

**The British Society of Rheology's**

**Non-Newtonian Club: Rheology for Processing**

**Thursday 19th September, 2019**

**University of Nottingham, School of Mathematical Sciences**

**List of Abstracts**

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### **RHEOLOGY FOR PROCESSING**

**'Disecting Dieswell'**

***Ian Robinson, Durham University, UK***

A facile method for predicting the optimal conditions for rapid, stable polymer extrusion, which relies only on gram-scale laboratory experiments for two commercial polystyrene samples with two molecular weights is demonstrated. Oscillatory rheology measured both molecular relaxation times and shear viscosity by the Cox-Mertz rule. These enables a shear viscosity map vs temperature and shear rate to be constructed, together with the positions for the major molecular timescales.

Alternative methods for characterising rheology, including melt flow index and capillary rheology measurements were also employed, but these do not give the same level of understanding of flow behaviour. The MFI test shows limited usefulness. The capillary tests generate shear viscosity vs shear rate at a series of temperatures. In addition, it measures die swell behaviour, where the melt lace makes a transition from stable to unstable behaviour at a range of shear rates for both polymers as a function of temperature at the expense of a larger sample volume. The complex die swell behaviour can be seen to collapse onto a single line regardless of temperature when plotted using the Rouse Weissenberg

number and using an empirical timescale measure defined in the paper. The full shear viscosity map, together with the polymer timescales thus serves as a design tool to predict processing behaviour for melt processors.

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**The CORAL project: Modelling toothpaste**

***Helen Wilson, University College London, UK***

I will talk about a joint project between UCL Mathematics, Chemical and Mechanical Engineering, aiming to model various processes and materials involved in the production of toothpaste. In Mathematics, we have been focusing primarily on aspects of suspension mechanics, including shear thickening and first steps towards incorporating a non-Newtonian fluid matrix.

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**Blending and degradation analysis of the heat sensitive biodegradable polymer poly(hydroxybutyrate-co-hydroxyvalerate)**

***Catherine Kelly, University of Birmingham, UK***

Poly(hydroxybutyrate-co-hydroxyvalerate) (PHB-co-HV) is a promising sustainable and biodegradable packaging material, however, progressive embrittlement caused by secondary crystallisation, and a poor thermal stability has limited widespread use. The addition of low molecular weight poly(ethylene glycol) (PEG) has been shown to reduce the rate of secondary crystallisation and therefore produce a more suitable material. The aim of this work was to analyse the melt miscibility of these two polymers and assess the effect of PEG on the thermal stability. Standard

frequency sweeps could not be performed due to thermal instability, and therefore time sweeps were utilised and the data superposed to generate a master curve. Rheological analysis, using the Han plot, showed PHB-co-HV and PEG to be miscible within the concentrations and molecular weights studied. The presence of PEG increased the degradation rate of PHB-co-HV at 185 °C, however, as PEG reduces the melting point and viscosity, the blends could be analysed at lower temperatures. This resulted in a 56% reduction in the degradation rate.

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### **Instability and interfacial segregation under flow**

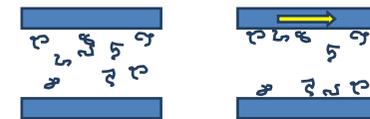
***Richard Thompson, Stephen Boothroyd, James Hart and David Hoyle***

***Department of Chemistry, Durham University, DH1 3LE, UK***

Engine lubricants should have as low a viscosity as possible under running conditions in order to minimise energy dissipation, yet usually require some polymer in the formulation to inhibit undesirable contact between moving surfaces. Managing these opposing demands, sustainably over the operating range of temperature and shear rate for an engine is a substantial challenge for lubricant formulations.

Recently, we have explored the idea that under certain shear conditions, the composition of a model lubricant could vary significantly from the bulk composition. The physics of shear banding suggests that this is certainly possible over certain ranges, and our experiments using a multi-pass rheometer show that shear flow near surfaces generates significant concentration fluctuations that are reversible. Using a hyperbolic die, we show that there is a characteristic onset shear rate for instability, and that this is most easily triggered close to the two-phase boundary measured in the quiescent state.

Very recent neutron reflectivity results will be presented that show surface enrichment of the model lubricant is possible at even modest shear rates, sketched in figure 1. This interfacial segregation is closely related to shear-induced concentration fluctuations in the bulk. Interestingly, when the mixture is not close to a bulk phase boundary, the shear induced surface segregation appears to be absent over the accessible range of experiments.



**Figure 1. Sketch of shear-induced segregation in model lubricant.**

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### **The interplay between polymer processing and polymer physics in nanocomposites**

***Nigel Clarke, University of Sheffield, UK***

The addition of nanoparticles to polymers to impart enhanced mechanical and functional properties presents new challenges for polymer processing, requiring us to develop an understanding of how nanoparticles impact polymer structure dynamics at a molecular level. We have shown how dynamics can be altered by nanoparticle size, shape, aspect ratio, surface area, loading and the nature of the interactions between the nanoparticles and the polymer matrix. We have observed various dynamic phenomena which appear to be uniquely associated with polymer nanocomposites. Unlike polymer melts, we have found that diffusion and rheology are decoupled in polymer/carbon nanotube nanocomposites.

We have observed a minimum in the diffusion rate of polymer chains as a function of nanoparticle concentration when the nanoparticles are rod-like (e.g., carbon nanotubes) and a collapse of the diffusion coefficient onto a master curve when the nanoparticles are spherical (e.g., silica nanoparticles). In the case of graphene and related two-dimensional materials, the high specific surface area nanomaterials in the graphene family alter the properties of the bulk polymer at very low concentrations. We have found that the graphene oxide within polymer nanocomposites, whilst locally flat up to length scales of  $\sim 16$  nm, is rough on a very wide range of length scales, implying extensive extrinsic wrinkling and folding. Our results demonstrate that well exfoliated sheets are key to achieving high interfacial areas between polymers and high aspect ratio filler in nanocomposites. We also show that the conformation of the polymer chains in the presence of graphene oxide mimics confinement at a solid interface, a molecular indicator of well-dispersed, high aspect ratio nanoparticles that are much larger than the polymer coil size. We show that this confinement causes a corresponding reduction in interchain entanglements.

## **FOCUS SESSION: Additive Manufacturing**

### **Crystallinity Development during Fused Filament Fabrication through Fast Scanning Chip Calorimetry**

*Peter van Puyvelde, KU Leuven, Belgium*

Although semi-crystalline polymers are associated with considerably better mechanical properties and thermal stability compared to their amorphous counterparts, using them as feedstock for Fused Filament Fabrication still poses some major challenges. Hence, the development of printed part crystallinity during printing should be fully understood in order to control the developed weld strength, as well as part shrinkage and warpage. Infrared thermography was utilized to record the thermal history of deposited layers while printing a single-layer wall geometry, employing two PA 6/66 copolymers with distinct molecular weights as feedstock. Print settings were varied to establish which settings are essential to effectively monitor final part crystallinity. The resulting temperature profiles were simulated in a Fast Scanning Chip Calorimetry device that allows for the rapid heating and cooling rates experienced by the printed polymer. Both liquefier temperature and print speed were found to have very little influence on the total attained crystallinity. It became apparent that the build plate, set at a temperature above the polymer's glass transition temperature, imposes a considerable annealing effect on the printed part. A reduced molecular weight was observed to enhance crystallinity even more strongly. The presented methodology proves that Fast Scanning Chip Calorimetry is an effective tool to assess the impact of both print parameters and feedstock characteristics on the crystallization behavior of semi-crystalline polymers over the course of printing.

### **In-situ optical detection of polymer crystallization during 3-D printing**

***Dario Cavallo, University of Genoa, Italy***

Fused Deposition Modeling (FDM) involves the extrusion of a molten polymer through a moving nozzle, followed by its rapid cooling to consolidate the object shape. When semicrystalline polymers are employed, the complex thermo-mechanical history likely affects the crystallization process and the final properties of the products. However, crystallization of polymers in FDM is still a largely unexplored topic. Some preliminary results on the tracking of polymer crystallization in-situ during 3-D printing will be presented. Two optical setups were used to measure either the transmitted or scattered light during printing a single-layer wall of amorphous and semicrystalline polymers. Limitations of the first proposed setup, arising from the large beam-size and strong scattering of the crystalline entities are highlighted. Exploiting the second strategy, distinctive signatures of filament crystallization during deposition could be observed for a nylon-6/nylon-6,6 copolymer. The variation of crystallization time with printing conditions (i.e., nozzle temperature and print speed) was preliminarily explored.

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### **The role of rheology in laser sintering of polymer particles**

***Patrick D. Anderson, Eindhoven University of Technology, Netherlands***

Merging of particle pairs during selective laser sintering (SLS) of polymers is vital in defining final part properties. Depending on the sintering conditions, polymers can undergo full or partial sintering whereby incomplete sintering results in poor mechanical properties. In the present work, a novel in-house developed experimental setup is used to perform laser sintering experiments on polymer particle

doublets while performing in-situ visualisation of the sintering dynamics. Sintering conditions such as heating chamber temperature, laser pulse energy and duration, laser spot size and particle size are precisely controlled and systematically varied. A non-isothermal viscous sintering model, extending the Frenkel model, is developed to qualitatively predict the observed effects of the various parameters. It is shown that the sintering kinetics is determined by a complex interplay between the transient rheology caused by the finite relaxation times of the polymer and the time-dependent temperature profile which also affects the polymer viscosity. The combination of a full material characterisation with sintering experiments under well-defined conditions has resulted in a general understanding of the effects of material and process parameters on laser sintering. Results are compared with a computational model using the finite element method. Firstly, we analysed the viscoelastic flow problem of the sintering process using both the Giesekus model and the extended Pom-Pom model to describe the complex behaviour of the polymer. Secondly, we included the temperature-dependent low behaviour of the system to study the effect of process and material parameters. Finally, we discuss the crystallisation kinetics to predict and tune the morphology of the products.

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### **Rheological Consideration for the Design and Development of 3D Printable Hydrogel**

***Zuoxin Zhou, University of Nottingham, UK***

Hydrogels are physical or chemical network trapping high content of water that have been used extensively in biomedical applications to mimic soft tissues. 3D printing has become important manufacturing techniques to process various hydrogels. The rheological requirements

for a 3D printable hydrogel are different from those for the conventional injection of hydrogels into a mould. This talk reviews how rheological behaviour of hydrogels affects the overall 3D printing process.

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### **Designing hydrocolloid based food-ink formulations for extrusion 3D printing**

***Azarmidokht Gholamipour-Shirazi, Ian T.Norton, Tom Mills, University of Birmingham, UK***

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The major challenge and complex applications of additive manufacturing are emerging in the field of gastronomy, or in other words, “food 3D printing”. The ability to selectively deposit material within a 3D volume and hence gradate the composition offers the possibility for the control of complex structures for altering texture, taste and morphology in food products. Manipulation of microstructures by regulating mix and selective deposition of materials can allow regulation of fracture, breakdown or dissolution mechanics during product use, giving the possibility of a range of functional and novel foods. Not every type of food can be printed and also there is a limited quality of ingredients. In order for a material to be used in extrusion-based printing, it should display shear thinning behaviour. This determines if it can be extruded from the nozzle. For a practical application of 3D printing in the field of food, a precise setting of all printing parameters should be performed as a function of mechanical properties of the material. Furthermore, the study of the rheological properties and their relationship with the printing variables will be of crucial importance to improve the quality of 3D food objects. There still

exists a knowledge gap in linking material structure to process printing variables in order to obtain the desired 3D printed product. This study investigates rheological properties and printability (shape fidelity) of food-grade hydrocolloid pastes. From this study, it was found that if the phase angle is in the range of  $3^{\circ}$ – $15^{\circ}$  and the relaxation exponent is in the range of 0.03–0.13 the paste material is printable, which means that it can support its own-weight if printed. As the demand for inks for 3D printing increases, rheological measurements can rapidly assist with the development of new ink feedstocks.

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### **Rheology of printable soft materials for enhanced performance in 3D manufacturing**

***Dr Esther García-Tuñón, Materials Innovation Factory & School of Engineering, University of Liverpool, UK***

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Extrusion-based 3D printing, also known as Direct Ink Writing (DIW) or robocasting, is an additive manufacturing technique that provides a unique approach to introduce advanced and high-added-value materials into lab-scale manufacturing. Robocasting involves the continuous extrusion of colloidal pastes or gels through a fine nozzle to create 3D structures layer-by-layer. Formulation design aims to ensure “printability” through careful control of rheology. The pastes must be shear thinning to easily flow through the nozzle at modest shear rates and then immediately set into a non-flowing structure once printed. They must also be able to support multiple layers on top and retain the shape across spans without deformation.

The definition of “printability” however is often ambiguous and based on experimental observations rather than theory. “Printability” is also a broad concept due to the diverse range of applications within the field, from bio printing to structural composites and energy devices. This talk will focus on the different protocols we have combined to create “printability maps” in order to guide formulation design and determine their performance. We use different rheological tests in shear, extensional and oscillatory rheology that enable quantifying the printability of soft materials [1]. 2D colloids of graphene oxide (GO) exhibit a fascinating rheology and can aid the processing of different materials to develop ‘printable’ formulations [2]. GO colloids in water form printable networks at relatively low concentrations and can behave as multifunctional additives. Due to unique surface chemistry GO, can be used to act as a rheology modifier that imparts a strongly shear-thinning behaviour and yield stress ( $\sigma_y$ ) to suspensions of other materials even when is used in small concentrations [2]. This talk will cover an in-depth rheological study of GO suspensions with a wide range of behaviours from Newtonian-like to viscoelastic ‘printable’ soft solids [1]. Our results demonstrate that the quantification of ‘printability’ can be based on three rheology parameters: the stiffness of the network via the storage modulus ( $G'$ ), the solid-to-liquid transition or flow stress ( $\sigma_f$ ), and the flow transition index, which relates the flow and yield stresses ( $FTI = \sigma_f / \sigma_y$ ). I will also discuss the range of formulations that our group is developing, their potential in energy applications, as well as the complex structures that can be made and approaches to overcome current limitations.

#### REFERENCES

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2. García-Tuñón, E.\* *et al.* Graphene Oxide: An All-in-One Processing Additive for 3D Printing. *ACS Appl. Mater. Interfaces*, 2017, **9**, 32977–32989