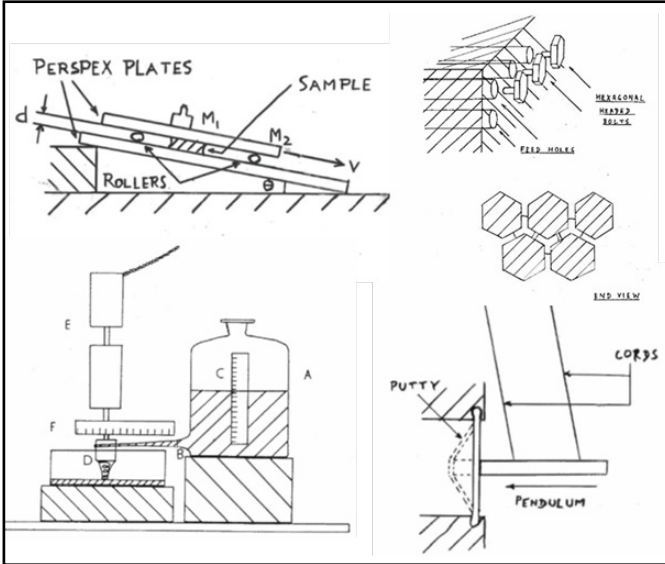


THE BRITISH SOCIETY OF RHEOLOGY

<http://www.bsr.org.uk>



# Rheology

# Bulletin

ISSN-1469-4999

VOL 62 No 3 2021

# THE BRITISH SOCIETY OF RHEOLOGY

## OFFICERS & MEMBERS OF COUNCIL 2021-2022

|                                |  |  |
|--------------------------------|--|--|
| President:                     | <b>Prof. Simon J. Cox</b><br>Institute of Mathematics and Physics,<br>Aberystwyth University, Aberystwyth SY23 3BZ                                   | T: 01970 622764<br>E: <a href="mailto:scx@aber.ac.uk">scx@aber.ac.uk</a>                                 |
| Immediate Past-President:      | <b>Dr Andrew Howe</b><br>Aqdot Ltd, Iconix Park, London Road,<br>Pampisford, Cambridge CB22 3EG  | T: 01223 928000<br>E: <a href="mailto:andrew.howe@colloidscience.org">andrew.howe@colloidscience.org</a> |
| Honorary Secretary:            | <b>Dr Claire McIlroy</b><br>School of Mathematics and Physics,<br>University of Lincoln, Lincoln LN6 7TS   | T: 01522 835 104<br>E: <a href="mailto:cmcilroy@lincoln.ac.uk">cmcilroy@lincoln.ac.uk</a>                |
| Honorary Treasurer:            | <b>Prof. Phil Threlfall-Holmes</b><br>23 Sefton Drive, Liverpool, L8 3SD   | T: 07775 413 499<br>E: <a href="mailto:phil@pthci.com">phil@pthci.com</a>                                |
| Web Editor                     | <b>Dr Andrew Clarke</b><br>Schlumberger Cambridge Research, High Cross,<br>Maddingley Road, Cambridge CB3 0EL.                                       | T: 01223 325222<br>E: <a href="mailto:andrew.clarke@physics.org">andrew.clarke@physics.org</a>           |
| Honorary Membership Secretary: | <b>Dr Manlio Tassieri</b><br>Biomedical Engineering Division, The University<br>of Glasgow, Glasgow, G12 8QQ   | T: 01413308116<br>E: <a href="mailto:Manlio.Tassieri@glasgow.ac.uk">Manlio.Tassieri@glasgow.ac.uk</a>    |
| EDI Champion                   | <b>Dr Shona Marsh</b><br>Netzsch Instruments, Element Court, Mercury<br>Point, Hilton Cross Business Park, Featherstone,<br>Wolverhampton, WV10 7FE. | T: 01902 306645<br>E: <a href="mailto:shona.marsh@netsch.com">shona.marsh@netsch.com</a>                 |
| Publications Manager           | <b>Dr Mónica S.N. Oliveira</b><br>University of Strathclyde, Mechanical and<br>Aerospace Engineering, Glasgow, G1 1XJ                                | T: 0141 5745060<br>E: <a href="mailto:monica.oliveira@strath.ac.uk">monica.oliveira@strath.ac.uk</a>     |
| Honorary Bulletin Editor:      | <b>Dr Richard L. Thompson</b><br>Department of Chemistry, Durham University,<br>Durham, DH1 3LE  | T: 0191 3342139<br>E: <a href="mailto:r.l.thompson@durham.ac.uk">r.l.thompson@durham.ac.uk</a>           |
| Ordinary Members of Council:   |  |  |
|                                | <b>Prof. Karl Hawkins</b><br>Institute of Life Science, School of Medicine,<br>Swansea University, Singleton Park, Swansea<br>SA2 8PP                | T: 01792 295058<br>E: <a href="mailto:k.m.hawkins@swan.ac.uk">k.m.hawkins@swan.ac.uk</a>                 |
|                                | <b>Mr Peter Hodder</b><br>TA Instruments Ltd, 610 Centennial Park,<br>Centennial Avenue, Elstree, Hertfordshire,<br>WD6 3TJ                          | T: 0208 238 6100<br>E: <a href="mailto:phodder@tainstruments.com">phodder@tainstruments.com</a>          |
|                                | <b>Mr Craig Smith</b><br>Anton Paar Ltd Unit F<br>The Courtyard<br>St Albans, Hertfordshire AL40LA UK  | T: 07972576350<br>E: <a href="mailto:craig.smith@anton-paar.com">craig.smith@anton-paar.com</a>          |
|                                | <b>Dr Richard Watson</b><br>School of Engineering, University of Warwick,<br>Coventry, CV4 7AL, UK   | E: <a href="mailto:thequarries@gmail.com">thequarries@gmail.com</a>                                      |

T: Telephone; E: Email

*The British Society of Rheology is registered as a Charity - Number 249967*

---

# THE BRITISH SOCIETY OF RHEOLOGY

---



**BSR BULLETIN**  
**2021, Vol. 62, No. 3**

## CONTENTS

|   |                   |
|---|-------------------|
| <b>Editorial</b>  | 74                |
| <b>Aims of the Society</b>  | 75                |
| <b>Simultaneous Quantification of Crystallinity and Rheological Properties of Coconut Fat via a Unique and Novel in-situ Combination of Rheology and 1H NMR. M. B. Özen, K.-F. Ratzsch and M. Wilhelm</b> | 76                |
| <b>Conference Report: Non-Newtonian Club, 17th September 2021<br/>Rheology of Multiphase Systems: Bubbles, Drops and Particles</b>  | 93                |
| <b>Commentary on the 363<sup>rd</sup> Council Meeting of the BSR</b>  | 97                |
| <b>Towards a Continuous Manufacturing Strategy for Complex Oral Health Formulations. Simona Migliozi</b>  | 99                |
| <b>Exploiting Rheology to Understand the Mechanical Properties of Multi-layered 3D Printed Hydrogel Systems. Ana M. Fuentes Caparrós</b>  | 103               |
| <b>BSR Awards</b>   | 107               |
| <b>Industry News</b>  | 112               |
| <b>Conference &amp; Courses Diary</b>   | Inside back cover |

## EDITORIAL

I hope that you enjoy this ‘midwinter’ issue of our bulletin. I am delighted to have some really excellent contributions from recent PhD graduates, which can only be good news for the long-term health of rheology. We have thesis summaries from two outstanding nominees for the Vernon Harrison Prize, and I’m very grateful to Begüm Özen for her fascinating overview based on her PhD work on rheo-NMR.

It’s been a busy year for the BSR; one in which we thank Andrew Howe for his excellent stewardship as BSR president and welcome Simon Cox into this role. Activities have thrived despite difficult circumstances with Mónica Oliveira and colleagues recently hosting a very successful online NNC, (See report in this issue). Over the last year, BSR has completed its first Equality, Diversity and Inclusion survey, and now offers additional support for members with caring commitments to help with participation in conferences and meetings. Please see the awards section for details of this and other support, and note that the Early Career Award eligibility criteria include members who may have taken a non-standard career path.

Members will be glad to hear that there is now an extensive collection of back issues of Bulletins is now available to BSR members via our website. The cover illustration is a small tribute to many contributions to our bulletin from the late Ralph Oliver, who is much missed and fondly remembered.

Richard Thompson, December 2021.

## SUBMISSIONS TO THE BULLETIN

Submissions to the Bulletin are welcome at any time. Electronic submissions by email to the Editor ([r.l.thompson@durham.ac.uk](mailto:r.l.thompson@durham.ac.uk)) are preferred in word format (e.g. .doc or .docx). Please always provide a contact name, address, e-mail, or telephone number in case of problems. The deadline for submission is Feb. 15<sup>th</sup>, July 15<sup>th</sup> and Oct. 15<sup>th</sup>, respectively, for three issues annually.

## COVER ILLUSTRATION

A selection of hand-drawn figures and diagrams created by D. Ralph Oliver, a regular contributor to BSR bulletins over many years. Back issues including these are now available to members via the BSR website.

## **AIMS OF THE SOCIETY**

The way liquids flow and solids deform affects all aspects of life.

Extraction and processing of crude oil, moulding of plastics, use of toothpaste, spreading of margarine, painting and the lubrication of joints in the human body are all examples of processes depending upon rheological behaviour. Rheology is defined as the science of the deformation and flow of matter.

If your work is concerned with rheology in any way, then you have much to gain by joining the British Society of Rheology, including

- advance your knowledge by attending our conferences
- receive publications including Rheology Abstracts, Bulletin and Rheology Reviews
- learn of current instrumentation and accessories plus new developments.
- access to non-Newtonian Club linking industry and academia
- travel Grants, Poster Prizes, Career Opportunities
- network with fellow members who, while working in a different discipline or industry, may be facing similar problems to yours

The Society is non-profit making and is registered as a charity. For the details, you are warmly welcome to visit our web site <http://www.bsr.org.uk/>, and to apply for membership on-line.

## Simultaneous Quantification of Crystallinity and Rheological Properties of Coconut Fat via a Unique and Novel in-situ Combination of Rheology and $^1\text{H}$ NMR



M. Begüm Özen<sup>a,b\*(L)</sup>, Karl-F. Ratzsch<sup>c,d</sup>, Manfred Wilhelm<sup>c(R)</sup>



<sup>a)</sup> Nevşehir Hacı Bektaş Veli University, Faculty of Art and Sciences, Chemistry Department, 2000 Evler Mah. Zübeyde Hanım Cad., 50300, Nevşehir, Turkey. E-mail: [begumozen@nevsehir.edu.tr](mailto:begumozen@nevsehir.edu.tr), \*corresponding author

<sup>b)</sup> Nevşehir Hacı Bektaş Veli University, Science Technology Application and Research Center, 50300, Nevşehir, Turkey.

<sup>c)</sup> Karlsruhe Institute of Technology (KIT), Institute for Chemical Technology and Polymer Chemistry, Engesserstr. 18, 76128, Karlsruhe, Germany. E-mail: [manfred.wilhelm@kit.edu](mailto:manfred.wilhelm@kit.edu)

<sup>d)</sup> Bruker Biospin GmbH, Rheinstetten, Germany.

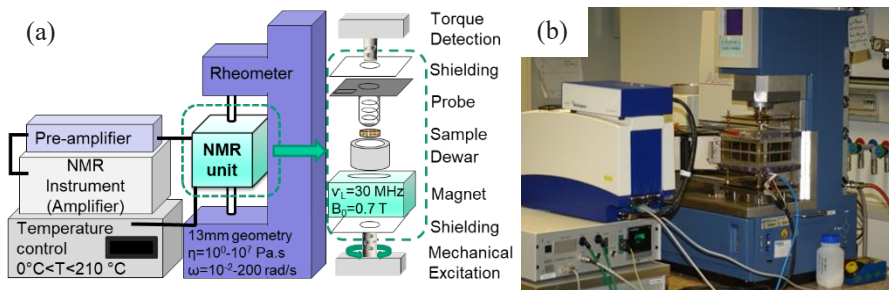
Crystallization of fat has received much interest in research over the last decades due to the effect of microstructure on physical, specifically mechanical properties [1]–[4]. Manufacturing of the fat-based product consists of a controlled interference to preserve, alter or destroy a microstructure during processing [3]. During processing, various parameters change at the same time e.g. cooling rate and applied shear and elongation deformation. These have a large impact on the fat crystallization behavior such as polymorphic transitions, oil migration, fat bloom development, aggregation of crystals, differing crystal size, and solid fat content [5], [6]. Correlating the influences of processing parameters on fat crystallization is advantageous for

scientists to understand and predict the principles for the fat and food industry, to control final product characteristics: the stability of the processed food, and thus, safe, diversified, convenient, and good quality fat products are produced [5].

Advanced characterization techniques provide a major contribution to the engineering sciences in fat research, with an investigation in micron length scales, such as those found in self-assembly colloidal structures, crystal networks, crystals of many types, and interfaces. These micron-sized (1 -10  $\mu\text{m}$ ) identities together with the solid fat content (SFC) are critically involved in the final mechanical properties, rheological and processing behavior, textural and sensory properties of food [3]. These properties can be altered by varying shear flow and/or temperature profiles during crystallization to attain customer needs. Commonly used characterization techniques to investigate fat crystal structure formation and their fractal properties are microscopy techniques e.g. polarized light microscope, environmental scanning electron microscopy (ESEM), and other physical methods e.g., X-ray diffraction (XRD), differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), light diffraction, and rheology.[3], [5] All of the mentioned methods provide quantitative analysis. Nevertheless, a direct correlation of the investigated properties for different methods is not possible due to the non-identical calibration (shear rate, cooling rates, etc.). Therefore, multidisciplinary approaches have been used for better understanding the impact of processing conditions on the fat microstructure. Mazzanti *et al.* [7], [8] used a Couette shear cell with the combination of XRD to study shear-induced crystallization of cocoa butter, milk fat, stripped milk fat, and palm oil. They observed accelerated crystallization and oriented crystals along the shear direction by applied shear. For their later study [9] they used Rheo-NMR, comprising a 10 mm NMR tube with a Teflon shaft, creating a mini Couette cell, to investigate the SFC and its impact on crystallized fat properties. They used the free induction decay (FID) signal to determine the SFC of the blends of canola stearin (CS) in canola oil (CO) under different shear rates (58 - 460  $\text{s}^{-1}$ ), however, did not see a significant difference between sheared and non-sheared samples.

In previous studies, shear was applied within the NMR spectrometer, while rheological parameters were not determined. The studies in the past twenty years conducted by Rheo-NMR setups rely dominantly on the NMR part to determine SFC and simplified rheology part with the application of steady shear flow via Couette

geometries for studying limited to low viscosity complex fluids [10, 11] without quantification of the steady-state viscosity or the complex viscosity under oscillatory deformation. Therefore, a reliable, robust, fast method to determine the SFC correlation with rheological quantities (e.g.  $G'$ ,  $G''$ ) under applied large deformation would be desirable. Only very recently the newly developed low-field RheoNMR setup simultaneously measures the full rheological shear characterization ( $G'$ ,  $G''$  ( $\omega$ ,  $\gamma_0$ ,  $t$ ), allowing for the application of large amplitude oscillatory deformation “LAOS” and the related data analysis via  $I_{3/1}$  [12], FT-Rheology [13], [14]) etc. via a high end rheometer and the quantitative molecular mobility by  $^1\text{H}$  NMR [15]–[18] and  $T_2$  relaxation time determination. Thus, a precise investigation of sample crystallization under identical and identified conditions has become possible with this unique Rheo-NMR setup (see Figure 1). Additionally, this technique provides a correlation between the time evolution of the sample’s macroscopic material properties and microscopic molecular dynamics under applied nonlinear deformation.



**Figure 1:** (a) Illustration of the developed set-up and (b) a photograph of the RheoNMR setup adapted from the ref. [17] with permission.

To demonstrate the capabilities of this new low-field RheoNMR technique, coconut fat was chosen as a model substance for a fat isothermal crystallization kinetic study. Although coconut fat is extensively used in several applications from food to industrial purposes, the kinetic study of coconut oil crystallization has rarely been published. The easy accessibility of coconut fat also makes it favorable for this study.



## 1. Isothermal coconut fat crystallization

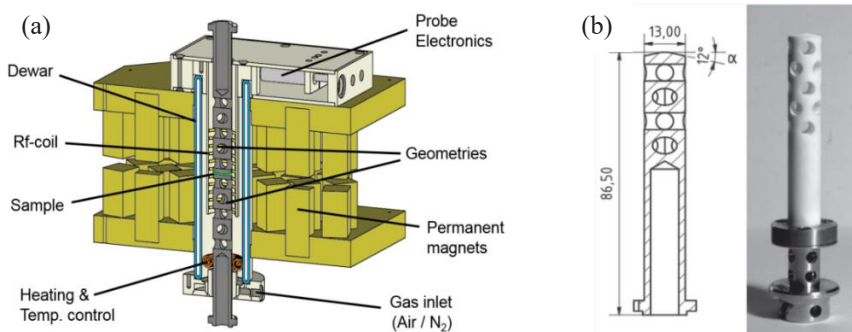
The isothermal crystallization experiments of coconut fat samples were conducted via Rheo-NMR using ceramic, proton-free, and non-conducting rheological 13 mm cone-plate geometry (see Figure 2b). The low-field Rheo-NMR, introduced by Ratzsch *et al.* in 2017 [17], consists of a combination of a Halbach designed low-field permanent magnet ( $\nu_{Larmor} = 30$  MHz,  $B_0 = 0.7$  T) in a commercial strain-controlled TA ARES (TA Instruments, New Castle, DE, USA) shear rheometer. The Bruker minispec (ND series) is used as the console/amplifier for the NMR probe. A combination pulse sequence with magic-sandwich echo (MSE) and the Carr-Purcell-Meiboom-Gill pulse sequence (CPMG) was used in the NMR method. The purpose of the CPMG sequences is to refocus only on the magnetization of the more mobile phase of the sample, and the MSE sequence provides refocusing on the initial transverse magnetization. By analyzing the magnetization decays using a bi-exponential model with pre-factors ( $I_A$  and  $I_B$ ) and transverse relaxation times as  $T_{2A}$  and  $T_{2B}$ , the back-extrapolated initial intensities  $I_{CPMG}$  at the time of NMR equals to zero “ $t_{NMR} = 0$  ms” were determined [15]–[19].

$$I_{CPMG}(t_{exp}) = I_A \exp(-t/T_{2A}) + I_B \exp(-t/T_{2B}) \quad (1)$$

Calculated  $I_{CPMG}(t_{exp})$  values along the time of experiment “ $t_{exp}$ ” were compared with the  $I_{CPMG}$  of a supercooled melt, which shows the maximum value of the  $I_{CPMG}$  ( $I_{CPMG,max}$ ), for achieving the mass-fraction crystallinity  $X_C$  during the crystallization process with the following equation;

$$X_C(t_{exp}) = (1 - (I_{CPMG}(t_{exp})/I_{CPMG,max})) \quad (2)$$

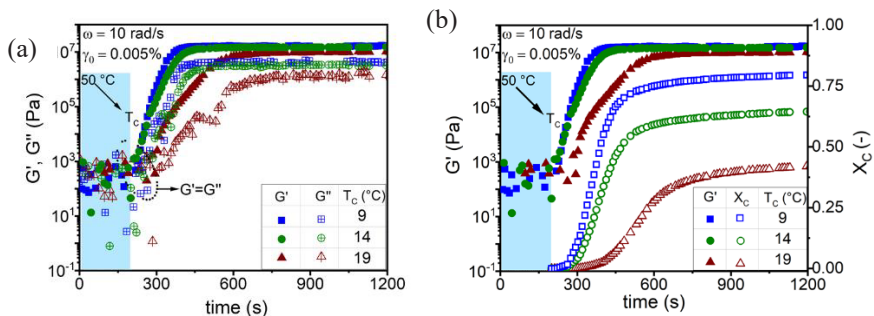
The resulting  $X_C$  evolution by time shows the developing crystallization or SFC during the isothermal crystallization process. All experiments in this study were conducted with the following settings values in the NMR method: the  $90^\circ$  pulse length= 2.4  $\mu$ s, and the  $180^\circ$  pulse length= 4.8  $\mu$ s, the recycle delay  $\tau_{rd}$ = 2.5 s with 16 scans and  $\tau$ = 20  $\mu$ s ( $\tau$ - waiting time) between subsequent  $180^\circ$  pulses for the applied CPMG sequence.



**Figure 2:** (a) Schematic overview of the used Halbach magnet with the NMR probe of the Rheo-NMR setup and the rheometry counterparts. (b) Drawing and the photo of the machinable ceramic cone geometry for the rheometer which has 13 mm diameter and 86.50 mm length. It has holes for fast thermal stabilization. Figures adapted with permission from the ref. [17].

### 1.1 Temperature dependence

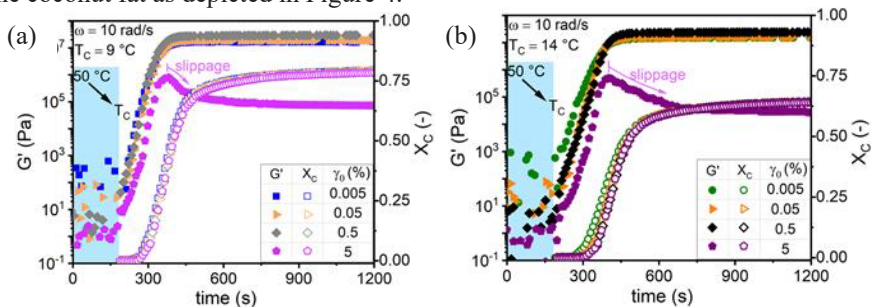
All isothermal crystallization experiments were conducted by melting the sample at 50 °C for 15 min to obtain an isotropic melt sample and then, cooling it to the crystallization temperature ( $T_C$ ) as fast as possible. The sample was kept at  $T_C$  until it was fully crystalline. Sample curves are presented in Figure 3. For the temperature dependence experiments a low deformation amplitude ( $\gamma_0 = 0.005\%$ ,  $\omega = 10$  rad/s) was applied to not disturb the crystal network formation. A gelation (as defined via  $G' = G''$ ) occurred at the SFC of less than  $X_C = 0.01$ . Then, the increasing  $X_C(t)$  and the moduli ( $G' > G''$ ) reflects the crystallization kinetics. While the moduli reached the final maximum stable value ( $G_{\infty}^I$ ), the  $X_C$  continued to rise for another 100 s to achieve the final SFC ( $X_C^{\infty}$ ) due to developing secondary crystallization (see Figure 3b). The strong effect of the increased  $T_C$  from 9 to 19 °C is observed with the  $X_C^{\infty}$  reduction from 80% to almost its half. Presumably, the increasing  $T_C$  led to larger spherulites, which had a more amorphous phase.



**Figure 3:** (a) The time evolution of  $G'(t)$  and  $G''(t)$  from the Rheo part. (b) The  $G'(t)$  and simultaneously acquired the  $X_C$  via the NMR part of the RheoNMR. With a 10  $^\circ\text{C}$  increase in the crystallization temperature,  $T_C$ , a slower crystallization was observed with a strongly influenced final SFC ( $X_C^\infty$ ), seen as a reduction in  $X_C^\infty$  from 80% to almost 40%.

## 1.2 Deformation dependence

Various strain amplitudes ( $\gamma_0$ ) were imposed during the isothermal crystallization of the coconut fat as depicted in Figure 4.



**Figure 4:** Simultaneously monitoring of  $G'(t)$  and  $X_C(t)$  under imposed various  $\gamma_0$  (a) at  $T_C = 9^\circ\text{C}$ , and (b) at  $T_C = 14^\circ\text{C}$ . A change in the microstructure is indicated by a delay in the  $X_C$  and the reduction in  $G'_\infty$  with increasing  $\gamma_0$  at  $T_C = 14^\circ\text{C}$ .

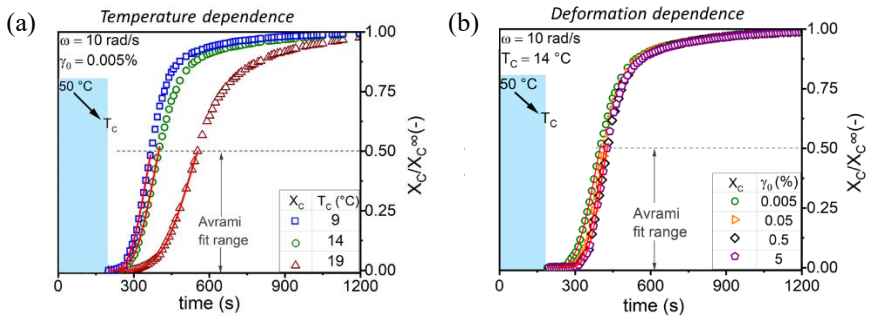
The increase of  $\gamma_0$  from 0.005% to 5% at both  $T_C$  caused a significant decrease in  $G'$  by a factor of  $\sim 100$  and led to slippage or fracture when the sample was fully crystalline. No significant effect was observed on the  $X_C$  development for applied deformation range at  $T_C = 9$  °C. Although the  $X_C^\infty$  was not influenced, a delayed crystallization can be seen with increased deformation at  $T_C = 14$  °C.

### 1.3 Kinetic analysis

It has been known that the bulk fat nucleation is predominantly heterogeneous [20], and this results in a noninteger value of  $n$  [5], [21]. Additionally, the interaction of fat crystals with each other in the network has a very complex nature [22]. Within this framework, the kinetic analysis of the coconut fat crystallization system in this study was done by applying an Avrami model to the plotted relative crystallinity ( $X_C / X_C^\infty$ ) data. The general expression of the Avrami model is

$$\left(\frac{X_C}{X_C^\infty}\right) = 1 - \exp(-(K(t - t_i))^n) \quad (3)$$

where the rate constant  $K$  (time)<sup>-1</sup> and exponent  $n$  (-) being the Avrami parameters [23]–[25]. The exponent  $n$  reflects both the dimensionality of the growth and the nucleation mode [26]. The Avrami approach describes the primary crystallization periods, and thus, provides a good fit up to 50% of the final crystallinity of the whole crystallization curve [27]. Therefore, the relative crystallinity ( $X_C / X_C^\infty$ ) as a function of time for a variety of temperatures and shear deformation were fitted by the Avrami model (see equation 3) up to  $X_C / X_C^\infty = 0.5$  as depicted in Figure 5. The extracted kinetic parameters from the Avrami fit are shown in Figure 6. The dimensionality  $n$  increased by about 1 within  $\Delta T_C = 10$  °C rise for quiescent crystallization. However, the  $n$  value increased by almost 3 via the application of a large deformation  $\gamma_0 = 5\%$ . This resulted in  $n > 4$ , which presumably indicates the complexity of the crystallization mechanism with a multi-dimensional growth and different morphology of the coconut fat. Another intriguing point is: if the experiment was conducted at  $\gamma_0 = 5\%$ , first this slowed down the crystallization, and after some time, accelerated it. In total the duration of crystallization did not show any difference. The explanation could be that the crystals at the early stage of crystallization were destroyed due to the applied large deformation which led to a slower crystallization. Then, applied large deformation increased the contact surface, increased convection, and led to more compact and/or stretched aged crystals, and

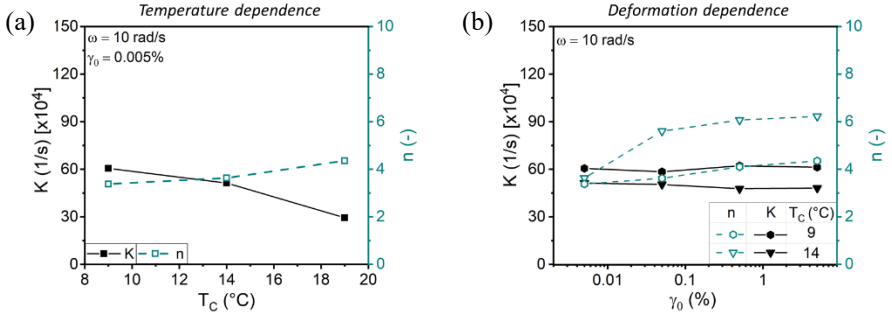


**Figure 5:** Visual comparison of fitted the Avrami model (see equation 3) to the isothermal crystallization  $X_C / X_C^\infty$  time evolution curves for (a) the temperature-dependent experiments at the  $\gamma_0 = 0.005\%$ , and (b) the deformation-dependent experiments at  $T_C = 14^\circ\text{C}$ . The Avrami model was fitted up to  $X_C / X_C^\infty = 0.50$  and shown as a red line. An intriguing point here is that the conducted  $\gamma_0 = 5\%$  during isothermal crystallization, decelerated the crystallization at an early stage, and later on, accelerated it. Thus, applied large deformation shows no impact on the duration of total crystallization.

hence, speeded up the crystallization. Therefore, the applied large deformation ( $\gamma_0 = 5\%$ ) increased the  $n$  value over 4, but it has no significant effect on the calculated  $K$  value. This finding is in agreement with the report of Kloed in 1998 [20] that shear-induced crystallization caused compaction of the fat crystals.

#### 1.4 Fractal dimension analysis

The fat crystal network is composed of packed fractal flocs throughout the sample. The analysis of fractal geometry is important for understanding the link between the microstructure of the fat crystal network and the macroscopic rheological properties of the network. The fractal dimension is a measure of the relationship between the mass and size of a cluster [28], [29]. According to the study of Narine and Marangoni [29], the fractal dimension is strongly influenced by mass and heat transfer which are governed by processing conditions, i. e., temperature history. With the here



**Figure 6:** Kinetic parameters (a) for the temperature-dependent experiments; and (b) for the deformation-dependent experiments at  $T_C = 14$  °C with varying  $\gamma_0$ . Parameters-  $n$ : Avrami exponent,  $K$ : Avrami rate constant (see equation 3). Application of large deformation ( $\gamma_0 \geq 0.05\%$ ) increased the  $n$  value over 4, but it has almost no influence on the  $K$  value.

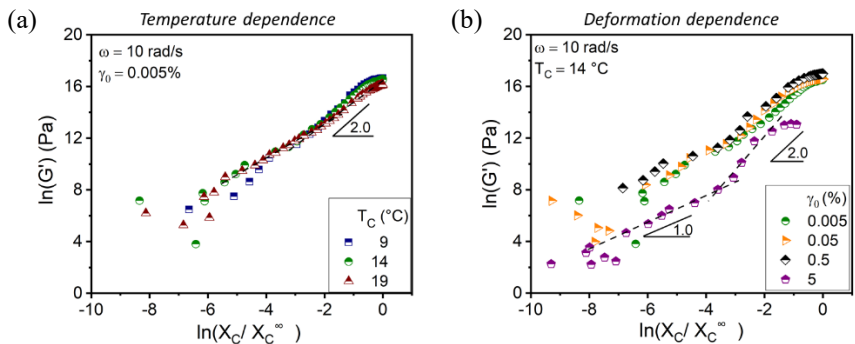
presented Rheo-NMR method, the crystallization processing conditions are identical with simultaneous measurement by  $^1\text{H}$  NMR and a high-end rheometer. Thus, the direct correlation of  $G'$  as a function of the  $X_C$  can be evaluated based on the weak-link regime for colloidal dispersion. Above the gelation threshold, the gel network consists of closely packed fractal flocs [30]. The flocs are divided into two, as a strong and weak-link regime [29], [30]. In the strong-link regime, the particle concentration is low, and the individual floc is large. Each floc behaves as a weak spring [30]. However, in the weak-link regime, particle concentration is high with very small and stiff fractal flocs [30], [31]. Thus, the  $G'$  exhibit a power-law increasing behavior with increasing SFC [30]–[33] as described by;

$$G' = \psi X_C(t)^p \quad (4)$$

$$\ln(G') = \ln(\psi) + p \ln(X_C(t)) \quad (5)$$

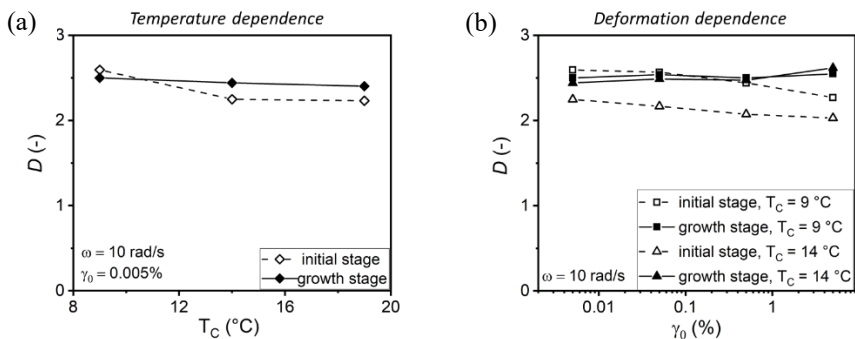
where  $\psi$  is a constant, independent of  $X_C$ , but it depends on the polymorphic nature such as particular lipid or triglyceride composition of the fat crystal network, and  $p$  is a chemical length exponent, which depends on the fractal dimension  $D$  of the network in the following manner:  $p = 1/(3 - D)$  in the weak-link regime for a

three-dimensional system. The linear slope ( $p$ ) of  $\ln(G')$  and  $\ln\left(\frac{X_C(t)}{X_C^\infty}\right)$  correlations are used to calculate  $D$  values, as depicted in Figure 7. Different slopes were observed from three different stages in coconut fat crystallization experiments. A low SFC was presented at an early stage of the crystallization. Consequently, this stage is called the initial stage. Another stage consists of the higher SFC, and hence, it is called the growth stage. Then, an observed plateau indicated no further change in the fractal dimension. Determined  $D$  values from the plots in Figure 7 are displayed in Figure 8. The resulting  $D$  value was stable at the growth stage by changing  $T_C$ . However, it was a factor of 1.2 higher with a decrease in  $\Delta T_C = 10$  °C. According to Narine and Marangoni (1999) [29] a sample has instantaneous nucleation at a lower temperature, and thus, nucleation sites dissipate the heat effectively throughout the network. Therefore, in the systems at low  $T_C$  with a rapid nucleation stage have a higher fractal dimension.



**Figure 7:** Correlation between  $\ln(G')$  and  $\ln\left(\frac{X_C(t)}{X_C^\infty}\right)$  (a) for the temperature-dependent Rheo-NMR experiments; and (b) for the deformation-dependent experiments at the  $T_C = 14$  °C for various  $\gamma_0$ . Linear fit as represented with a dashed line and the observed two different slopes are called the initial and the growth stage of the crystallization. The slope of the linear fits provides the chemical length exponent  $p$ , and hence, the fractal dimension  $D$  of the network can be calculated via  $p = 1/(3 - D)$ .

In the case of the application of LAOS, the  $D$  value gradually decreased up to a factor of 1.1 as compared to the initial stage. This may originate from the constrained heat and mass transfer due to the deformed crystalline nuclei in the sample if a higher  $\gamma_0$  was applied. Lower  $D$  values were indicative of a disordered packing of the microstructural elements within the network [29] compared to experiments with higher  $D$  values. Nevertheless, the  $D$  value did not change significantly by increasing  $\gamma_0$  at the growth stage in the crystallization process.



**Figure 8:** Fractal dimension ( $D$ ) of the isothermally crystallized coconut fat (a) under the quiescent condition with varying  $T_C$ ; and (b) under varying deformation at  $T_C = 9$  °C and 14 °C.

While at low  $T_C$  with a rapid nucleation, higher  $D$  values were extracted; the  $D$  value remained similar at the growth stage for different  $T_C$ . Additionally, the existence of oscillatory deformation influenced the early stage of the crystallization and decreased the  $D$  value up to a factor of 1.1. However,  $D$  had the same value at the growth stage regardless of applied deformation.

## 2. Further potential for the Rheo-NMR combination

The importance of the unique Rheo-NMR method is that it offers the possibility of a deeper understanding of the relation between microscopic molecular dynamics and macroscopic material properties under identical thermal and oscillatory shear conditions. The study of the deformation impact on crystallization is interesting



since a lot of processing techniques apply shear and elongation forces in the linear and non-linear regime within fat processing e.g., the dry fractionation process. The Rheo-NMR could close a knowledge gap in the development of kinetic models for crystallization under applied shear to determine the required deformation or shear stress in fat or polymer processing, and hence, optimize the manufacturing processes. Understanding the effect of varying processing conditions (i.e. deformation, cooling rate) and the impact of additives on the fat crystal network and the resulting mechanical properties allows further tailoring of the properties such as spreading to obtain innovative products for specific applications. Thus, the Rheo-NMR method opens up the possibility to relate macroscopic structural, mechanical, and even sensory properties of the fatty product with the molecular origin as determined via  $^1\text{H}$  NMR relaxometry.

The RheoNMR method is very general and can be applied to a variety of soft matter e.g. polymers, fats, resins, rubbers, etc., and can provide a new and unique possibility for studying crystallization, gelation, curing with the application of flow [17], [18], [34]–[37] in the linear and non-linear regime both under steady and non-steady e.g. oscillatory conditions.

### **Acknowledgements**

M. Begüm Özen acknowledges funding by the Republic of Turkey Ministry of National Education. The authors thank Volker Röntzsch, who used the RheoNMR setup in their own work and provided ideas for the improvement.

### **References**

- [1] L. deMan, J. M. deMan, and B. Blackman, “Physical and textural evaluation of some shortenings and margarines,” *J. Am. Oil Chem. Soc.*, vol. 66, no. 1, pp. 128–132, 1989.
- [2] J. M. Aguilera and D. W. Stanley, “Microstructural Principles of Food Processing and Engineering,” *Trends Food Sci. Technol.*, pp. 158–159, 1990.
- [3] J. M. Aguilera, “Why food micro structure?,” *J. Food Eng.*, vol. 67, no. 1–2, pp. 3–11, 2005.
- [4] G. Calliauw, E. Fredrick, V. Gibon, W. De Greyt, J. Wouters, I. Foubert, K. Dewettinck, “On the fractional crystallization of palm olein: Solid solutions and eutectic solidification,” *Food Res. Int.*, vol. 43, no. 4, pp. 972–981, 2010.

- [5] A. G. Marangoni, *Fat Crystal Networks*, New York, Marcel Dekker, 2005.
- [6] A. P. B. Ribeiro, M. H. Masuchi, E. K. Miyasaki, M. A. F. Domingues, V. L. Z. Stroppa, G. M. de Oliveira, and T. G. Kieckbusch, "Crystallization modifiers in lipid systems," *J. Food Sci. Technol.*, vol. 52, no. 7, pp. 3925–3946, 2015.
- [7] G. Mazzanti, S. E. Guthrie, E. B. Sirota, A. G. Marangoni, and S. H. J. Idziak, "Orientation and Phase Transitions of Fat Crystals under Shear 2003," *Cryst. Growth Des.*, vol. 3, no. 5, pp. 721–725, 2003.
- [8] G. Mazzanti, A. G. Marangoni, and S. H. J. Idziak, "Modeling phase transitions during the crystallization of a multicomponent fat under shear," *Phys. Rev. E*, vol. 71, no. 4, pp. 1–12, 2005.
- [9] G. Mazzanti, E. M. Mudge, and E. Y. Anom, "In Situ Rheo-NMR Measurements of Solid Fat Content," *J. Am. Oil Chem. Soc.*, vol. 85, pp. 405–412, 2008.
- [10] P. T. Callaghan, "Rheo-NMR: A new window on the rheology of complex fluids," *Encyclopedia Nucl. Magn. Reson.*, vol. 9, pp. 737–750, 2002.
- [11] C. Schmidt, "Rheo-NMR spectroscopy," in *Modern Magnetic Resonance, Part 3, Applications in Materials, Food and Marine Sciences*, edited by G. A. Webb, Springer, New York, 2006, pp. 1495–1501.
- [12] M. A. Cziep, M. Abbasi, M. Heck, L. Arens, and M. Wilhelm, "Effect of Molecular Weight, Polydispersity, and Monomer of Linear Homopolymer Melts on the Intrinsic Mechanical Nonlinearity  ${}^3Q_0(\omega)$  in MAOS," *Macromolecules*, vol. 49, pp. 3566–3579, 2016.
- [13] K. Hyun, M. Wilhelm, C. O. Klein, J. G. Nam, K. H. Ahn, S. J. Lee, R. H. Ewoldt and G. H. McKinley, "A review of nonlinear oscillatory shear tests: analysis and application of large amplitude oscillatory shear (LAOS)," *Progress in Polymer Science*, vol. 36, no. 12, pp. 1697-1753, 2011.
- [14] M. Wilhelm, "Fourier-Transform Rheology," *Macromol. Mater. Eng.*, vol. 287, no. 2, pp. 83–105, 2002.
- [15] V. Röntzsch, M. Wilhelm, and G. Guthausen, "Hyphenated low-field NMR techniques: Combining NMR with NIR, GPC/SEC and rheometry," *Magnetic Resonance in Chemistry*, 2015.
- [16] M. B. Özen, V. Röntzsch, K.-F. Rätzsch, G. Guthausen, and M. Wilhelm, "Low-Field RheoNMR: Newly Developed Combination of Rheology and  ${}^1\text{H}$  TD- NMR to Correlate Mechanical Properties with Molecular Dynamics in Soft Matter M.," in *Annual Transactions of the Nordic Rheology Society*,

- 2016, vol. 24, pp. 38–40.
- [17] K.-F. Ratzsch, C. Friedrich, and M. Wilhelm, “Low-field rheo-NMR: A novel combination of NMR relaxometry with high end shear rheology,” *J. Rheol.*, vol. 61, no. 5, pp. 905–917, 2017.
- [18] V. Röntzsch, M. B. Özen, K.-F. Ratzsch, E. Stellamanns, M. Sprung, G. Guthausen, and M. Wilhelm, “Polymer Crystallization Studied by Hyphenated Rheology Techniques: Rheo-NMR, Rheo-SAXS, and Rheo-Microscopy,” *Macromol. Mater. Eng.*, vol. 1800586, p. 1-14, 2018.
- [19] V. Röntzsch, M. Haas, M. B. Özen, K.-F. Ratzsch, K. Riazzi, S. Kauffmann-Weiss, J. K. Palacios, A. J. Müller, I. Vittorias, G. Guthausen, M. Wilhelm, “Polymer crystallinity and crystallization kinetics via benchtop 1 H NMR relaxometry: Revisited method, data analysis, and experiments on common polymers,” *Polymer*, vol. 145, pp. 162–173, 2018.
- [20] W. Kloed, “Mechanical properties of fats in relation to their crystallization,” Wageningen Agricultural University, the Netherlands, 1998.
- [21] S. D. Campbell, H. D. Goff, and D. Rousseau, “Modeling the Nucleation and Crystallization Kinetics of a Palm Stearin/Canola Oil Blend and Lard in Bulk and Emulsified Form,” *JAACS, J. Am. Oil Chem. Soc.*, vol. 81, no. 3, pp. 213–219, 2004.
- [22] J. M. DeMan and A. M. Beers, “Fat Crystal Networks: Structure and Rheological Properties,” *J. Texture Stud.*, vol. 18, no. 4, pp. 303–318, 1987.
- [23] M. Avrami, “Kinetics of Phase Change. I General Theory,” *J. Chem. Phys.*, vol. 7, no. 12, pp. 1103-1112, 1939.
- [24] M. Avrami, “Kinetics of phase change. II Transformation-time relations for random distribution of nuclei,” *J. Chem. Phys.*, vol. 8, no. 2, pp. 212–224, 1940.
- [25] G. Strobl, *The Physics of Polymers*, Third Revi. Heidelberg, Germany: Springer, 2007.
- [26] L. H. Sperling, *Introduction to Physical Polymer Science*, 4th ed. New Jersey: Wiley Interscience, 2006.
- [27] E. Piorkowska and G. C. Rutledge, *Handbook of Polymer Crystallization*, New Jersey, John Wiley, 2013.
- [28] Y. Shi, B. Liang, and R. W. Hartel, “Crystal Morphology, Microstructure, and Textural Properties of Model Lipid Systems,” vol. 82, no. 6, 2005.
- [29] S. S. Narine and A. G. Marangoni, “Relating structure of fat crystal networks to mechanical properties: A review,” *Food Res. Int.*, vol. 32, no. 4, pp. 227–

- 248, 1999.
- [30] W. Shih, Y. Shih, S. Kim, J. Liu, and I. A. Aksay, “Scaling behavior of the elastic properties of colloidal gels,” *Phys. Rev. A*, vol. 42, no. 8, 1990.
- [31] L. G. B. Bremer, “Fractal aggregation in relation to formation and properties of particle gels,” Ph.D. thesis, Wageningen University, 1992.
- [32] L. G. B. Bremer, T. Van Vliet, and P. Walstra, “Theoretical and experimental study of the fractal nature of the structure of casein gels,” *J. Chem. Soc. Faraday Trans. 1*, vol. 85, no. 10, pp. 3359–3372, 1989.
- [33] G. A. Marangoni and S. S. Narine, *Physical Properties of Lipids*. New York, Basel: Marcel Dekker, 2002.
- [34] M. B. Özen, K.-F. Ratzsch, V. Rätzsch, and M. Wilhelm, “Correlating Crystallization Kinetics and Rheological Properties of Polyethylene Using a New RheoNMR Setup,” *Proceedings of 4th International Polymeric Composites Symposium, Exhibition and Brokerage event (IPC)*, 2015, pp. 308–310.
- [35] F. Rebry, A. Declercq, K.-F. Ratzsch, M. Wilhelm, K. Dewettinck, and P. Van Der Meeren, “Rheo-NMR to investigate fat crystallization under shear,” *Curr. Res. Food Sci.*, 2021.
- [36] S. Nie, K.-F. Ratzsch, L. S. Grage, J. Keller, A. S. Ulrich, J. Lacayo-Pineda, and M. Wilhelm, “Correlation between Macroscopic Elasticity and Chain Dynamics of Natural Rubber during Vulcanization as Determined by a Unique Rheo-NMR Combination,” *Macromolecules*, vol. 54, no. 13, pp. 6090–6100, 2021.
- [37] M. B. Özen, “Crystallization of Polyethylene as Detected via RheoNMR,” Ph.D. thesis, *Karlsruhe Institute of Technology*, 2020.



*Link to ref 37*



Find out more on  
[www.netzsch.com/rh7-10](http://www.netzsch.com/rh7-10)

# When Shear Power Meets Super Strength

**NETZSCH**  
Proven Excellence.

NETZSCH-Gerätebau GmbH UK Branch Office  
[uk.thermal@netzsch.com](mailto:uk.thermal@netzsch.com) · [www.netzsch.com](http://www.netzsch.com)

## The Reliable and Powerful Rosand Capillary Rheometer

- High force and wide dynamic speed capillary rheometer
- Understanding rheological behavior of materials by replicating processing conditions
- Measurements of absolute shear and extensional viscosity
- Interchangeable pressure transducers, dies and accessories
- Open design for ease of cleaning
- Intuitive Flowmaster™ software

**DISCOVER** the **RHEOMETER** with the...  
Sensitivity • Ease-of-use • Versatility



**TO ADDRESS THE MOST  
DEMANDING APPLICATIONS**



The **NEW** Discovery Hybrid Rheometer

**Waters™**



[tainstruments.com](http://tainstruments.com)

## Conference Report

### Non-Newtonian Club, 17<sup>th</sup> September 2021 Rheology of Multiphase Systems: Bubbles, Drops and Particles

Organised by Mónica Oliveira, Konstantinos Zografos, Paul Grassia and Mark Haw at the University of Strathclyde and hosted virtually on Zoom platform on Friday 17<sup>th</sup> September.



The BSR Non-Newtonian Club meeting on the theme of “Rheology of Multiphase Systems: Bubbles, Drops and Particles” was hosted on Sept 17<sup>th</sup> 2021 on-line at the University of Strathclyde. It was an excellent day, with a great mix of industrial and academic talks. Over 230 people registered, with more than 130 participants attending on the day. There were attendees from five continents and many time zones (including countries such as New Zealand, Japan and Brazil in addition to UK and other European countries), which emphasises the broad international interest of rheology and the new found reach of the online NNC meetings.

The technical programme was launched with a direct industrial insight into the challenges related to papermaking and specifically how foams can be used to enhance the strength of paper. **Ari Jäsberg and Tuomo Hjelt** (VTT Technical Research Centre of Finland Ltd) explained how strength aids need to be added during the papermaking process, but there can be advantages of adding them in the form of a foam after a paper fibre network has already formed. Sometimes the foam application leads to a uniform foam layer covering the fibre network, whereas sometimes it does not. Understanding the rheology of the foam is then a step towards controlling how foam will behave when applied to a paper fibre network. Work at VTT has demonstrated that the foams that they use tend to shear thin which is unsurprising, but slip velocities turned out to be surprisingly large. Another challenge is that large pressure changes can occur, meaning that foam bubbles expand and foam density changes during the process.

We continued on the theme of foams with a beautiful and very insightful talk by **Isabelle Cantat** (University of Rennes). The focus now switched to the local scale of the foam films and specifically how surfactant moves around on these films. Towards this end, the group at Rennes has built a device consisting of just five foam films. Motors are used to stretch certain films and compress others. How foam films displace within the device allows determination of surface tension in different films, and looking at how film thicknesses evolve gives insight into how surfactant is transported around Plateau border menisci. Key to understanding the surfactant transport process is recognising that a geometric frustration occurs at the menisci at which three films meet. It is not possible to have uniform motion both along and across each and every film. Instead some films must have different velocity on different sides, meaning they are sheared. These ideas then lead to a constitutive relation between surface tension between films and surfactant flux around the menisci.

In the last talk of the morning session, **Nathanael Inkson** (Siemens Digital Industries Software) gave us an update of the evolving Siemens computational fluid dynamics software, Simcenter STAR-CCM+. The talk focused on the modified Eulerian finite-volume code and Nat discussed the recent changes to allow modelling of particle suspensions and stabilised emulsions, and covered a number of test cases, including rheological behaviour of suspensions in flows between parallel plates and shear induced particle migration, and stabilised water/oil emulsions laminar and turbulent flow in pipes.

In the first session of the afternoon, **Anke Linder** (ESPCI, Paris) discussed the fascinating world of complex microscopic particle behaviour under flow at low Reynolds numbers, looking at number of examples of particles with complex shapes and/or deformability. The first case shown looked at hydrogel particles with a variety of shapes fabricated *in situ* in such way that their shape and material properties are well-controlled. By tracking these particles in confined flow, Anke discussed how shape governs particle trajectories (e.g. lateral drift, oscillatory movement and rotation), highlighting the role of asymmetry. This was followed by two cases involving bioparticles: actin filaments and bacteria. Anke's group used a range of tracking techniques to follow the particles in well-controlled flows, producing beautiful videos. Using a combination of experiments and simulation we were shown



how filaments buckle into helicoidal shapes in strong compressional flows, and how motile bacteria accumulating at surfaces are reoriented by flows, leading to upstream swimming and changes in bacterial motility.

**Elizabeth Jamie** (Schlumberger Cambridge Research) introduced us to the complexity of industrial non-Newtonian fluid formulation in oil and gas engineering, with a talk focussed on understanding the behaviour of multiphase non-aqueous drilling fluids. These fluids, a mix of brine droplets, clay, additional solid particulates, and other components suspended in oil at a moderate disperse phase volume fraction, demonstrate both complex rheology and sensitive time-dependent structural and mechanical behaviour. Through macroscopic and microscopic visualisation, Liz demonstrated that a ‘model’ fluid, representative of the commercial drilling fluid, behaves like a weak colloidal gel, in particular showing a delayed collapse behaviour familiar from research literature on simpler colloid-polymer depletion systems. Innovative multi-channel confocal microscopy, in collaboration with the Petekidis group at FORTH in Crete, revealed the gel’s internal microstructure, a highly inhomogeneous network with large empty voids. Liz’s talk reminded everyone of the important and sometimes surprising connections that can be made between basic research on highly simplified ‘model’ systems and applications under ‘extreme’ industrial conditions, such as the temperatures, pressures and performance requirements found in heavy-duty drilling operations.

In the last talk of the day, **Adam Townsend** (University of Durham) spoke about microorganisms swimming through structured networks following a microscale approach in which the anisotropic structure of the background fluid was specifically modelled. Inspired by an electron microscope image of a sperm cell making its way through cervical mucus, he discussed the importance of the mucus structure on helping or obstructing the sperm cell. Adam argued that the system can be considered as a swimmer moving through a viscoelastic medium, but wondered whether this approach ignores the physics at the small scale. To understand how the swimmer moves, he modelled the mucin fibres, approximating them as individual, flexible, inextensible, rods, which were allowed to interact with a swimming filament representing the swimmer. He investigated the effect of different concentrations described by two different types of networks: rigid and flexible. He observed that at low concentrations the swimmer swam with similar speeds

independent of the network. For high concentrations, a speed boost was found for the flexible networks, while for rigid networks the swimmer was seen to slow down. Adam's talk concluded with a very entertaining table, with references to Greta Thunberg, in an attempt to explain that the speed of these swimmers is drastically affected by the flow environment.

The meeting closed with an address by the president of British Society of Rheology, **Simon Cox**, highlighting the work of the BSR and the range of benefits for members.

This latest meeting of the BSR Non-Newtonian club demonstrated the enormously varied challenges presented by non-Newtonian complex fluids in both research and applications, as well as the continuing innovation being brought to bear on those challenges by scientists and engineers worldwide. Techniques ranging from cutting-edge microscopy to high-power computation highlight that BSR researchers and engineers are not only pushing the boundaries of non-Newtonian fluids science but also developing and using the very latest methodologies, tools which will undoubtedly go on to have wider application in many other areas. That the online conference drew such a large and varied audience, at a time of continuing challenge for all of us globally, is a further testament to the resilience and commitment of the BSR community.

Finally, we cannot finish without thanking Alan McCleave for technical assistance with setting up the online webinar sessions, Andrew Clarke for help with the online registration, and all our speakers and audience for a very inspiring set of talks and discussions.

**Mónica, Kostis, Paul and Mark**

## **British Society of Rheology 363rd Council Meeting**

The meeting was held virtually via Zoom on 20th September, 2021, Chaired by Professor Simon Cox with Claire McIlroy as secretary.

BSR is well represented on the European Society of Rheology Council, with Simon Cox now the BSR representative to the Executive Council, joining and Mónica Oliveira who was elected as Member at Large (congratulations, Mónica). Manlio Tassieri was elected as a Representative of Individual Members (congratulations to Manlio, too). Simon is also the BSR representative to the International Congress of Rheology (ICR).

Council encourages members who have ideas about promoting rheology more widely and who seek financial support to contact Simon Cox to discuss whether the idea may be eligible to access the Rheology Engagement Fund.

Council encourages members who would like to organise a Non-Newtonian Club Meeting to contact Simon Cox. These events are typically 1-day meetings and will be supported by BSR to ensure that there is no registration fee (important when in-person events return). Increasing the range of people organising meetings can help us cover a wider range of rheological topics and give opportunities to a wider range of speakers.

Discussions were held on whether the membership renewal date should be “rolling” or remain fixed at 1<sup>st</sup> October. Rolling renewal has many advantages in spreading loads throughout the year and may be enabled should there be a change in web services provider.

Simon attended the ESR council meeting and reported the Weissenberg award will now be awarded every year (although not clear what happens on ICR years) and rheologists from anywhere in the world are eligible. It has not yet been confirmed if AERC, Seville will be online or face to face.

Phil Threlfall-Holmes (Treasurer) reported that the BSR finances remain healthy and in surplus.

Claire proposed a new “BSR Carers Grant” to cover care costs that may be incurred as a necessary consequence of a member attending a rheology meeting. Andrew Clarke (Web Editor) is keen to have the back issues of the BSR Bulletin uploaded to the Website and has included an article search function for digital bulletin copies by extracting a title and authors list.

The September NNC (organised by Mónica Oliveira) on 17th September 2021 - “Rheology of Multiphase Systems: Bubbles, Drops and Particles” - was very successful with 230 registrations and nearly 140 attendees at each session (and even attendees from New Zealand). Delightfully, there was a perfect academic-industry and male-female balance amongst the 6 speakers.

The BSR Mid-Winter Meeting will be held online (Zoom most likely because of its broad familiarity) w/c 10<sup>th</sup> January 2022. Organisers are Andrew Clarke and Andrew Howe and, in addition to Award Lectures, the likely theme will be around rheology of concentrated suspensions.

Manlio Tassieri (Membership Secretary) reported that BSR counts 13 Council Members, 81 Honorary, and 154 Members; for a total of 248 Members.

Richard Thompson (Bulletin Editor) encourages and welcome submission of articles!

Andrew Howe, September 2021

# Towards a continuous manufacturing strategy for complex oral health formulations

Simona Migliozi  
Department of Chemical Engineering  
University College London



The conversion of traditional batch operations into continuous processes represents an important goal towards process intensification. The rigorous design of continuous manufacturing operations poses several challenges, especially for processes involving complex fluids, whose rheological properties change during processing. The scope of this thesis was to provide a new approach for the development of a continuous process aimed at the production of a non-aqueous Carbopol gel used in oral health formulations, based on the understanding and detailed exploration of the rheological properties of the materials and of the physical interactions among its components. The dissertation addressed two main challenges related to the process: (i) in-line mixing of complex liquids and (ii) control over the Carbopol gelation. First, the impact of complex rheological properties on the mixing stage was investigated experimentally and numerically. Concentration maps, obtained at different mixer lengths via Planar Laser Induced Fluorescence (PLIF) experiments and Computational Fluid Dynamics (CFD) simulations, revealed that mixing of viscoelastic fluids reduces when the elastic rheological response becomes significant. Independently of the mixer geometry, clear deviations from the Newtonian benchmark were observed as soon as the *Deborah* number exceeded unity (Fig.1), revealing the onset of viscoelastic instabilities induced by an increased solid-like response of the material to changes of the shear rate field. Different transitions were observed as the mean flow rate increased, the nature of which appeared to be influenced by both the rheological properties of the fluid and the flow field induced by the complex geometries considered.

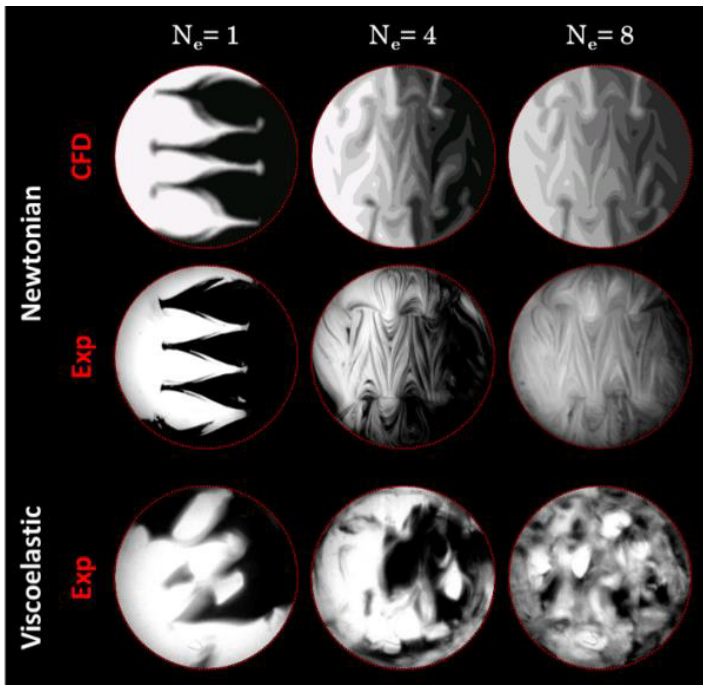


Figure 1. Experimental (from PLIF) and numerical concentration maps of two liquid streams (black and white) after  $N_e = 1, 4$  and  $8$  elements of the SMB-R mixer; Newtonian case (first two rows from the top) and Viscoelastic case (bottom row).

To prevent these effects and control the evolution of the rheological properties over the entire process, the kinetics of the gelation process were investigated via time-resolved rheometry and UV-Vis spectroscopy. This study yielded insights into the mechanism of gelation (Fig.2), leading to a kinetic relation to describe the time-evolution of the linear elastic properties of the Carbopol matrix in non-aqueous solvents.

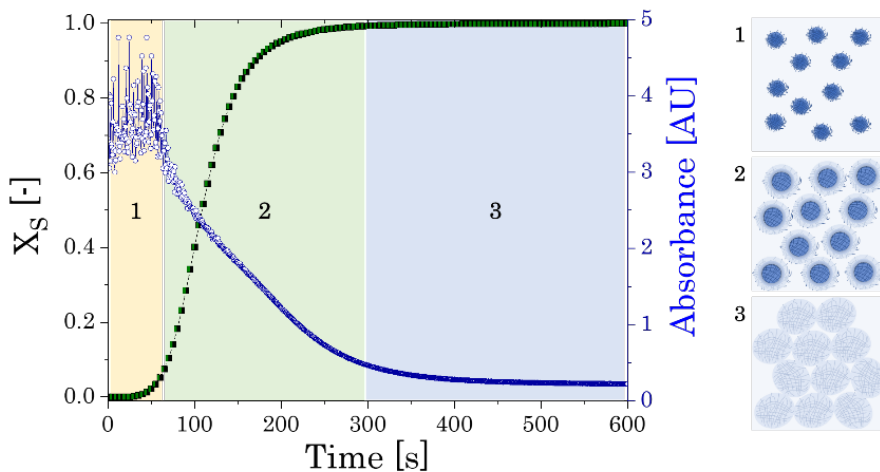


Figure 2. Evolution of the normalised storage modulus (left-hand axis) and of the absorbance (right-hand axis) during the gelation process. The trends suggest a diffusion-controlled process, where the particles are progressively swollen through the diffusion of solvent in the crosslinked structure of Carbopol.

To link the kinetic findings with the evolution of the flow properties, the rheological properties of Carbopol dispersions and the impact of different solvents on the swollen configuration of the microgels were further investigated. In the presence of co-solvents, the kinetic aspect of the swelling process is critical in determining the final swollen state. Overall, the results highlighted the possibility of treating, from a rheological perspective, Carbopol gels as fully packed suspensions of soft elastic particles, independently of the solvent used, and a generalized scaling behaviour of the flow properties could be retrieved as function of the particle volume fraction.

Finally, the scaling laws and the kinetic model were implemented in a CFD model to enable the simulations of the gelating flow in different operating conditions (Fig.3). By exploiting fundamentals of reaction engineering, the approach allows incorporating the kinetics of gelation with the inherent changes of the rheological properties induced by the gelation itself, thus providing a simple and cost-effective solution to achieve a more detailed design of the new process.

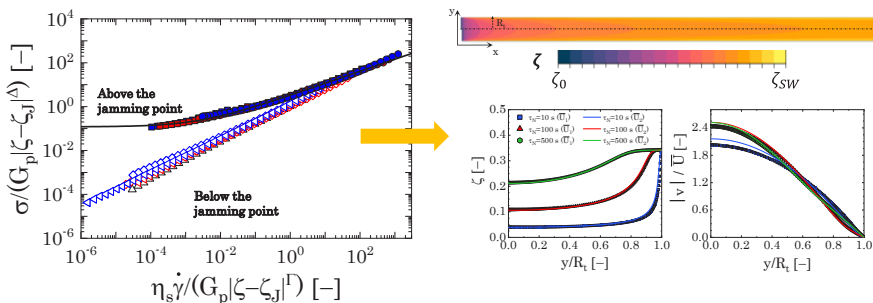


Figure 3. Scaled flow curves of the Carbopol dispersions (left). For all solvents used the curves collapse onto two branches, one above and one below the jamming point. The scaling law can be used, together with the kinetics of gelation, to model the gelating flow. The approach was tested in the case of a steady-state laminar flow in a circular channel. An example of the results obtained is shown on the right, where the radial profiles of volume fraction of the swelling Carbopol particles ( $\zeta$ ) and the corresponding velocity profiles are reported at different residence times, for two different inlet velocities.



## **Exploiting Rheology to Understand the Mechanical Properties of Multi-layered 3D Printed Hydrogel Systems**

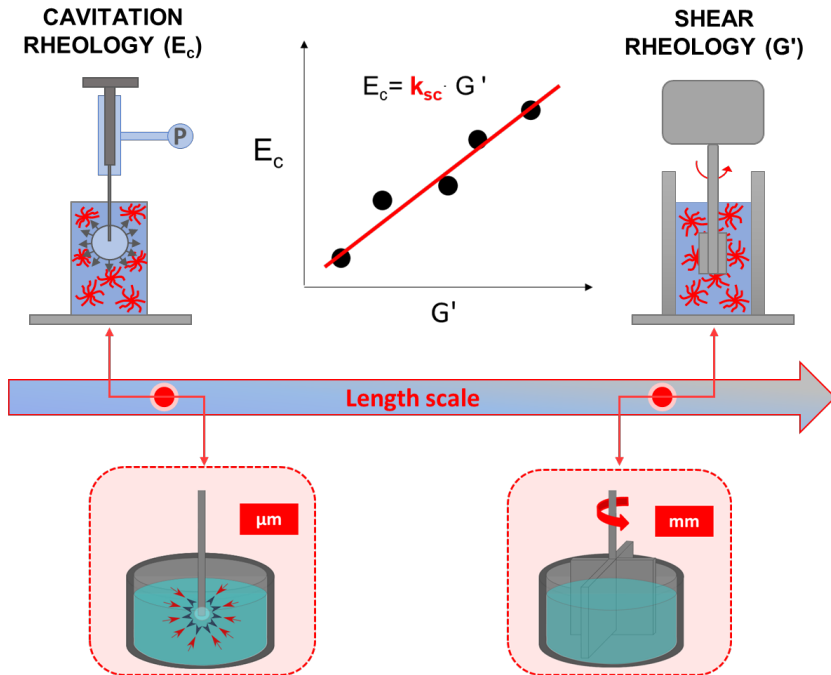
Ana M. Fuentes Caparrós  
University of Glasgow



Hydrogels are present in our everyday life: electronic devices, hygiene products, water purification systems, biomedical sciences, and so on. The characterisation of the mechanical properties of such class of soft material is key in determining whether these materials are potentially suitable for specific applications. Hydrogels used for tissue engineering, for example, are committed to 3D scaffolds that mimic the natural extracellular matrix, which supports cell adhesion, migration, differentiation and proliferation. As such, there is special interest in the study of the mechanical properties of hydrogels. Over the last few decades, 3D (bio)printing has emerged as a promising technology to construct biomaterials over layer-by-layer deposition with precise shape, structure and architecture of target tissues and organs. Thus, a wide range of hydrogels have been reported to be suitable for 3D printing. In most cases, the mechanical properties of such hydrogel's candidates are assessed before the 3D printing process, with little if any rheological characterisation of the gels after they have been printed. Thus, it is normally assumed that the resulting mechanical properties of the printed materials are not affected by the printing process. This lack of measuring post-printing is undoubtedly due to the difficulty in carrying out such measurements. Furthermore, the mechanical properties of hydrogels are normally measured using traditional shear rheology, which needs millilitres of sample and assesses the bulk properties of the material. However, very often in biology, for example, the volume of gels samples for rheological characterisation is limited. As such, their characterisation using traditional shear rheology is restricted. Furthermore, it is important to not only measure the bulk mechanical properties, but also interpret the properties of hydrogels at a smaller length scale, especially if they are to be used in biomedical sciences.

In my thesis, I focused on developing rheological methods to characterise multi-layered hydrogels for 3D printing technology as well as finding a way to characterise

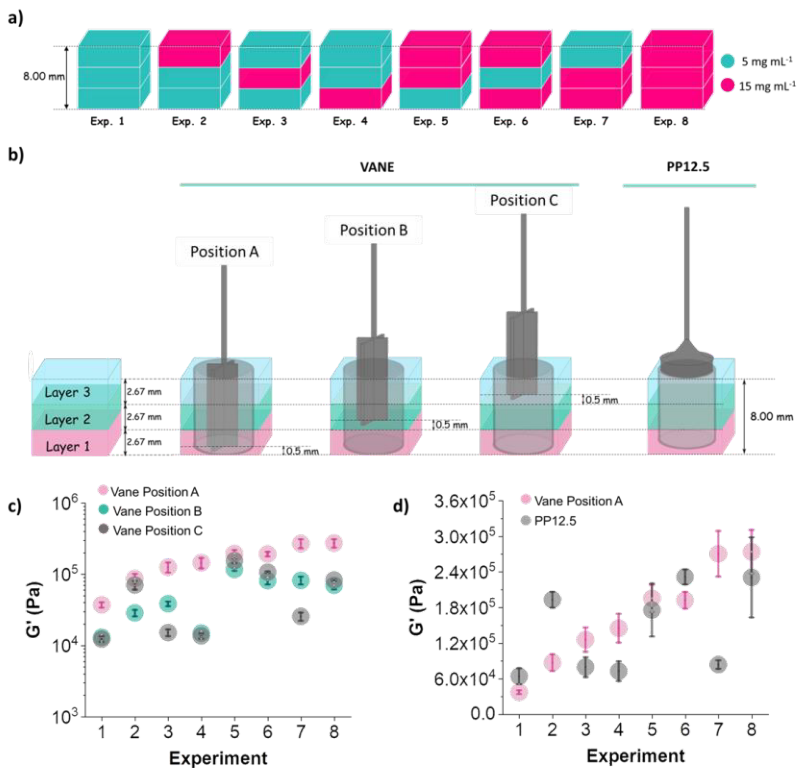
the mechanical properties of hydrogels at multiple length scales. Specifically, we used traditional shear rheology and cavitation rheology to assess the mechanical properties of a series of hydrogels at the mm and  $\mu\text{m}$  scales respectively (Figure 1).



**Figure 1.** Schematic representation of a cavitation rheometer (top left) and a shear oscillatory rheometer (top right). The relationship between both techniques is given by a proportionality constant,  $k_{sc}$ , determined by the ratio of the moduli obtained from the two techniques (top middle). Closer diagram showing how both techniques work at different length scales (bottom).

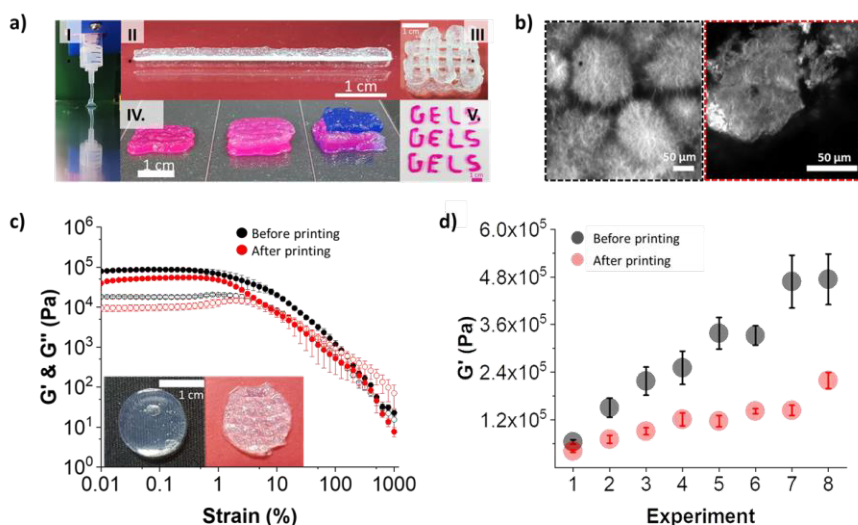
We analysed the quantitative relationship,  $k_{sc}$ , to interconnect between both rheological techniques.  $k_{sc}$  was assessed for gels with different microstructures and we found that the resulting values were dependent on the type of microstructure present in our gel. The resulting measurements showed that cavitation rheology

gives a greater insight into the networks that have been formed as compared to bulk rheology where the slight differences in absolute moduli are difficult to interpret.



**Figure 2.** (a) Cartoons showing gel layers in experiments 1-8. Each gel stack is made up of 3 layers, where the cyan and deep pink layers represent 5 mg mL<sup>-1</sup> and 15 mg mL<sup>-1</sup> of the gelator respectively. The different concentrations result in different gel stiffnesses. (b) Schematic representing three different positions used for the vane measurements in an 8 mm three-layered gel; position A, B and C correspond to the vane located at 0.5 mm above the bottom surface of layers 1, 2 and 3 respectively. (c)  $G'$  values for experiments 1-8 in log scale using the vane in position A (pink circles), B (green circles) and C (grey circles). (d) Comparison of  $G'$  for experiments 1-8 using both the vane in position A (pink circles) and the PP12.5 (grey circles). The error bars represent the standard deviation of three different measurements.

Furthermore, we developed a rheological method to characterise the mechanical properties of multi-layered hydrogels with a high degree of control. We demonstrate that not only the mechanical properties of individual layers within a multi-layer gel system can be measured, but also the contribution of each layer to the combined gel can be assessed as well as the contribution of the neighbouring layers (Figure 2). Lastly, we demonstrated the effect of 3D printing on the mechanical properties of the resulting multi-layered hydrogels (Figure 3).



**Figure 3.** (a) Photographs of 3D printed gels at a concentration of  $5 \text{ mg mL}^{-1}$ ; (a.I.) A 50 mm printed line. (a.II.) Deposition of a gel filament onto the printing bed; (a.III.) Scaffold of three printed layers; (a.IV.) (left to right) 1-layer, 2-layer and 3-layer systems using a serpentine pattern and dyed with Rose Bengal (layer 1), no dye (layer 2) and Nile Blue A (layer 3). (a.V.) Printed text. All scale bars represent 1 cm. (b) Confocal images for a gel at a concentration of  $5 \text{ mg mL}^{-1}$  (left) before and (right) after printing. The scale bars represent  $50 \mu\text{m}$ . (c) Strain sweep for a gel at a concentration of  $5 \text{ mg mL}^{-1}$  and 2 mm height before printing (black data) and 1 layer after printing (red data). The rheological measurements were carried out using the vane at a measuring position of 0.5 mm. The insets show photographs of a gel at concentration of  $5 \text{ mg mL}^{-1}$  (left) before and (right) after printing. (d) Evolution of  $G'$  for experiments 1-8 (black data) before and (red data) after printing. The error bars represent the standard deviation of three different measurements.

## **BSR AWARDS**

### **Undergraduate Summer Research Bursaries**

#### **Nature of Bursaries**

The purpose of the bursaries is to give experience of research to undergraduate students to explore the potential of becoming a researcher and to encourage them to consider a career in rheology. Two such awards will be granted in 2022. The bursaries provide support for the student at a rate of £200 per week for a period of between 6 and 8 weeks if full time. Applications from students wishing to work part – time will also be considered. The awards will be transferred to the successful applicant's Institution; it is the responsibility of the applicants to inform their respective administrative departments of the award.

The closing date for receipt of applications is 5pm, Friday 25th February 2022. Successful candidates will be informed by end of March.

#### **Eligibility**

Students may only take up the bursary during the summer vacation between the intermediate years i.e. students must have completed their second year of their undergraduate degree. Students in the final year of their degree intending to undertake a taught Master's degree immediately following their undergraduate degree may apply. Applications on behalf of first-year undergraduate students will not be considered.

Researchers in rheology at universities and research laboratories in industry within the UK are eligible to apply. A supervisor may support no more than one student application. Priority will be given to projects supervised by postdoctoral researchers or early career academic staff. Students will normally be expected to be on track for a first-class or upper second-class degree in order to be considered. Students must be registered at a UK institution for the majority of their undergraduate degree.

Supervisors and students do not necessarily have to be based at the same institution, however we expect that they will work together at the same institution for the duration of the project and have regular meaningful personal contact (an average of

1 hour per week meeting in person is the minimum expected). Bursaries will only be granted for the student named on the application form; awards are not transferable between students.

### **How to apply**

The completed application form should be emailed by the student applicant to the BSR secretary at [secretary@bsr.org.uk](mailto:secretary@bsr.org.uk), by the above deadline. A bonus payment of £100 will be made on receipt of a report (word format) suitable for publication in the Bulletin of the Society.

## **\*New\* BSR Carer Grant**

### **Purpose**

The purpose of the BSR Carer's Grant is to enable parents and carers to attend conferences and other research schools, meetings or visits by making a supplementary contribution towards caring costs. The BSR will award up to £250.

### **Eligibility**

Applicants must be a member of 9 months standing and may only apply for one carer's grant in any 12-month period. You may apply for a travel grant simultaneously.

### **Application**

Submissions should include your name, position and organisation, and a short summary of the activity to be supported. Please explain how this activity will support your research and include a break-down of the projected costs.

Applications should be sent to the Secretary ([secretay@bsr.org](mailto:secretay@bsr.org)) and must be received at least 1 month prior to the activity. Up to a maximum of 4 grants will be granted per annum. Payment of the award will be made on the receipt of a short report suitable for the Bulletin of the Society. Advance payment may be made in certain circumstances; please send enquiries to the Secretary.

## **Vernon Harrison Award**

The British Society of Rheology welcomes applications for the Vernon Harrison Award for the most distinguished PhD thesis in rheology. The aim of this award is

to recognise excellence, creativity and novelty in research. It will be awarded to the postgraduate student who, in the opinion of the adjudicating committee, has made the most original and significant contribution to any branch of rheological research (experimental, computational or theoretical) leading to the award of a PhD degree in a given academic year. This prize is partly supported by the Vernon Harrison Bequest. Deadline for receipt of applications is 30<sup>th</sup> September annually.

### BSR Annual Award

The Annual Award is intended to recognise a significant contribution to rheology, either through a single paper (in which case a group of co-authors can receive the award) or more sustained activity of a single individual. The Award is decided based on scientific merit. Long service is not a factor, and nominations of early career scientists / research workers are welcomed. The final decision is taken by the Council of the British Society of Rheology. If, in a given year, there is no suitable nominee, then the Award will not be given. Deadline: 31<sup>st</sup> July annually

### BSR Student Travel Awards

The British Society of Rheology seeks applications for travel awards from its student membership, with the objective of encouraging students to disseminate their research. Travel awards are available to student members of the Society to present their research by paper or poster at a conference that contains a strong rheological element. The awards are expected to supplement existing sources of funding that would not cover the whole cost of attending the conference on their own. Suitable meetings include the Non-Newtonian Club in September and the Mid-Winter Meeting in December.

Applications for a travel award should be sent to the Secretary ([secretary@bsr.org.uk](mailto:secretary@bsr.org.uk)). Submissions should include the name and location of the conference, the title, authors and abstract of the paper submitted to the conference, a breakdown of the projected costs of attending the meeting and a brief supporting letter from the research supervisor. The support of the British Society of Rheology should be mentioned in the conference presentation, and the Society's logo may be used for this purpose. Payment of the bursary will be made on receipt of a conference report suitable for publication in the Bulletin of the Society.

## **BSR Early Career Travel Award**

The purpose of the BSR Early Career Travel Award is to assist early-career researchers with disseminating rheological research and building their research network by either supplementing travel to a national/international conference, or supplementing funding for a short research visit. Research visits that connect academia and industry are especially encouraged.

BSR will award up to £150 for UK-based and £300 for European-based conference travel, and up to £500 for conference travel in the rest of the world. In the case of research visits (or combined conference and research visit), BSR will award up to £500 for UK-based and £1000 for non-UK-based research activity.

### **Eligibility**

Applicants must be a BSR member of at least 9 months standing.

This travel award is intended to assist those in the “early stage” of their careers; that is an academic post-doctorate position, transitioning to an established independent researcher, or new to an industrial role. (PhD students, please see student travel award.)

There are no eligibility rules based on years of post-doctoral experience or whether the applicant holds a permanent position. Consideration will be given to applicants who have taken a non-standard career path after their primary degree. Applications are also welcomed from candidates who wish to re-establish themselves after a career break or any other period of absence from active research.

Please note applicants may only apply for one travel award in any 12 month period. Individuals may receive no more than one award within a 3-year period.

### **Application**

In the case of conference travel, submissions should include the name and location of the conference, the title, authors and abstract of the paper submitted to the conference. The support of the British Society of Rheology should be mentioned in the conference presentation, and the Society's logo may be used for this purpose.



In the case of a short research visit, submissions should include the name and location of the host institution/company, and a short synopsis of the intended research.

Applicants should justify why they consider themselves an “early-career” researcher in their submission.

A breakdown of the projected costs and a brief supporting letter from the head of school/line manager (and the host institution/company in the case of a research visit) should also be included.

Applications will be judged on the following criteria:

1. Scientific excellence in the area of rheology, including theory and application.
2. Benefits to applicant's career progression.

Applications should be sent to the Secretary ([secretary@bsr.org.uk](mailto:secretary@bsr.org.uk)). Applications must be received at least 1 month prior to conference travel and 3 months prior to a research visit. Up to a maximum of 4 awards will be granted per annum.

Payment of the award will be made on receipt of a report suitable for publication in the Bulletin of the Society.

Claire McIlroy  
BSR Honorary Secretary

## Industry News

NETZSCH have recently launched their NETZSCH online academy (NOA) e-learning platform. With over 150 courses offered and new courses being added regularly, the platform can start with learning basics of instrument use through to understanding measurement of specific applications and advanced techniques. With 10 languages and a variety of user levels you can enjoy flexible learning that is fully adaptable to your training needs.

NOA training courses are created by experienced specialists in the field of thermal analysis and rheology. In-line with your professional development, training certification is provided upon course completion. To learn more, watch the video on the website page highlighted below.

The rheology section is rapidly growing with 50 courses to currently choose from, you can enrol and start watching content for free via this NOA page:



[NOA - NETZSCH Online Academy - NETZSCH Analyzing & Testing \(netzsch-thermal-analysis.com\)](https://www.netzsch-thermal-analysis.com/NOA)

## CONFERENCE DIARY

| <b>2022</b>       |   | <b>CONFERENCES &amp; MEETINGS</b> |
|-------------------|---|-----------------------------------|
| April             | <b>BSR AGM</b>  |                                   |
| Date tbc          |   |                                   |
| 12-14 Jan<br>2022 | <b>Midwinter meeting – Particles, Emulsions and Gelation-<br/>controlling the rheology of concentrated colloidal systems.</b> |                                   |
| Cambridge         |   |                                   |
| 26-28 April       | <b>Annual European Rheology Conference (AERC), Seville.</b>   |                                   |
| Dec/Jan           | <b>Midwinter meeting – details to follow</b>  |                                   |
| Durham            |   |                                   |
| <b>2023</b>       |   |                                   |
| 17-19 July        | <b>UK Colloids, Liverpool</b>   |                                   |
| Liverpool         | <a href="https://www.bsr.org.uk/conference/uk-colloids-2021-49/">https://www.bsr.org.uk/conference/uk-colloids-2021-49/</a>   |                                   |
| 29 July           | <b>ICR 2023 International Conference on Rheology, Athens.</b>   |                                   |
| – 4 Aug           | <a href="https://www.hsr.gr">https://www.hsr.gr</a>   |                                   |
| <b>2024</b>       |   |                                   |
| April             | <b>Annual European Rheology Conference (AERC), Leeds</b>  |                                   |



## MASTER THE FLOW WITH THE MCR RHEOMETER SERIES

- Extensive accessory portfolio, quickly and easily adapted to meet your rheological needs
- Renowned EC motor technology for highly accurate results across a vast viscosity range
- Breakthroughs in user-friendliness with patented features like Toolmaster™, TruGap™, and T-Ready™
- Dedicated software for customized test and analysis definitions, and simplified data retrieval

