory prediction. This effect is more prominent for polyelectrolytes in low-ε solvents. These results also provide evidence for the Fujita free volume theory[4] indicating an important role played by the monomeric friction factor on the dynamic properties of polymer solutions at high volume fractions, such as the solution viscosity. This observation was also found to extend to PSS with other counterions with a lower degree of hydrophobicity.

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Hidden symmetry in polymer field theory and its implications for self-consistent field theory and field-theoretic simulation

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Polymer field theory has long been a cornerstone for investigating the nanostructures of heterogeneous polymers, offering robust methodologies for analysis. There are two primary approaches within polymer field theory: Field-Theoretic Simulation (FTS), which samples an ensemble of fluctuating fields, and Self-Consistent Field Theory (SCFT), which identifies the saddle points of polymer fields. Traditionally, SCFT has been used to determine the mean field solution of polymer systems, under the assumption that the fields and ensemble average densities in SCFT solutions are real-valued functions, and that the real-valued saddle points are isolated points in the field configuration space.

Contrary to this assumption, we demonstrate that the saddle points form a continuously connected family sharing the same Hamiltonian value. This study reveals that the Hamiltonian of polymer field theory inherently possesses symmetry under both real and imaginary spatial translations. This hidden symmetry not only generates a family of interesting complex SCFT solutions but also provides insight into the behavior of Complex Langevin FTS (CL-FTS), where field configurations are sampled around these connected saddle points. Additionally, we propose a translation scheme for CL-FTS to manage its intrinsic instability. Our findings aim to facilitate more realistic polymer field simulations, better aligning them with experimentally observed polymeric nanostructures.

Equilibrium and dynamical polymer networks for flow

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Intracellular structures such as cytoskeletal networks can contribute to transport within the confinement of the cell. We show how a monomer ensemble approach (Azote and Muller-Nedebock, 2019) for networks of directed filaments leads to the derivation of possible transport by active machinery travelling along this network, leading to understanding of the properties of macroscopic flow (for example, of organelles) between the centre and periphery of a cell. We show how this may be related to properties of autophagic flux. The monomer ensemble approach can be recast for the dynamics of formation of such networks and accompanying behaviour of flow within the geometrical confines of the networks.

Polymer dynamics in active nematic turbulence

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Polymers play a key role in many complex biomaterials in which activity drives the system out of equilibrium. While previous studies have focused on active polymers in passive fluids [1] or passive polymers in athermal baths [2], passive polymers in actively flowing liquid crystals are particularly interesting because of the interplay between anisotropy, activity and internal degrees of freedom. This work reports the first study of a passive polymer in active nematic flows. To study the dynamics of flexible polymers in 2D active turbulence, we employ a hybrid Multi-particle Collision Dynamics [3] and Molecular Dynamics [4] simulation. We find diffusivity increases with activity until the onset of turbulence. The high-activity saturation is due to competition between active forcing and conformational changes. Long polymers are stretched by activity, while short polymers are compressed. Surprisingly this is due to their interaction with +1/2 and -1/2 topological defects, respectively. This demonstrates how activity represents a pathway by which biological systems can control polymer properties.

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Wetting, adsorption, and desorption behaviour of single polymer chains: a closer look

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Polymer interactions with surfaces play a significant role in applications ranging from polymer composites and nanocomposites where macromolecules are in contact with fibres, fillers, and additives to tribology and adhesion where the polymeric products must perform well near a solid surface.

Atomic force microscopy (AFM), analytical theory, and Monte Carlo simulations were used to study the behaviour of polymers on surfaces. The phenomena studied include the differences in the nanoscale wetting behaviour when different substrates were used and the increased elastic modulus of polymer nanodroplets due to surface ‘pinning’. Single polymer chain droplets were observed to lie flatter and wet the substrate more than chemically identical multi-chain droplets of the same size (same total number of

monomers), which attain a more globular shape. The simulations revealed that isolated chains exhibit a monotonic adsorption fraction trend with chain length, while chains in multi-chain droplets decrease or increase their adsorbed fraction with chain length depending on their population. This mode of internal chain adsorption allows the droplet as a whole to arrange the chains at the droplet–substrate interface in the most thermodynamically preferable way. Furthermore, it leads to significant differences in the wetting behaviour in agreement with the AFM observations.

Moreover, the desorption force of poly(styrene-co-butadiene) random copolymer thin films on mica, silicon, and graphite substrates was quantified at the single polymer chain level by AFM force-distance curves. The results include single-chain pull-out and desorption phenomena from their films on different substrates. Single chain pull-out events were found to be dominated by surface energy contributions. The polymer desorption force was strongest on the graphite substrate and weakest on the mica. The single-chain adhesion and friction effects are discussed in terms of scaling theory and the implications to rubber compounding are highlighted.

Invited: Capturing the structural evolution and mechanics of protein assemblies during network formation

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A major challenge in the field of soft matter is to understand how the mechanical properties of an individual biopolymer translates to the collective response of a biopolymer network. By combining protein engineering, structural and mechanical characterisation and modelling we are developing a fundamental understanding of protein network formation and function. This approach is revealing a diversity of viscoelastic and structural properties that originate on both the nanoscale and the mesoscopic scale, providing powerful opportunities for engineering responsive and functional biomaterials. In this talk I will share our recent efforts to engineer protein aspect ratio and mechanical malleability and demonstrate its role in defining network architecture, mechanics and function. By modelling folded proteins as colloids, there are rich opportunities to explore network formation mechanisms, revealing an important crossover between diffusion and reaction limited cluster aggregation and the importance of the structure of the network at the percolation point. By taking an integrative small- and wide-angle scattering approach coupled with computational modeling we reveal the multiscale structure of hierarchically self-assembled proteins in aqueous solution. Finally, I will share our collaborative efforts to exploit these novel biomaterials for application in triggered drug delivery, as scaffolds for disease modelling and to understand the physics of living systems.

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Breath figure assembly on evaporating polymer solution droplets in levitation

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We report the drying of isolated polymer solution droplets, employing acoustic levitation, and demonstrate the spontaneous generation of breath figures (BF) on the resulting polymer particles and capsules with controlled surface pore arrays. By contrast with supported polymer thin films, the evaporative cooling experienced by suspended droplets suffices to yield ubiquitous BF formation, owing to their thermal insulation and the synchronous condensation and self-assembly of water microdroplets, accompanied by capsule skin formation and kinetic arrest. A simple model describes simultaneously the radius and temperature evolution along the droplet-to-particle transformation, and the scaling of surface pore dimensions, with environmental parameters. The generality of the approach is demonstrated with a range of model polymers, and the coupled roles of solution thermodynamics and droplet environment are shown to permit the facile design of capsules with tunable transport and dissolution kinetics.

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A biodegradable scaffold for bioelectronic applications

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In vivo bioelectronic applications require properties tailored to their specific usage. Devices need to be inert to the body, possess the requisite mechanical properties, act

upon appropriate electronic signals, and be easily destroyed or removed at the end of its life.

I shall present data describing a robust, stable, and transducing 3D hydrogel bioelectronic scaffold based on hyaluronic acid. Hyaluronic acid is found naturally in the body and provides inherent biocompatibility and predetermined routes of degradation.

The crosslinked hydrogels are stable in water beyond 25 days of submersion demonstrating that the crosslinks are not susceptible to rapid hydrolysis. Hyaluronidase, an enzyme present in the body, on the other hand does cause degradation of the scaffold on timescales of weeks, which would not preclude useful applications for the scaffold.

The body is full of soft tissue, and so the hydrogel should not be more rigid than this tissue. Measuring such mechanical properties is not trivial and choosing the right model requires some consideration. Different models are discussed, and measurements presented. Here, the modulus of the scaffold is of the order of tens of kPa, which would make it an ideal match for the spinal cord.

The bioelectronic device functioning as an OECT contains an active layer of a conductive polymer. Here, two thiophene based polymers have been compared: poly(3,4-ethylenedioxythiophene) (PEDOT) and a polymerised trimer, bis[3,4-ethylenedioxythiophene]-3-thiophene butyric acid, sodium salt (PETE-S). Hyaluronic acid acts as a natural dopant to PEDOT and has not displayed an incompatibility with the other polymers. Both of these scaffolds present credible transistor performance, which is noteworthy given that PEDOT and PETE-S were dispersed within the hydrogel rather than deposited as a pure conducting layer.

The effects of substrate glass transition temperature and hydrophobic heterogeneities on the wetting dynamics of a model infant milk formula

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Fat heterogeneities found on the surface of spray-dried infant milk formula are known to impede the instantaneous rehydration of these products. The poor rehydration limits the overall formulation, thereby impacting on the nutritional quality. Recent studies investigating model powder systems have highlighted the complex mechanisms governing the spreading of water on soluble polysaccharides as a model system for a solvent spreading on a homogeneous film of its solute. In such systems, water diffuses ahead of the contact line where it alters the surface energy, contact angle, and contact line speed. Although the presence of surface fat slows down the wetting of spray-dried infant formula and similar products, this phenomenon is not yet understood quantitatively. In this research, the interactions between water and hydrophobic surface heterogeneities on soluble films with two different glass transition temperatures were investigated. Defined surface heterogeneities were created by the ink-jet printing of cocoa butter onto water-soluble thin films of maltodextrin to produce either periodically-ordered or randomly distributed hydrophobic deposits with a range of area coverages. The spreading dynamics of water on the heterogenous surfaces was studied under a fixed relative humidity. Area coverages of cocoa butter above 1.2% were found to decrease the contact line speed and increase the contact angle. The contact line was deformed by the deposits of cocoa butter, causing - in some cases - periodic deceleration followed by an acceleration during spreading. Area coverages above 26% led to a three-fold increase in the spreading time. The presence of surface heterogeneities was found to impact the spreading more strongly than the glass transition temperature of maltodextrin in the substrate. These novel insights could help to design soluble heterogeneous surfaces on powders to increase the nutritional value of infant formula.

Characterization of water adhesion on hydrophobic electrospun polymer fibers

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Previous studies have shown little correlation between the wettability of a material and its water adhesion properties. Despite these differences, applications involving droplet-surface interactions, such as self-cleaning surfaces, oil-water separation, and fog water harvesting, often emphasize wettability, with contact angles being a widely used method, while water adhesion is frequently overlooked. This study focused on examining water adhesion properties of various electrospun fibres composed of Polycaprolactone with different concentrations of Poly(l-lactide-co-ε-caprolactone). Using an adhesion tensiometer, we measured water adhesion and compared it with both static and dynamic water contact angles. The findings demonstrate a weak correlation between wettability and water adhesion, indicating that the two properties are influenced by different factors. This discrepancy underscores the importance of studying water adhesion in polymers and highlights the necessity for developing new techniques to accurately measure this property. Furthermore, a greater focus on water adhesion can enhance our understanding of polymer chemistry and surface properties, potentially leading to innovations in material design for specific applications. Addressing this often-ignored parameter can give deeper insights into the behaviour of polymers in various environmental conditions and improve the efficiency and effectiveness of materials used in practical applications involving droplet interactions.

Hydrogels for solar-driven water purification

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Providing access to safe water is a major global challenge due to expansion of industrialization, growth of the global population, and contamination of freshwater resources. According to the United Nations, in the last century, global water requirements grew at a rate more than twice that of the population growth rate. In the United State alone, the Environmental Protection Agency has identified over 70,000 water bodies in the United States alone that are impaired by pollution. The health issues associated with consuming contaminated water are well-known: waterborne disease outbreaks, leading to gastrointestinal illness, reproductive complications, and neurological disorders, amongst others. More than 1.5 million people die each year from diarrhea caused by the intake of unsafe drinking water. Therefore, developing advanced water purification technologies that provide access to safe water to more of the global population remains an enduring challenge.

Hydrogels have emerged as promising soft materials for sustainable and off-grid water purification and harvesting. However, the low water production rate well below daily human demand is a current impediment to technology translation. To make progress towards addressing this challenge, we present work on the development of a rapid-response solar absorber gel membrane capable of producing potable water from various contaminated sources at a rate of ~ 26 kg m-2 h-1, which is sufficient to meet daily water demand. The membrane—produced at room temperature via aqueous-based processing using an ethylene glycol (EG)-water mixture—uniquely integrates the attributes of poly(N-isopropyl acrylamide) (PNIPAm), polydopamine, and poly (sulfobetaine methacrylate) to enable off-grid water purification with enhanced photothermal response and the capacity to prevent oil- and bio-fouling. The use of the EG-water mixture was critical to forming the loofah-like structure with enhanced water transport. Remarkably, under various sunlight irradiations of 1 and 0.5 sun, LSAG required only 10 to 20 min to release ~ 70 % of its stored liquid water, respectively. Equally important, we demonstrate the ability of the membrane to purify water from various harmful sources, including those containing small molecules, oils, metals, and microplastics.

New methodology for anisotropic nanoparticles characterization by Depolarized Light Scattering measurements: length and diameter determination of rod-like nanoparticles

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In this work, we introduce a new setup and a method for characterizing anisotropic nanoparticles using a multi-angle polarization dynamic light scatteringtechnique. This method is based on the measurement of the correlograms of scattered light intensity fluctuations both in the parallel and crossed polarizer configurations, and possibly concomitantly, from which the rotational and translational diffusion coefficients are extracted. By inversing the mathematical expressions of these coefficients, this approach allows the rapid determination of length and diameter of the anisotropic nanoparticles, enabling kinetic measurements. A comparison of experimental results obtained with this multi-angle depolarized DLS (DDLS) method to classical TEM images is discussed.

Invited: Optimising the performance of biodegradable polymers: design of fillers and plasticisers to tune polymer crystallization

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Poly(hydroxybutyrate) (PHB)-based polymers are promising candidates for replacing petroleum-based plastics. Fillers and plasticisers are typically added to improve the properties, which are largely controlled by the crystallinity and microstructure. Despite many studies reporting crystallization in plasticised and filled polymer formulations, there is limited systematic understanding on the crystallization behaviour of polymers in these systems [1], which results in a lack of control of the final product. We will present simulations and experimental results on how the interaction between fillers and plasticisers influence polymer crystallization [2-5]. Our findings show that we can predict polymer crystallization behaviour, which can be used to provide design guidelines to control polymer crystallinity and hence mechanical and barrier properties. These results can therefore enable the future design and optimisation of polymer composites, and accelerate the development of sustainable plastic products.

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A Comparison of crosslinking methods for the formation of atomistic crosslinked structures

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Atomistic models of crosslinked polymers enable the investigation of properties that are challenging to understand through experiments alone. Combining simulations with experimental observations can provide understanding of polymer properties such as mechanical response and diffusion of small molecules. Crosslinked structures can be created by forming crosslink bonds while allowing the growing chains to move and relax. However, chemical reactions are typically not possible in molecular dynamics simulations due to strict definitions of bonded atoms. We aim to compare two of the approximate reaction methods available to determine the effect of this choice on the cured structure.

As a model crosslinking polymer, an epoxy-amine system of diglycidyl ether of bisphenol A (DGEBA) and m-xylylenediamine (MXDA) has been used. The first method can form only one bond at a time, which requires replacing reactive functionalities with intermediates, simplifying the reaction to the formation of a single bond. This is commonly used for bulk epoxides but produces unrealistic behaviour when the reaction takes place near a surface. By forming initially weak bonds that are gradually strengthened, the crosslinked structures can be equilibrated. The second method can form multiple bonds in a single step and removes the need for activation of functionalities. In this method, a brief speed limit is applied to recently reacted atoms to allow the relaxation of new bonds.

We compare cure kinetics and structural properties during and after cure for both methods. We find clear differences in kinetics and network structure at low conversion. However, at high conversion negligible differences in network structure are observed. This indicates that either method may be used depending only on the validity of use of activated functionalities and ease of implementation for the system of interest.

A framework for a high throughput screening method for polymeric systems using molecular dynamics

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Polymer composite materials require softening to reduce their glass transition temperature and improve processability. To this end, plasticizers, which are small organic molecules, are added to the polymer matrix. The miscibility of these plasticizers has a large impact on their effectiveness and therefore their interactions with the polymer matrix must be carefully considered. Many plasticizer characteristics, including their size, topology and flexibility, can impact their miscibility and, because of the exponentially large numbers of plasticizers, the current trial-and-error approach is very ineffective. In this work we show that using coarse-grained molecular simulations of a small dataset of 48 plasticizers, it is possible to identify topological and thermodynamic descriptors that are proxy for their miscibility. Using ad-hoc molecular dynamics simulation set-ups that are relatively computationally inexpensive, we establish correlations between the plasticizers' topology, internal flexibility, thermodynamics of aggregation and their degree of miscibility and use these descriptors to classify the molecules as miscible or immiscible. With all available data we also construct a decision tree model which achieves a F1 score of 0.86 \pm 0.01 with repeated, stratified 5-fold cross-validation, indicating that this machine learning method can be a promising route to fully automate the screening. By evaluating the individual performance of the descriptors, we show this procedure enables a 10-fold reduction of the test space and provides the basis for the development of workflows which can efficiently screen plasticizers with a variety of topological features. The approach is used here to screen for apolar plasticizers in polyisoprene melts but similar proxies would be valid for other polyolefins, while, in cases where polar interactions drive the miscibility, other descriptors are likely to be needed.

Quantifying the free volume distribution in acrosslinked epoxy coatings through a combined PALS and molecular dynamics simulation study

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The free volume of epoxy coatings gives us a unique insight into the network structure. Free volume voids exist within all polymeric systems; understanding them allows us to formulate better, longer-lasting coatings systems. Ultimately saving resources and

protecting environments. Our main questions are: what size are the voids? Are they interconnected? Do these voids provide pathways for water and ion ingress?

In this work, we have measured average free volume void size and size distribution using positron annihilation lifetime spectroscopy (PALS). We have then compared these results with those calculated via molecular dynamics simulations and found coherent results. The combination of these results gives a more in-depth image of the systems.

Electrospun polymer nanofibres for enhanced through-thickness electrical conductivity of CFRP composites

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Detecting internal damage in carbon fibre reinforced polymer (CFRP) composites has been gaining importance in recent years to ensure their structural integrity, safety, and performance. Electrospun lightweight veil interleaved CFRP composites have been developed. The effect of embedment of polymer nanofibre based veils on the through-thickness electrical conductivity (TTEC) and mechanical properties of CFRP composites has been measured. Subsurface or bulk matrix cracks and delamination in composite structures cannot be seen with the naked eye and can lead to the premature failure of the whole structure. CFRP composites are conductive in the fibre direction, where carbon fibre acts as a sensor due to its anisotropic conductive nature. Self-sensing techniques use electrical conductivity to check the integrity of composites under inspection. In-plane fibre fracture can be self-sensed, but this approach is not applicable for detecting delamination or matrix cracking as the polymer matrix is an insulator. Electrical sensing in composites relies on a conductive material, which can be attained by introducing conductive moieties in the polymer matrix. In this work, two variants of electrically-conductive polymers, polyaniline emeraldine base (PANI-EB) and polyaniline emeraldine salt (PANI-ES) were combined with polyvinylpyrrolidone (PVP) as a carrier polymer to produce nanofibers on carbon fibre reinforcement fabrics in a one-step electrospinning process using nozzle-free electrospinning setup. The through-thickness electrical conductivity of PANI-EB/PVP and PANI-ES/PVP electrospun veil interleaved composites improved from 0.0117 to 0.592 and 0.852 S/m, respectively, compared to the control specimens. The electrical conductivity of interleaved laminates increased 3 to 6 folds under uniaxial pressure in elastic deformation range. The TTEC of PANI-EB/PVP and PANI-ES/PVP electrospun veil interleaved composites enhanced from 0.0117 to 1.80 and 5.20 S/m, respectively, compared to the control specimens under 4.6 bar pressure. The samples tested for Interlaminar shear strength (ILSS) exhibited multiple matrix cracks. The cracked specimens had a sharp decline in TTEC of PANI-EB/PVP and PANI-ES/PVP electrospun veil interleaved composites 6.2 × 10-4 and 7.6 × 10-4 S/m, respectively under similar uniaxial pressure conditions. In comparison, the TTEC of commercially available silver plated nylon fibres veil interleaved CFRP composites is 0.122 S/m [Guo et al., 2019]. This study reveals that conductive electrospun nanofibres interleaved composites have the potential to meet the functional integration requirements of the aerospace and renewable energy structures for electrical properties and can find applications in electromagnetic interference (EMI) shielding and structural health monitoring.

Telephone cord blister formation in solvent swollen elastomer films

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Video imaging was used to study large-slope folded telephone cord blister formation in solvent swollen films of polydimethylsiloxane (PDMS) elastomers. Chlorobenzene, chloroform, heptane and toluene were used to swell PDMS films with thickness values in the range $15 < h < 223$ microns supported on glass substrates. Measurements of the blister width, corrugation wavelength and blister growth speed were studied as a function of the film thickness for all four solvents. Modified theories of buckling were shown to accurately predict the film thickness dependence of the width and corrugation wavelength and a modified fracture mechanics approach was shown to reproduce the non-monotonic thickness dependence of the blister growth rates. A critical blister width (and film thickness) was identified for films swollen by each solvent which is consistent with the existence of mixed modality in the growth of the crack tip at the interface. These critical dimensions are shown to scale with the strength of the adhesive interactions between the film and the substrate.

Auxetic liquid crystal elastomers: fundamentals, applications and future outlook

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Liquid crystal elastomers are lightly cross-linked elastomeric materials containing liquid crystal components. The liquid crystal units are usually incorporated within the backbone itself (main-chain liquid crystal elastomer) or as pendant chains (side-chain liquid crystal elastomer). The coupling of liquid crystal order with the polymer conformation leads to remarkable mechanical behaviour and stimuli responsiveness. [1] The auxetic response (negative Poisson's ratio) was discovered in liquid crystal elastomers in 2018. [2] Auxetics are a class of materials which get thicker with applied strain. The LCEs displaying an auxetic response are a family of acrylate materials. The

auxetic response occurs at a molecular level and the material remains non-porous (volume conserving) throughout. The auxetic mechanism in LCEs is therefore very different from conventional (re-entrant) auxetic materials which are engineered, porous materials in which the pore size increases on strain.

Here, I will present the experimental evidence for the underlying mechanism of the auxetic response in these systems. With strain, the nematic, auxetic LCEs become biaxial. With increasing strain, the uniaxial order parameter decreases while the biaxial order parameter increases. [3,4] Reconstructing the orientational distribution function from the order parameters [3] reveals that an out-of-plane population of mesogens begins at the onset of the auxetic response. The increase in thickness beyond a certain threshold strain is caused by a sufficiently large population of molecules rotating out of plane. The design guidelines for these materials have been explored experimentally. These guidelines will be covered in addition to possible applications and the future outlook for these materials.

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Solvent uptake in epoxy resins used as anti-corrosive coatings

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Two-part epoxy resins display good moisture and corrosion resistance as well as strong mechanical properties as well as being adhesive. They therefore see use as anti-corrosive coatings on ships, aeroplanes, trains, wind turbines and other civil infrastructure. The water and methanol over time was measured for samples of model epoxy resins of different stoichiometries, cured with and without solvent and homopolymerizer. These uptake measurements were related to information on their network structures so that possible failure mechanisms could be ascertained.

Topological understanding of degradability of polymer networks with cleavable strands or crosslinks

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Designing degradable or re-processable polymer networks, such as thermosets or elastomers is a formidable challenge due to their crosslinked structure. Among them, networks based on vinyl polymers such as polyacrylates, or polystyrene are particularly challenging as they contain exclusively carbon-carbon backbones.

Using crosslinkers with cleavable groups (e.g., disulfides) seems like a straightforward method to develop fully degradable vinyl polymer networks. However, networks/gels prepared by conventional free radical polymerization (FRP) typically cannot be degraded even when they contain cleavable crosslinkers.

I will present the recent work in our group aimed at better understanding of (non)degradability of networks/gels prepared from different classes of vinyl monomers, by analyzing their polymerization kinetics and the resulting network topologies, specifically formation of spatial inhomogeneities during crosslinking.

Additionally, I will discuss how reversible degradability can be enabled in polyacrylate networks by incorporating cleavable units in the backbone (strands) rather than in the crosslinks.

Founders Prize: Development of quantitatively accurate simulations for block copolymer materials

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Block copolymers self-assemble into a rich array of periodically-ordered microstructures that can be exploited for various applications. While the existing theories have been remarkably successful, they have nevertheless lacked the ability to provide quantitatively accurate predictions. However, this is poised to change. Firstly, it has been demonstrated that block copolymer phase behaviour becomes universal at high molecular weights, which implies that these molecules can be accurately represented by simple coarse-grained models, in particular, the standard Gaussian-chain model. Secondly, an accurate method has been developed for calibrating the Flory-Huggins interaction parameter, χ. Thirdly, the development of field-theoretic simulations has overcome many of the limitations of conventional particle-based simulations. These advances will be discussed in the context of the diblock copolymer melt. The resulting ability to perform quantitatively accurate simulations is likely to open a new chapter in block copolymer research, in much the same way self-consistent field theory did 30 years ago.

Invited: Entropic phase-separation in polymer grafted nanoparticle blends

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Polymer grafted nanoparticles (PGNP) systems tend to maximize the system's configurational entropy by dispersion of the NPs, and the polymer chains' conformational entropy and enthalpic interactions by mediating the interactions between the NPs. We examine a binary blend of PGNPs with chemically distinct brushes, with respective to entropic and enthalpic and overall miscibility behavior. First, we document that the binary PMMA/PSAN (AN content14%) homopolymer blend (i.e. without attached nanoparticle) films remain in the 1-phase for all blend compositions, wherein for both homopolymers, their Mw is matched to PGNP brush Mw, and studied at same sets of temperature. In contrast, end-grafting of the polymer chains to the NPs apparently significantly reduces the chains' configurational degrees of freedom, and the PGNP blends phase separate. We hypothesize that the reduced entropic miscibility interactions due to tethering of PGNP brushes, allowing the weakly unfavorable enthalpic interaction to drive 2-phase behavior. This is despite the fact that the enthalpic interactions are themselves reduced in PGNP brush/brush interdigitation contacts compared to untethered systems, due to limited interdigitation within only the semi-dilute polymer brush (SDPB), zone but not in the concentrated polymer brush (CPB) zone. We demonstrate these results in a binary PGNP blend system with chemically distinct grafted-polymers of PMMA-g-SiO2 /PSAN-g-PSAN that undergoes this this kind of phase separation, and that too, only in a narrow window in vicinity of the 50/50 PGNP blend composition, where enthalpic interactions are maximal. In summary, while an identical matched in every respect, chemically distinct PMMA/PSAN homopolymer blend system is miscible at all temperatures and compositions studied, its tethered PGNP/PGNP blend system is not miscible in a limited composition window around 50/50. A delicate balance of reduced entropic degrees of freedom of PGNP brushes and enthalpic interactions is responsible for this phenomena.

The effect of solvent quality on porous Poly(2,6-diphenyl-p-phenylene oxide) formation

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Porous organic polymers (POPs) play a crucial role in adsorption processes, catalysis, and gas sensing. These metal-free materials offer simplicity, well-defined porosity, high surface area, and valuable surface chemical functionality. Poly(2,6-diphenyl-p-phenylene oxide) (PPPO) is a popular POP used in gas sensing albeit not frequently studied due to the complexity of sample preparation and material processing. However, PPPO's high thermal stability (Tg 220-230 °C, Tm 420-510 °C), high porosity, and hydrophobicity makes it ideal for gas chromatography and specific gas sensing. The current approach for achieving porosity is via non-solvent induced phase separation (NIPS), upon the addition of non-solvent to a binary mixture of PPPO/good solvent leading to demixing and then kinetic arrest. One of the key parameters which will influence NIPS and consequently pore formation is the interaction between PPPO and the solvent.

Therefore, this work aims to identify good solvents for PPPO and examine polymer conformation before non-solvent addition. Binary solutions of PPPO (0.5-20 w/w%) in DCM, chloroform, THF and toluene are analysed using optical microscopy, viscometry, and small angle neutron scattering (SANS). We identify that above a specific composition threshold, phase separation occurs, leading to a kinetically arrested soft-solid structure ("polenta-like"). Due to slow kinetics of this transformation, temperature jumps are employed to quickly assess the stability of the binary solutions and measure polymer conformation, spinodal, or nucleation and growth decomposition. These experiments measure gyration radii, correlation lengths, overlap concentrations, and viscosities, providing insight into polymer conformations and solvent quality. Finally, we relate these findings to the porosity in PPPO materials formed via NIPS with different solvents establishing a relationship between molecular parameters and physical properties.

From this work, we establish that understanding the thermodynamics and kinetics of these binary mixtures can guide decisions for porous PPPO production methods leading to better surface area and pore size control.

Relaxation dynamics in poly(methyl methacrylate)/poly(4-tert-butylstyrene) systems produced via thermal initiated random co-polymerization

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Poly(methyl methacrylate)/poly(4-tert-butylstyrene) (PMMA/PTBS) systems were developed by means of thermal initiated random co-polymerization at various monomer-to-monomer ratios. The relaxation dynamics of various co-polymers have been developed utilizing either PMMA [1] or PTBS [2] but to the best of our knowledge, this is the first time PMMA/PTBS random copolymers have been prepared for dielectric experiments. PMMA exhibits three dielectric relaxation processes, namely the α-, β-, and γ-relaxation, from high to low temperatures respectively [3], whilst PTBS only exhibits an α-relaxation. In this work, we aim to examine the temperature dependence of the recorded relaxation processes, particularly of the segmental dynamics (α-relaxation) that is attributed to the dynamic glass-to-rubber transition process and is the major thermal event of amorphous polymers.

Broadband Dielectric Spectroscopy measurements were conducted employing a Phecos temperature system with an integrated dielectric cell, and an Alpha-A frequency analyzer, all provided by Novocontrol Technologies, Germany. The dielectric experiments were performed in a parallel 'sandwich' plate configuration employing gold electrodes, in the temperature and frequency ranges of -48 – 198 °C and $10^{(-1)}$ – $10^{(6)}$ Hz, respectively.

[1] V. Raja, et al., Materials Letters, 2004, 58, 3242 – 3247. doi: 10.1016/j.matlet.2004.05.061
[2] H. Watanabe, et al., Macromolecules, 2007, 40, 5389 – 5399. doi: 10.1021/ma070696h
[3] E. Logakis, et al., Composites Science and Technology, 2011, 71, 854 – 862. doi: 10.1016/j.compscitech.2011.01.029

Testing the theory of Akcasu et al. for the time evolution of the scattering intensity during polymeric spinodal decomposition and dissolution using simulated scattering data

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The field of polymer blending aims to combine the properties of polymers to create functional materials. In general, polymer blends are prone to phase-separating, leading to the formation of immiscible microstructures, which affect the properties of the resulting material.

Thermally induced spinodal decomposition and dissolution offer a route between miscible and immiscible microstructures. The evolution of the microstructure can be probed using small angle scattering techniques. While the time evolution of the scattering intensity can be measured relatively easily, modelling it has proved to be much more difficult.

Perhaps the most commonly used equation to study the time evolution of the scattering intensity during polymeric spinodal decomposition or dissolution is the linear Cahn-Hilliard-Cook equation. While this equation has proved to be a useful tool in the analysis of scattering data, it is only applicable under a restrictive set of conditions and assumptions. Motivated to improve this situation, Akcasu et al. set out to derive a non-linear equation of motion [1,2]. The inclusion of non-linear terms causes the equation of motion to become unclosed. In other words, the 'full' equation of motion is an intractable infinite hierarchy of coupled differential equations. Therefore, a truncation scheme is required to solve it.

There is very little in the literature aimed at testing the equation derived by Akcasu et al. To rectify this, we tested the Akcasu equation using scattering data derived from simulations. In the context of dissolution, the Akcasu equation performed well at describing the time evolution of the simulated scattering data. In the case of spinodal decomposition, we determined that improvements are required.

[1] Akcasu et al., J. Chem. Phys., 97(8) :5782-5793, 1992
[2] Akcasu and Klein, Macromolecules, 26(6) :1429-1441, 1993

Optically white porous polyethylene manufacture via thermally induced phase separation

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Opaqueness (i.e. whiteness) in a material arises from scattering of impinging light due to high refractive index. The most frequently used pigment for whiteness is titanium dioxide (TiO_2) with a range of industrial applications (e.g. paints, cosmetics, pharmaceuticals). However, TiO_2 has been found to have adverse pulmonary health effects and poses industrial processing challenges, such as inhomogeneous mixing. Consequently, recent research efforts have focused on taking inspiration from nature where low refractive index (n = 1.4-1.6) biopolymers exist in highly scattering nanostructure arrangements (e.g. chitin nanopillars in Cyphochilus beetle wings). Therefore, at the centre of controlling light management in polymer systems is understanding how to modulate nanostructure size and arrangement. Frequently, this is achieved through phase inversion via thermally or non-solvent induced phase separation.

In this work, we investigate optical whiteness of semi-crystalline high-density polyethylene (HDPE) particles and films formed via thermally induced phase separation (TIPS). By using a single axis acoustic levitator, we develop a methodology for studying drying kinetics of HDPE/o-xylene solutions. We determine the effect of polymer concentration (0.05-5 w/v%) and particle size (0.01-0.3 µL) on the nanofeature formation with optical microscopy, thermal imaging, and SEM.

Following these insights, we develop a scalable approach for optically white HDPE thin film manufacture. We quantify the optical properties with transmission and reflectance measurements and measure the porosity with BET achieving comparable characteristics to optical pigments from current state-of-art research. Finally, we test the thermal stability of the HDPE films before and after annealing to determine their potential for industrial applications.

Optimizing the performance of NMC622 battery half-coin cells by using amphiphilic aqueous binders to modulate the percolation of carbon black

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N-methyl-2-pyrrolidone (NMP) is the conventional solvent for processing high-nickel cathodes as it dissolves the polymer binder polyvinylidene fluoride (PVDF) and does not leach nickel from the cathode material. NMP is restricted under REACH regulations as a 'substance of very high concern'. Aqueous processed cathodes with hydrophilic binders offer advantages over conventional processing with NMP, namely nontoxic, unrestricted use, and cost-effectiveness being 100 times less expensive than NMP/PVDF.

Aqueous binders have generally yielded unimpressive battery performance; therefore, a novel binder system has been studied. Here, an amphiphilic polymer (pluronic F68) was used to control the dispersion of carbon black in the slurry, and a high molecular weight polyethylene glycol (PEO) was used as a viscosity modifier. Zeta potential measurements were taken to assess the degree of carbon-black dispersion in the slurry. Measuring oscillatory strain measurements, a narrow viscosity range in which carbon black percolates in the cathode slurry was identified and validated by conductivity data. Working within this viscosity range, a series of formulations were developed that maximize the mass fraction of active material whilst ensuring enough binder is present to disperse the carbon black in water Ultimately, the formulations presented have a constant viscosity, attained by controlling the solids loading.

An optimal ratio of 25% PEO to 75% pluronic-F68 was identified; half-coin cells outperformed those made with NMP/PVDF. Through adsorption measurements, it was found that the affinity between the binder and carbon-black correlates with the size of carbon-black flocs that form, enabling tuning of carbon-black percolation in the slurry. By controlling the viscosity, it was shown that electrochemical cell performance correlates very strongly with both the PEO to pluronic ratio and the slurry conductivity for this system. The results indicate that the affinity of the polymer binder(s) to carbon-black can determine the electrochemical performance of the cell.

Binder matters! Balancing viscosity with molecular weight in lithium-ion battery cathodes

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Commercial lithium-ion batteries require 2-5 wt% binder to retain their capacity over thousands of cycles; but there is a fundamental lack of understanding about how the polymer chemistry, chain architecture and molecular weight affect the processing and performance of battery cathodes. Reproducibly formulating slurries remains a bottleneck to testing and optimising new battery materials. This study resolves the effects of viscosity on the structure of cathode slurries and the performance of the dried electrodes.

The viscosity of a solution containing the conventional battery binder, polyvinylidene fluoride (PVDF), is systematically varied across two decades, and the rheological characteristics of the slurries are measured. In all instances, the viscosity of the slurry is dominated by the aggregation of carbon black flocs, which are added to increase the conductivity of the electrode. In general, the size of carbon black flocs increases with the viscosity of the polymer solution, suggesting that the mixing step is less successful at deagglomerating carbon black powder in high-viscosity dispersions. Interestingly, the structure of the slurry depends on whether it is prepared from a homopolymer or a blend of two homopolymers selected to match the viscosity of the homopolymer solution. Higher molecular weight binders seem to provide greater colloidal stability at the price of requiring higher shear conditions to deagglomerate the carbon black. The highest capacity battery half-cells result from slurries with liquid-like rheology. This work finds that blended binder systems (in contrast to homopolymer formulations) offer a higher degree of control over the slurry and resulting electrodes, potentially streamlining battery testing and improving the reliability of manufacturing processes.

Reprogrammable 3d printed liquid crystal elastomer actuators

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[1]University of Leeds, UK

Soft robotics has recently become an exciting field of research due their flexible and versatile properties, making them ideal for applications in biomimetics and artificial muscles [1]. Liquid crystal elastomers (LCEs) are unique materials that combine rubber-like elasticity with the orientational order of liquid crystals and display the actuation properties required for these applications [2]. Here, we demonstrate the fabrication of a 3D-printed LCE actuator, which is modified to allow reprogrammable operation.

Our LCEs are crosslinked main-chain LC polymers, where the chains consist of mesogens interspersed with spacer units. The mesogens within these LCE networks can align, resulting in a polydomain aligned LCE. To produce an effective actuator, however, overall alignment provided by a monodomain LCE is required, but such overall alignment is not inherent to the material and generally must be induced.

Here, we achieve excellent overall monodomain alignment using the shear profile of 3D printing, where the final crosslinking is achieved by UV-curing [3]. The resulting LCE can be reversibly switched from the aligned state to the unaligned state upon temperature change, thus undergoing a macroscopic shape. Whilst this actuation is reversible, the crosslinking of the LCE means the material cannot be re-shaped after curing and can thus only actuate in a single ` mode’. The fabrication of a multimodal LCE actuator is desirable, as this would mimic the performance of naturally occurring actuation such as that seen in muscle tissue [1].

We present 3D-printed LCEs laminated with a semi-crystalline polymeric material. This bi-layered LCE composite is malleable upon melting of the crystalline domains and can be reshaped before reversibly actuating into its new shape. This composite LCE demonstrates ideal multi-mode actuation, and correspondingly acts as a reprogrammable actuator.

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[2] Actuators. 2020, 9, 3
[3] ACS Appl. Mater. Interfaces. 2017, 9(42), 37332-37339

Equilibrium and non-equilibrium behaviour in thin-film mixtures of polymers and small-molecule organic electronic materials

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The miscibility of materials and the nature of interfaces within organic electronic devices is of key significance for their performance. This presentation will highlight recent work on materials for organic photovoltaics, focussing on fundamental mixing behaviour in model thin-film systems. By investigating narrow molecular-weight-distribution polymers blended with various fullerene derivatives, we have established a framework in which polymer/small-molecule mixing in these systems can be studied in comparison to equilibrium thermodynamic theories. Understanding equilibration (and non-equilibrium behaviour) is important in relation to i) device efficiency and ii) morphological stability, within working organic photovoltaic devices. In-situ neutron reflectometry measurements that probe mixing behaviour during thermal annealing will be presented. These measurements involve extensive annealing at elevated temperatures that enable investigation of two key requirements for properly equilibrated systems; i) convergence to the same state from different starting points (thin-film composition profiles) and ii) thermal reversibility of behaviour. Extensive mass-transfer occurs in all cases, on thermal annealing, but the layer compositions, layer thicknesses and interfacial widths do not always attain their equilibrium values. Results from two recent studies will be presented, revealing the circumstances under which equilibrium behaviour is confirmed (A. M. Higgins et al, J. Mater. Chem. C, 2023, 11, 2107), and the circumstances under which these systems can become trapped in non-equilibrium states and display hysteresis (A. M. Higgins et al, Soft Matter, 2024, 20, 2532).

The microstructure formation in multifunctional electrolytes using small angle neutron scattering

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Materials and devices which could perform simultaneously more than one function are becoming increasingly popular as they can provide weight and/or volume savings. One of the examples of such materials is a multifunctional electrolyte (ME) for energy storage devices and more specifically for structural supercapacitors [1]. To achieve true multifunctionality, it is essential that the electrolyte has both high ionic conductivity and good mechanical properties. However, there is an inverse relationship between these two properties, i.e. as mechanical properties increase, mostly due to the rigidity of the polymer chains, ionic conductivity falls.

To date, the most promising performance has been shown by MEs obtained through reaction or polymerisation induced phase separation (RIPS or PIPS) [2, 3]. These systems have a bicontinuous structure in which one of the phases is responsible for the ion conduction while the other phase provides mechanical strength and modulus. Research has mainly focused on the development of new MEs and their characterisation. Curing kinetics of MEs has been studied mainly using DSC, a technique that does not provide an understanding of the microstructure formation which has indisputable effect on the properties of the final ME.

Here, a RIPS kinetic study leading to formation of MEs is reported, using small angle neutron scattering (SANS). The MEs are based on bisphenol A diglycidyl ether (DGEBA), isophorone diamine (iPDA) and the ionic liquid 1-ethyl-3-methylimidazolium bis (trifluoro methyl sulfonyl) imide (EMIM-TFSI). By following structural changes as a function of time, analysis of the SANS data provides an insight into the effect of composition and temperature during curing.

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[2] Q. Wendong, et al . Multifunct. Mater., 4, 2021, 035003.
[3] L. M. Schneider et al, ACS Appl. Energy Mater., 2019, 2, 4362−4369.

Conductive Polymer Binders for Lithium-Ion Batteries

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Lithium-ion (Li-ion) batteries are at the forefront of the global energy storage market, used in a wide range of applications from portable electronics to electric vehicles. Li-ion electrodes are composites, consisting of: active lithium-containing particles, a fine scale carbon dispersion for electron transport, and a binder that holds everything together. Conventionally, a polyvinylidene fluoride (PVDF) binder is used, which is an insulating polymer. This forms no other function than a mechanical one. Conductive polymers are an attractive alternative, because of their ability to conduct electrons, which reduces the need for as much carbon additive. Hence this increases the energy density of the final battery. Furthermore, improving the conductivity of the electrode may lead to faster charging/discharging times. Conductive polymers exhibit a backbone with an extended pi-electron network, and dopants can be introduced to create charge carriers. However, despite their promising functional properties, conductive polymers exhibit low solubility, thus making their processing for Li-ion electrodes a challenge.

In this work polyaniline, poly(3-hexylthiophene) (P3HT) and poly(9,9-di-n-octylfluorenyl-2,7-diyl) are studied in a range of organic solvents to try and improve the performance of lithium-ion electrodes. Batteries are assembled and a range of electrochemical tests conducted: constant current/constant voltage cell cycling, galvanostatic intermittent titration technique and electrochemical impedance spectroscopy. The type of binder used was found to greatly affect lithium removal/insertion behaviour from the electrode. The light-emitting fluoride outperforms PVDF at higher charge/discharge rates. Thermal annealing improves the conductivity of the P3HT polymer. Importantly, it was found that the processing of the electrode – the type of solvent and mixing conditions, had a profound effect on end performance of the electrochemical cell.

Multi-scale model of the conductivity of diblock copolymer system filled with conductive fillers

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We investigate the electrical response of the insulating diblock copolymer system (DBC) filled with conductive fillers depending on the following factors: (i) composite temperature and morphology; (ii) affinities of fillers for copolymer blocks; (iii) interaction between fillers. By performing the consistent phase-field and Monte-Carlo simulations of the filled DBC system, we demonstrate that the location of fillers in DBC essentially depends on the above three factors. The simulated distribution of fillers in DBC, in turn, proves to be directly related to the electrical response of the composite calculated by the developed model. In particular, the order-disorder transition in DBC system is found to co-occur with the insulator-conductor transition in the filler network provided a sufficient difference between the affinities of fillers for dissimilar DBC blocks. The order-order transition between the lamella and cylindrical morphologies of DBC is found to cause a spike in the composite conductivity.

Posters

P1. Physical Properties of Chitosan with Varying Degrees of Deacetylation

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Chitosan is a biodegradable copolymer of β[1,4]-linked 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose[1] (see Fig. 1), which is obtained via the deacetylation of chitin. Chitin can be derived from fungi, molluscs, and crustaceans. Chitosan is classified as "generally regarded as safe" (GRAS) notification in the USA, and it is sold as a dietary supplement in the UK. Chitosan has been reported to have one of the lowest water permeabilities of all sustainable bio-based materials. [1]. Hence, there is growing interest in using chitosan in packaging as a sustainable alternative to petroleum-derived plastics. Despite this interest, the data in the literature offers conflicting values of the thermal, rheological, and barrier properties. Furthermore, deacetylation can be used to alter the hydrophilicity but at the same time reduces molecular weight, Mw. In this work, the effects of varying Mw and the deacetylation have been investigated. The thermal breakdown temperature, water sorption isotherms, and water contact angle were found to be independent of the molecular weight. There is no evidence for a glass transition in differential scanning calorimetry. As the enthalpy of water evaporation from chitosan was measured to be greater than that of free water, there is evidence for strong binding of water. Increasing the de-acylation time (which coincides with a decrease in the Mw) decreases the viscosity of solutions. The biomolecules show no evidence for chain entanglement. This deepened understanding of chitosan properties lays a foundation for future development as a sustainable packaging material.

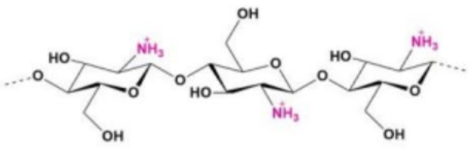

Figure 1. Molecular structure of the repeating group of chitosan. Taken from ref. 1

[1] A. Guarnieri et al., (2022) Sci Rep 12, 8084.
[2] P. Tyagi et al., (2021) Trends in Food Science & Technology, 115, 461-85.

P2. Equilibrium and non-equilibrium behaviour in polymer/small-molecule mixtures for organic photovoltaic (opv) applications

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In recent years, Organic Photovoltaics (OPVs) have shown improvement in efficiency, with some solar cell architectures reaching over 18%. The stability of OPVs still remains the major setback for the commercialization of the devices, and this has been traced to the thermal stress, photodegradations and the morphological instabilities within the organic semiconductor materials. The bulk heterojunction photovoltaics of polymer/small-molecule mixtures are essential in achieving high efficiency. In these mixtures, factors that are of key importance for device performance are the: (i) miscibility of the components (ii) segregation within the blend and (iii) morphology of the blend. This research investigates in one part, the novel Non-Fullerene-Acceptors (NFAs), which have led to significant recent increases in the efficiencies of OPVs and on the other part, the hysteresis in the polymer-fullerene bilayers. Recent research has shown that equilibration occurs within organic bilayers but does so in a way that cannot be rationalised within the framework of Flory-Huggins' theory; under certain circumstances, it has also been found that extensive mass-transfer occurs, but the system does not attain equilibrium. In this project, Neutron Reflectivity (NR) technique would be employed to study these changes in compositions and interfacial width of bilayer samples and ascertain if there is either true equilibrium or the existence of hysteresis (when and why it occurs).

P3. The role of internal strain in a nematic liquid crystal elastomer

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Liquid Crystal Elastomers (LCEs) are formed of liquid crystal polymers loosely crosslinked, resulting in flexible materials which can exhibit properties such as high order and birefringence when templated in a nematic phase. Previous work has been done to understand the role of crosslinking on nematic LCEs undergoing a temperature induced phase transition from an ordered nematic to a disordered isotropic phase [1,2]. In this work, the role of order and internal strain is investigated for a unique family of LCEs first developed by Mistry et al [3] which exhibit 'auxeticity' (negative Poisson's ratio under strain). This family of materials is of particular interest considering their auxeticity, high nematic ordering and their potential for applications such as impact resistance. Therefore, understanding how these materials behave with temperature is crucial to determine optimal temperatures for operation.

Using Raman Spectroscopy, we demonstrate that for an increase in temperature across an ordered nematic LCE, the order parameters ⟨P_2⟩ and ⟨P_4⟩ significantly decrease with ⟨P_2⟩ reducing from 0.65 at 25°C to 0.14 at 130°C. This reduction in order parameter is evidence of a continuous phase transition from nematic to isotropic (T_NI). Further techniques such as Transmission Spectroscopy and Fluorescence Spectroscopy reveal an onset of the continuous transition around ~ 80°C.

The order parameters, ⟨P_2⟩ and ⟨P_4⟩, can be seen to increasingly diverge from classic maximum entropy theory with an increase in temperature. Interestingly, we demonstrate that using a modified mean field theory achieves good agreement to experimental order parameter results to reveal the role of internal strain during the continuous T_NI.

[1] Disch, S. et al. Macromol. Rapid Commun. 1994, 15, 303-310.
[2] Selinger, J.V. et al. Phys. Rev. Lett. 2002, 89 (22), 225701.
[3] Mistry, D. et al. Nat. Commun. 2018, 9 (1), 5095.

P4. Dissolution of wool yarns by 1-ethyl-3-methylimidazolium acetate studied with time-temperature superposition

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The dissolution of wool yarns in the ionic liquid 1-ethyl-3-methyl-imidazolium acetate [C2mim][OAc] has been investigated. Wool yarns were submerged into [C2mim][OAc] and dissolved for various times and temperatures before coagulating with water. Optical microscopy was used to track the yarn's cross-sectional area. We propose that there are two competing dissolution processes, one rate-limited by disulfide bonds at low temperatures (LTs), and a second by hydrogen bonds at high temperatures (HTs), with a crossover point between the two regimes at 70 ℃. The corresponding activation energies were ELT = 127 ± 9 kJ/mol and EHT = 34 ± 1 kJ/mol. The remaining area of the dissolved wool yarn could be shifted via time–temperature superposition to plot a single master curve of area against time for both regions. Finally, the dissolution could be modelled by a diffusion process, giving self-diffusion coefficients for the [C2mim][OAc] ions (0.64–15.31 × 10^{-13} m^2/s).

P5. Investigating the influence of crosslinker concentrations on the phase templating of liquid crystal elastomers

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Polymer templating has been an attractive field as 'templating' can be used to control the structure and the morphology of the polymer. Liquid crystals (LC) have been uilized as a templating medium to create LC polymer networks, which show stimulus-response and enhanced functionality [1, 2]. Liquid crystal elastomers (LCEs) are a class of polymeric materials that combine the properties of LC anisotropy and rubber elasticity, resulting in stimuli-responsive properties and unique mechanical behaviors [3].

Cross-linkers play an important role in the mechanical and optical properties of LCEs and also in elastomer-templated networks. Studying the influence of synthesis and crosslinker concentration on LC order and phase templating allows for understanding the properties and behavior of LCEs and decoupling the effects of composition from structure and order[4]. In this work, the influence of crosslinker concentrations on phase templating of LCEs has been investigated. Isotropic LCEs were produced by diluting the monomers with a range of solvents, while nematic LCEs were created by adding a nonreactive mesogen 6OCB. A combination of polarising optical microscopy and differential scanning calorimetry have been used to measure the phase transition temperatures of the mixtures. Isotropic LCE samples showed an increase in TNI and Tg by increasing crosslinker concentration and at a value of the crosslinker ~6 $mol\%$, the isotropic phase was stabilized and persisted following the drying of polymerised materials. Moreover, the addition of 6OCB and ~6 $mol\%$ crosslinker resulted in the formation of isotropic LCE at 60°C polymerisation, while monodomain nematic LCE was produced at 22°C polymerisation. By contrast, at lower crosslinker concentrations, LCEs that polymerised in the precusor’s isotropic phase exhibited a transition to a polydomain nematic state at room temperature upon 6OCB removal. The ability of templating phases with ~6 $mol\%$ of crosslinker was further demonstrated by adding the chiral dopant CB15 to the nematic precursor. The resultant LCE exhibited an oily streak texture, consistent with the chiral nematic phase.

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P6. Utilising microorganisms encapsulated within hydrogels for agricultural applications

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Food is a bedrock of human civilisation, which every person is reliant on. Unfortunately, there is a large disparity in food access across the world meaning up to 783 million people despite the UN sustainable development goal of eliminating world hunger by 2030. Resource constraints on the manufacturing of agrochemicals has driven the pursuit of alternative crop products, namely biologicals. These products are highly scalable, exhibit extended availability in the soil, foster a more diverse biological community (improving crop productivity) whilst preserving soil structure and tend not to leach outside of their area of application. At present the transportation and application of living microbes remains challenging; hydrogel encapsulation has been proposed as a method for protecting the living payload. This project aims to develop a scalable method of encapsulating soil microbes in micron-sized hydrogel beads towards delivering a more sustainable agricultural product.

A range of biopolymers, including chitosan, alginate and cellulose are cross-linked with a range of crosslinking agents to form biodegradable gels. The mechanical properties of the gels and the kinetics of crosslinking are measured by rheology. In parallel, various microbes are cultured to form a broth. The broth is then loaded with a crosslinkable biopolymer and controllably crosslinked to measure viability for different biopolymers and different crosslinking densities. The loaded biopolymer precursor is then sprayed into the crosslinking agent to form microparticles. The shear stress required causes a tradeoff between particle size and viability of the microbe. Identifying and tuning the operational parameters on a pilot scale rig enables fast screening for different microbe/hydrogel/crosslinker combinations. This project develops an inexpensive, scalable product that supports sustainable farming and economic growth.

P7. Thermomechanical recycling of PET based textiles

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The textile industry faces major sustainability issues due to the very large volume of waste produced. 84-92 million tonnes of pre and post-consumer textile waste is collected globally per year of which 66-75% ends up in landfill. In fact, of the 10% of textiles that are recycled globally less than 1% are recycled back into new textiles, leading to a growing global textile waste problem and pressure on virgin resources. One of the most common textile fibres is poly(ethylene terephthalate) (PET). PET may be chemically or thermo-mechanically recycled. Although ‘recycled polyester’ clothing is available, to date, this is almost exclusively obtained from recycled plastic bottle waste. Textile-to-textile PET recycling is a much more complex process that is yet to be developed on large scale.

Starting from different textile waste samples supplied by Project Plan B, we have performed sequential thermomechanical extrusion cycles of PET monofilaments. Changes in the chemical and physical properties of the filaments from textile waste are being compared to those of pure PET to determine whether PET textiles can undergo repeated thermomechanical recycling. Machine learning is being used to predict the changes in PET viscosity that occur during extrusion and to determine the amount of virgin material needed to reach optimum physical properties. This will help to determine if it is worthwhile recycling certain textile waste feedstocks. Additionally, we show that solid state polymerisation (SSP) could be used to improve the physical properties of recycled PET based textiles, without the need to add virgin materials. PET used for textiles has relatively low molecular weight/ viscosity. We believe that that short residence times are sufficient to increase properties such as viscosity to usable standards, making the process sustainable and economically viable.

P8. Modelling polymer crystalline microstructure and gas barrier properties

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There is an urgent societal need to accelerate the development of sustainable plastics, and transition away from fossil sourced plastics. Plastic thin films are used in a variety of applications, ranging from low cost food packaging to high end electronics, where mechanical strength and flexibility, and gas and water barrier properties are of critical importance. Typically, filler particles and plasticisers are added to improve the film performance, and these additives change the crystallinity and microstructure of the polymer. We will present a model for spherulitic growth in a thin film following Avrami theory combined with filler-induced nucleation. The spherulitic microstructure will be characterised in terms of its statistical properties, such as the distribution of domain sizes, which will provide a framework for understanding experimental microstructures, whose statistical properties will also be characterised and compared to the models. The dependence of the gas barrier properties on the microstructure, based on a Fickian diffusion model will be presented.

P9. Optimisation of frontal photopolymerisation for non-planar material assembly

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FPP is a light-driven directional solidification process which yields conversion profiles that propagate in time, in the form of travelling waves, generally under conditions of strong light attenuation and limited mass transfer. Under certain conditions, the travelling conversion profiles are time-invariant, while in general these evolve with time due to a complex interplay of mass or hear diffusion, and network properties. In the simplest form, our models comprise a single equation of motion for a (scalar) conversion fraction ϕ and a generalised Beer-Lambert law accounting for the spatio-temporal evolution in conversion. The non-trivial coupling of these equations can describe a range of systems, but higher order chemical conversion schemes are needed to account for experimental observations of solidification kinetics, light attenuation and spatio-temporal monomer-to-polymer conversion, acquired by profilometry, AFM and spectroscopic imaging. Our framework provides a range of simple descriptive models, with a small number of system parameters, yet providing predictive ability for ubiquitous solidification and patterning processes, including 3D printing and non-planar assembly of materials generated via photopolymerisation.

P10. Machine Learning-Enhanced Metadata Analysis for Identifying Polymer Compositions

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High-volume, low-cost polymers offer numerous solutions to various industrial challenges, such as lightweight aircraft cabin components and high breakdown strength polymers for high-voltage insulation. The affordability and continually improving properties of these polymers have led to widespread industrial applications. However, a critical challenge for the polymer industry is enhancing the processes used to produce, form, and dispose of polymers.

A major issue in disposal is the identification and composition analysis of polymers. Current techniques, such as Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), are used to identify polymers. However, the significant amount of additives in commercially available polymer materials complicates the comprehensive determination of their composition and identification. This necessitates the use of multiple methods and expert analysis, making the process time-consuming. Historically, polyethylene, polypropylene, and other hydrocarbon-based polymers have been extensively used, but with current and future developments, polymer structures are becoming more complex. Therefore, the need to automate identifying polymer compositions is becoming more significant.

For instance, in the cable industry, subsea cables which consist large volume of plastics are recycled after a long operation time; due to various patents the exact composition remains unknown. If a company ceases operations, this information may be lost. Instead of processing everything together, which can result in harmful byproducts, separating materials based on their unique compositions allows for safer and more efficient recycling processes.

This research aims to address these challenges by developing a data-driven metadata analysis method utilizing a machine learning approach that leverages different classifier pipelines to correlate polymers, fillers, and volume fractions with their measured properties. For a given combination of measured property values, the system can offer a confidence percentage for various filler-polymer-volume fraction combinations. Additionally, the system would suggest potential further property measurements that would most significantly increase confidence in identifying the likely combination of polymer, filler, and volume fraction. This approach aims to streamline the identification process, reduce the number of necessary measurements, and support a more sustainable and efficient polymer industry. Currently filler only represents nanoparticles but can be extended to other forms of additives, provided enough data.

Data has been collected from NanoMine: An Online Platform of Materials Genome Prediction for Polymer Nanocomposites from the Brianson research group.

P11. Using coupled phase field models to understand microstructures induced by dual transition processes.

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Understanding the spinodal decomposition of polymer blends is of great importance in fields such as biological cells, polymer composites, solar cells and many more. Spinodal decomposition is a spontaneous process which governs self assembly in both biological and polymer mixtures leading to the formation of membraneless organelles or material microstructures, for example.

In the case of polymer blends, the mixtures may be composed of materials with very different glass transition temperatures, such that during phase separation, portions of the polymer (rich in materials with higher glass transition temperature) become glassy whilst the rest of the material remains liquid. This asymmetry changes the morphology compared to a transition from pure spinodal decomposition, hence produces a material with different characteristics, therefore gaining an insight into such a process will lead to a better material manufacturing. A key piece of physics required to understand the microstructure formation in materials that become glassy is to capture the shrinkage that the phase undergoes, in addition to the increase in viscosity.

To model this, we are investigating the morphology from a dual process transition (spinodal decomposition coupled with glass transition) by combining two phase field models, a compressible diffusive spinodal decomposition model coupled with hydrodynamics which enables shrinkage of the bulk material via the dynamics of a free surface, simulated via a custom mesh-free simulation framework on GPU.

P12. Enhancing electrical properties of epoxy resins using bio-based modifiers

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Epoxy resins are a class of materials which play a vital role in the performance of electrical applications such as high voltage transformers, bushings, wind turbine blades, etc. Bio-based additives offer numerous advantages, including reductions in environmental impact, and the potential to enhance electrical, thermal, and mechanical performance of epoxy resins. Bio-based calcium carbonate filler (CCF), derived from sustainable materials such as limestone, seashells, or eggshells, provides an alternative to traditional fillers. Additionally, bio-based modifiers can integrate within the polymer network, resulting in systems with enhanced properties. An example of a bio-based modifier is cashew nutshell liquid (CNL), which contains monofunctional epoxy-terminated monomers. This study aims to investigate the effects of CCF and CNL on the electrical and mechanical properties of epoxy resins.
Various percentages of CCF and CNL were incorporated into an epoxy resin matrix cured with an amine-based hardener. The manufactured samples were characterized via DC conductivity, AC breakdown, dielectric spectroscopy, and tensile tests.

The results indicated that both CCF and CNL led to a decrease in the dielectric permittivity. Notably, the addition of 8 wt% CNL resulted in a 30% increase in the breakdown strength of the modified samples. In contrast, adding up to 4 wt% CCF caused only a negligible change in breakdown strength. Furthermore, samples with 4 wt% CCF exhibited the highest ultimate tensile strength, while samples with 8 wt% CNL demonstrated the highest Young's modulus.

Investigating the use of bio-based fillers and modifiers to enhance the electrical and mechanical properties of epoxy resin systems is rather essential. The findings of this study are pivotal in promoting sustainability, reducing environmental impact, improving health and safety, meeting regulatory requirements, and addressing the market demand for eco-friendly dielectric materials.

P13. Hyperbranched Polymer Drug Delivery Vehicle

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Cancer is a leading cause of mortality worldwide and 50% of people in the UK will be diagnosed with cancer at some point in their life. Chemotherapy is a common treatment for all cancer types but has several limitations, most chemotherapy drugs are hydrophobic, non-specific, and toxic to healthy cells. The genetic instability of cancer makes drug discovery difficult due to the constant evolution of cancer cells. An alternative approach to these issues is to develop novel formulations of existing chemotherapy drugs to improve their effectiveness. Polymeric nanocarriers offer the potential to improve drug solubility, transport and targeting of existing drugs. This project aims to develop a drug delivery vehicle comprised of a hyperbranched polymer maximising drug loading efficiency whilst minimizing the time and cost of processing.

Polyethylene glycol chains are functionalised and then grafted onto the surface of a dendrimer. The structural properties of the dendrimer can be characterised by DLS, FTIR and NMR. The functionalised dendrimer is loaded with drug by the solvent inversion process whereby the drug preferentially migrates to the core of the dendrimer due to the hydrophobic effect. The concentration of loaded drug is quantified using UV-vis spectroscopy. Varying the solubility of the dye and measuring drug loading will lead to the development of a predictive relationship that can be applied to any dye. The thermodynamics of drug-polymer and drug-solvent interactions are coupled with the kinetics of processing, so the first step is to develop a robust, scalable processing route. Systematically varying the time of the inversion step, preliminary results suggest that faster inversions result in greater drug loading. Once the loading process has been optimized for nile red, I will use the same conditions to compare a range of other dyes and drugs.

P14. Multiplexed microfluidic setup for analysing interaction of complex blend of triacylglycerols with surface active agents

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We demonstrate experimental approaches that will aid in predictively designing surfactant formulations of greater efficiency and sustainability, leading to a reduction in water and energy consumption and a lower environmental footprint. We examine the emulsification ability of model surfactants and mixtures, employing representative complex hydrophobic films, namely blends of triglycerides. We utilise microfluidic techniques, able to control the thermal and flow fields, and quantify the removal process using a combination of experimental probes and process conditions.

We study the removal of triglycerides in a single microfluidic channel, and then introduce ways to incorporate multiple channels in a single microfluidic setup, that is, multiplexing. Multiplexing in microfluidics enables multiple, comparative experiments, simultaneously within a small chip. We demonstrate that the microfluidic chip can incorporate tens and hundreds of channels in a single chip and then comparatively study the removal of triglycerides by varying the surfactant formulations in different channels. The model hydrophobic substrate, a combination of three triglycerides that mimics tallow, is deposited within microfluidic channels by capillary flow technique. The multiplexed setup consists of multiple outputs attached to reservoirs of surfactant solutions and a single input connected to a pump, where the single pump is pulling the solution, and between the input and output cleaning occurs in channels. Different pressure conditions were experimented with to realize a uniform flow in different branches of the multiplexed setup. This experimental setup enables efficient screen surfactant's molecular structure, mixture, and concentration for specific water hardness and process temperature, by varying a single parameter at a time and only utilising a small amount of materials.

P15. Nanophotonic taste buds for biomedical applications

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The most commonly employed disease diagnostics and monitoring systems for detecting biological moieties rely upon antibody-antigen pairings due to their high selectivity and strong binding affinities. Whilst antibodies can provide reliable and accurate results, they are susceptible to denaturation and deactivation of their binding sites and are unsuitable for small molecule detection due to size limitations. Furthermore, production and genetic engineering of bioreceptors is expensive, technically challenging, and time-consuming. Molecularly Imprinted Polymers (MIPs), coined 'artificial antibodies', rectify the shortcomings of antibody-antigen pairings by displaying increased stability, the ability to detect small molecules as well as biological markers, and straightforward synthesis mechanisms. Additionally, MIPs are easily adapted to detect a huge library of specific markers within biosensing.

Typical biosensors operate through a 'lock and key' system, i.e. they are only capable of detecting singular analytes. Whilst this system is important, it struggles to keep up with the growing interest in simultaneous sensing. Sensors capable of interrogating one sample for a variety of biomarkers simultaneously holds interest for research into continuous monitoring and determination of novel biomarkers and pairings. In addition to this, simultaneous probing for biomarkers in one sample can significantly reduce the sample volume and testing time required to reach a diagnosis.

Here, we address these limitations by developing a novel nanoplasmonic sensing array consisting of lithographically fabricated gold nanostructures functionalised with a variety of MIPs. By designing each polymer to specifically bind to a particular analyte, our engineered metasurface will be capable of simultaneous biorecognition and small molecule detection for widespread analysis of markers simultaneously. The simultaneous reactivity of the sensor concept offers itself to a variety of applications including fingerprint analysis of patient samples, more accurate and specific diagnosis, and research into less monitored diseases in a way that current technologies struggle.

P16. Development of new sustainable adhesives promoting recycling using reversible conductive polyelectrolyte adhesion

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This work addresses the growing problem of electronic waste (e-waste) by developing a reversible conducting adhesive (RCA). The high demand for electronic devices and their short lifespans contributes to the annual rise of electronic waste, with only 17% of global e-waste being properly recycled 1. According to the United Nations Environment Programme (UNEP), electronic wastes contain substances that present a significant threat to human and environmental health 2. Furthermore, electronic waste should be involved in a circular economy by returning the e-waste to the production chain through reusing and recycling. Also, recycling these materials could minimise the demand for virgin mining for vital metal 1.

In this work, reversible conductive adhesive is introduced as a replacement for metal solder, allowing electronic components to be easily removed from PCBs. The adhesive reversibility can be achieved using chemical stimuli (pH change) in two different formulations. One by using polystyrene-butyl acrylate and poly acrylic acid (Pol st-ba/paa) as polyanions; another formulation involves using polystyrene-butyl acrylate and chitosan (Pol st-ba/chi) as polycations 3. The carboxylic groups (-COOH) in AA lead to electrostatic interaction with a surface to form an adhesive bond 4. At higher pH (above its pKa≈ 4.5) 3, the deprotonation of carboxylic groups occurs due to excess hydroxide ions (OH-), which reduce the adhesion strength and make the adhesive easily removed from the surface 5. On the other hand, chitosan consists of amino group (-NH2) that protonated at low pH (below its pKb≈ 6.5) to form an ammonium group (-NH3+), leading to chain expansion, thus reducing adhesion strength 6.

The glue was tested on various surfaces were tested, including glass, plastic, copper, stainless steel, steel, aluminium, and printed circuit boards (PCBs), which show good reversibility and adhesion strength for both formulations. The reversibility of the adhesive has several unique properties that set it apart from other adhesives. It can be debonded on demand without significant damage to the materials involved, allowing for recycling and reusing of materials. At the same time, the polyanions glue shows good conductivity to be considered as replacement for solder joints. Moreover, the adhesive can be produced from renewable sources with minimal environmental impact at a reasonable cost 7.

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P17. Mechanical characterization of PDMS samples with varying prepolymer molar mass

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Polydimethylsiloxane (PDMS) is widely used because of its excellent thermal stability, biocompatibility, and gas permeability. PDMS, a member of the important class of silicones, which has a wide range of commercial and industrial applications. This study focuses on analysing the mechanical properties of PDMS samples with variable prepolymer molar mass, synthesised using the hydrosilylation reaction method, through compressive and tensile tests conducted following ASTM standards (Johnston et al., 2014). Cylindrical samples for compression and dog-bone samples for tensile tests were produced, with Sylgard 184 PDMS as a reference material. Mechanical properties including elastic modulus, crosslinking density, contact angle, and yield of reaction were assessed. The elastic modulus was determined from the initial linear region of the stress-strain curves using Hooke's Law ($E = \sigma/\varepsilon$), while a power-law behaviour ($\varepsilon \propto \sigma n$) was used to study the non-linear region. Crosslinking density and molar mass between crosslinks were calculated using both mechanical tests and theoretical models. Mechanical tests involved direct compression and tensile testing, while theoretical models included using a Phantom model network (Petroli, 2018) and methods described by Chassé et al. (2015). The extractable fraction was determined to calculate the reaction yield and contact angle measurements were conducted to analyse surface characteristics. Preliminary results show that higher molar mass prepolymers result in lower crosslinking densities and higher molar mass between crosslinks. These trends were consistent across mechanical testing and theoretical models. The yield of reaction, assessed by the extractable fraction, indicated efficient crosslinking. Contact angle measurements demonstrated the hydrophobic nature of the PDMS samples. This study offers a comprehensive comparison of the mechanical behaviour of PDMS samples with variable prepolymer molar mass, allowing for the optimisation of PDMS formulations for improved mechanical performance in various applications.

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P18. Unravelling capsule formation mechanisms in interfacially initiated PEGDA hydrogels

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Bacteria are used in a range of industries, such as waste water treatment, bioremediation or as soil additives. Live bacteria are often encapsulated to protect them from mechanical damage, desiccation and to prevent release. Therefore, these capsules need to be mechanically robust, while permitting sufficient diffusion to support the metabolic activity of the bacteria.

Here, we produced covalent hydrogel capsules from a water-in-oil (W/O) emulsion of aqueous poly(ethylene glycol) diacrylate (PEGDA) in hexadecane, containing a UV-radical initiator. Upon initiation, PEGDA polymerisation begins at the W/O interface to produce hydrogel capsules.

The 3D polymer microstructures were visualised using cryo-SEM after freeze fracture in conjunction with qNMR reaction tracking to estimate internal polymer fractions with a range of processing parameters. Systematic investigation showed how the UV energy input and the PEGDA macromer concentration can be used to selectively create honeycomb, sponge-like or dense spherical capsules. For each structure, the water-holding capacity and network swelling were assessed via thermogravimetric analysis.

When considering these results together, we propose a capsule formation mechanism based on diffusion-limited aggregation of PEGDA microbeads. The structures resemble random walk simulations of sticky beads and further satisfy the theoretical volume fractions required for microbeads percolating throughout a sphere.

We successfully encapsulated live Mycobacterium smegmatis within the sponge structures, demonstrating biocompatibility and that the internal hydrogel structure does not prevent growth of bacteria. This mechanistic understanding is paramount for designing robust covalent capsules while optimising porosity within hydrogel structures.

P19. Structure and Rheology of Semicrystalline Dissociative Polyurethanes

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In 2022, almost 1 million tons of polyurethane adhesives and sealants were consumed, being used primarily in the automotive, packaging, and construction industries. As these adhesives are irreversibly bonded, recycling of the adhesives and their substrates is not economically viable and as a result their use generates landfill waste. Alternative thermoplastics with dissociative covalent bonds have been prepared to address this problem, making strong adhesives that melt readily upon heating. This project seeks to test and characterise the structures and properties of these new, thermally reversible polyurethane adhesives.

Methylene diisocyanate/polyester semicrystalline polyurethanes with reversible Diels-Alder chain extenders were studied. Differential scanning calorimetry was used to characterise the thermal transitions of the materials. Small-Angle X-ray Scattering (SAXS) indicated the polyurethanes exhibit a lamellar structure with d-spacings in the range of 103-158 Å. Simultaneous SAXS/WAXS/DSC melting studies were applied to elucidate morphological changes as the materials melt and dissociate, allowing the crystalline melting point and retro Diels-Alder reaction to be followed online.

To correlate morphological data with material dynamics, rheological measurements were performed on the polyurethane melts. Frequency sweeps were taken over a range of temperatures and used to construct Time Temperature Superposition (TTS) master curves for the polymers' terminal and transition to flow regions. Interestingly, the TTS principle could be applied to these materials suggesting they are thermorheologically simple up to the reversible bond dissociation temperature.

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