

September, 6-8



# Book of Abstracts

**The multidisciplinary  
science of Rheology**

ISBN 978-84-697-5122-0

Towards a  
healthy and  
sustainable  
development



## CONTENTS

	Page
Welcome .....	2
Schedule .....	3
Committees .....	4
Keynote lectures and Invited speakers .....	5
Awards .....	6
Practical information .....	7
Social programme .....	10
Detailed programme .....	11
Abstracts oral communications .....	17
Oral communications Keynote Lecturers and Invited Speakers .....	18
Oral communications Wednesday, 6 .....	23
Oral communications Thursday, 7 .....	39
Oral communications Friday, 8 .....	57
List of posters presented .....	65
Abstracts poster communications .....	71
Poster Session 1, Wednesday, 6 .....	72
Poster Session 2, Thursday, 7 .....	117

## WELCOME

We are delighted to welcome you at the Iberian Meeting on Rheology, IBEREO 2017. This Meeting is an international event organized every two years, jointly by the Spanish Group of Rheology (GER) and the Portuguese Society of Rheology (SPR).

The current edition is hosted by the Universitat de València and IATA-CSIC and it takes place in the ADEIT premises, located at Valencia historical centre. A special emphasis about the multidisciplinary character of Rheology is given, together with an important consideration to health and sustainable development, as main drivers in nowadays product development.

During the meeting the most recent trends in rheology are going to be addressed. More than one hundred scientists coming not only from Spain and Portugal, but also from other European and American countries are presenting oral and poster contributions on the following topics:

- Formulation and Product design
- Food Rheology
- Suspensions, Colloids and Granular Materials
- Pharmaceuticals and Cosmetics
- Advances in new Rheology Areas
- Modelling and Simulation in Rheology
- Rheometry and Experimental Methods
- Polymers and Biopolymers

Moreover, along the conference several keynote and invited lectures are going to be given by well-known European rheologists. Finally, considering the relevant role of rheology practical applications, a round table with representatives from Industry and Science is also organized to debate about it.

On the other hand, some social activities are prepared for you to know better the monuments, history, traditions and surroundings of the beautiful city of Valencia.

We do hope you enjoy meeting colleagues, discussing about rheology but also having some leisure, so you go back home with great memories of IBEREO 2017 and Valencia!

The Organizing Committee

	Wednesday, 6	Thursday, 7	Friday, 8
8:30	<i>Registration</i>		
8:45			
9:00	<i>Opening Ceremony</i>	SC-O1 Rasteiro et al.	
9:15		SC-O2 Félix et al.	
9:30	Keynote Lecture <b>CRISPULO GALLEGOS</b>	SC-O3 Galindo-Rosales et al.	PB-O1 Burgoa et al.
9:45		SC-O4 Ramírez et al.	PB-O2 Zubarev
10:00		Keynote Lecture <b>LEONARD SAGIS</b>	PB-O3 Fernández et al.
10:15			PB-O4 Raghunanan et al.
10:30			Invited speaker
10:45			<b>ANTXON SANTAMARIA</b>
11:00	<i>Coffee Break</i>	<i>Coffee Break</i>	<i>Coffee Break</i>
11:15			
11:30	Poster Session 1	Poster Session 2	PB-O5 López-López et al.
11:45	PDP1- PDP16/ FRP1-FRP29	SCP1-SCP6/PhCP1-PhP8/ANP1-ANP2 REP1-REP5/PBP1-PBP11	PB-O6 Gila Vílchez et al.
12:00			PB-O7 Sangroniz et al.
12:15	FD-O3 Collar et al.	SC-O5 de Vicente et al.	Round table <i>Rheology and Industry</i>
12:30	FD-O4 Cortés-Triviño et al.	PhC-O1 Ribeiro et al.	
12:45	FD-O5 Borrero-López et al.	PhC-O2 Marto et al.	
13:00	FD-O6 Tenorio-Alfonso et al.	PhC-O3 Bettencourt et al.	
13:15	<i>LUNCH</i>	<i>LUNCH</i>	<i>Closing Ceremony</i>
13:30			
13:45			
14:00			
14:15			
14:30			
14:45	<i>Best Thesis presentations</i>	MS-O1 Nobrega et al.	<i>The City of Arts and Sciences &amp; Albufera trip</i>
15:00		MS-O2 Troya et al.	
15:15		AN-O1 Leal et al.	
15:30		AN-O2 Ortigosa-Moya et al.	
15:45	FR-O1 Smoot et al.	AN-O3 Gracia Fernández et al.	
16:00	FR-O2 Fradinho et al.	RE-O1 Meyer et al.	
16:15	FR-O3 Mironeasa et al.	RE-O2 Braun et al.	
16:30	<i>Coffee Break</i>	<i>Coffee Break</i>	
16:45			
17:00	Invited speaker	Invited speaker	
17:15	<b>ISABEL SOUSA</b>	<b>JOSÉ MUÑOZ</b>	
17:30	FR-O4 Batista et al.	RE-O3 Lefevre et al.	
17:45	FR-O5 Dias et al.	RE-O4 Morillas et al.	
18:00	FR-O6 Alvarenga et al.	RE-O5 Teixeira et al.	
18:15	FR-O7 Ropciuc et al.	<b>SPR Meeting</b>	
18:30	FR-O8 Codina et al.		<b>GER Meeting</b>
18:45	FR-O9 Howarth		
19:00	<i>Guided visit</i>		
20:00	<i>Welcome cocktail</i>		
20:30		<i>Gala Dinner / GER MEDAL</i>	

Code	Meaning	Code	Meaning
FR	Food Rheology	PD	Formulation and Product Design
PhC	Pharmaceuticals and Cosmetics	PB	Polymers and Biopolymers
RE	Rheometry and Experimental Methods	SC	Suspensions, Colloids and Granular Materials
MS	Modelling and Simulation in Rheology	AN	Advances in New Rheology Areas
O	Oral presentation	P	Poster presentation

## ORGANIZING COMMITTEE

María Jesús Hernández Lucas (Universitat de València, Spain)  
Teresa Sanz Taberner (IATA-CSIC, Valencia, Spain)  
Ana Salvador Alcaraz (IATA-CSIC, Valencia, Spain)  
Francisco J. Rubio Hernández (Universidad de Málaga, Spain)  
Roberto Steinbrüggen (IFI, Vigo, Spain)

## SCIENTIFIC COMMITTEE

María Dolores Álvarez (ICTAN-CSIC, Madrid, Spain)  
María Teresa Cidade (Universidade Nova de Lisboa, SPR President, Portugal)  
José María Franco (Universidad de Huelva, Spain)  
Carlos Gracia (TA Instruments, Spain)  
Antonio Guerrero (Universidad de Sevilla, GER President, Spain)  
Catarina Rosa Leal (Instituto Politécnico de Lisboa-ISEL, Portugal)  
José Muñoz (Universidad de Sevilla, Spain)  
Miguel Nóbrega (Universidade do Minho, Portugal)  
Pedro Partal (Universidad de Huelva, Spain)  
María Graça Rasteiro (Universidade do Coimbra, CIEPQPF-UC, Portugal)  
Helena Ribeiro (Universidade de Lisboa, Portugal)  
Antxon Santamaría (Universidad del País Vasco, Spain)  
Isabel de Sousa (Universidade de Lisboa, Portugal)  
Clara Asunción Tovar (Universidad de Vigo, Spain)

## KEYNOTE LECTURERS

Leonard Sagis obtained an MSc in Chemical Engineering from Eindhoven University of Technology in 1990, and a PhD in Chemical Engineering from Texas A&M University in 1994. In 1998, after postdoc positions at the physical chemistry department of Leiden University and the Institute of Technical Chemistry of the University of Amsterdam, he joined Wageningen University, where he is currently a faculty member in the Physics and Physical Chemistry of Food Group. Since 2011 he is also a member of the Polymer Physics Group of the Department of Materials, at ETH Zurich in Switzerland.

Críspulo Gallegos obtained his PhD at the Chemical Engineering Department of the University of Sevilla (1982, Sevilla, Spain). Since May 2011, he is Vice-President & Head of I&D “Complex Formulations” of Fresenius Kabi Deutschland GmbH (Germany). He is also Full Professor of Chemical Engineering at the University of Huelva (Spain). Among other universities, he has worked as Visiting Professor (1989) at the University of Laval (Québec, Canada) and as BBVA Professor (1998) at the Chemical Engineering Department at Cambridge University (UK). Since 2006, he is an invited “Associated Member” of the Institute of Non-Newtonian Fluid Mechanics (UK).

## INVITED SPEAKERS

Antxon Santamaría earned his BS and MS in Physics from the University of Navarra and his PhD from the University of the Basque Country. He was a Research Associate at the University of Tennessee in 1982. Since 1992 he is Full Professor of Applied Physics at the University of the Basque Country. Vice-dean of the Faculty of Chemistry of San Sebastián from 1987 to 1989 and Director of the Department of Polymer Science and Technology from 1989 to 2009. President of the Spanish Polymer Group (GEP) from 1997 to 2003 and President of the Spanish Rheology Group (GER) from 2006 to 2015.

Isabel Sousa, PhD in Food Science by University of Nottingham UK, is associate professor with habilitation at the Department of Biosystems Science and Engineering from the Instituto Superior de Agronomia (ISA) of the Universidade de Lisboa. Is head of the Eco-novel Food and Feed group of the LEAF (*Linking Landscape Environment Agriculture and Food*) research center at the Portuguese foundation for Science and Technology (FCT). Member of the Coordination Board of the F3 *Food Farming & Forest* College from the ULisboa (from 2015). Actual President of the Association for the Development of ISA - ADISA. Former Vice-President of ISA (2007-2009). Member of the ISA School Board (2013-2017).

José Muñoz received his Ph.D. in Chemical Sciences at the University of Seville. He is Senior Lecturer at the same university and is accredited as Full Professor of Chemical Engineering. He is PERSAN Company Chair of Detergency at the University of Seville and Head of the Applied Rheology and Technology of Colloids Research Group. He was Head of the Chemical Engineering Department of the University of Seville from 2001 to 2002, Treasurer of the Spanish Group of Rheology (GER) from 1993 to 2006 and Member of the GER Council from 2006 to 2015.

## AWARDS

### BEST THESIS AWARD

An Iberian award will be given to the most distinguished PhD Thesis in Rheology, each two years, by the Portuguese Society of Rheology (SPR) and the Spanish Rheology Group (GER / RSEF and RSEQ). The final decision of the Adjudicating Committee will be taken after a 15 minutes presentation of the previously selected candidates: Manuel Félix, José Ruiz-Lopes and Paulo Teixeira (scheduled Wednesday, 6 at 14:45 h). The awarded candidates will be notified at the Closing Ceremony on Friday, 8 (13 h).

### BEST POSTERS

A total of four posters will be granted by the Journal Europhysics Letters (EPL) with 150 euros each. All registered students presenting a poster are eligible candidates. The winners of the best poster awards will be announced during the Closing Ceremony on Friday, 8 (13 h).

### GER MEDAL

Prof. M<sup>a</sup> Eugenia Muñoz Bergareche and Prof. Crispulo Gallegos Montes have been awarded with the Gold Medal of the Spanish Group of Rheology (GER). The award ceremony will take place during the Gala Dinner on Thursday evening.

## About the Venue



Fundación Universidad Empresa de Valencia  
Plaza Virgen de la Paz, 3  
(located behind Santa Catalina Church)  
Information Desk: Ground floor  
Conference rooms: Ground floor  
Salón de Actos  
Salón de Grados  
Room 0.1.

## Free wifi connection



The University-Enterprise Foundation of Valencia provides free access to internet in the building. The connection will be via password (the password is located in your accreditation) or please contact the info desk of the conference

## Coffee Breaks

Cafeteria and square (Ground floor)



## Lunches

Roof terrace (Fourth floor)



## Sessions Area (Ground Floor)



## PHONES OF INTEREST

**Conference Venue. ADEIT**

Phone + 34 96 326 26 00

**RENFE (Train transport)**

Phone 902 320 320

**AENA (Spanish Airports)**

Phone support 902 404 704 / +34 91 321 10 00

**Tele taxi (taxi services company)**

Phone +34 96 357 13 13

**Metro Valencia**

Customer information phone 900 46 10 46

**Bus EMT Customer Service**

Phone +34 96 315 85 15

Monday to Friday from 8am to 9pm and Saturdays from 9am to 2pm

**Police of Valencia**

Phone 092

**Emergency**

Phone 112

**Tourist info**

Phone +34 96 398 64 22

## SOCIAL PROGRAMME

### WEDNESDAY, 6

#### **Visit to the city center of Valencia and welcome cocktail at the Botanical Garden of the University of Valencia**

Guided walking tour visiting the most noteworthy streets, squares and monuments of Valencia's historical center, such as the Gothic "Lonja"(World Heritage Site by UNESCO), the Modernist Central Market, the City Hall Square, the Baroque Palace of the "Marques de Dos Aguas", the Ancient University, the Cathedral and the Medieval "Torres de Serranos" Gateway, among others. The visit will end with an open air welcome cocktail at the Botanical Garden.

**Meeting point: 19 h. Main hall Conference venue**

### THURSDAY, 7

#### **Gala Dinner at the Ayre Astoria Palace Hotel**

The Gala dinner will take place on the roof terrace of the iconic Ayre Astoria Palace Hotel which offers wonderful views of the city's historical center. With an emblematic history and location (only five minutes walking from the conference's venue) the hotel –which was partially renovated in 2013 with a contemporary style- proffers an impeccable service and exceptional cuisine (it is specialized in rice dishes and Mediterranean cuisine)

**Meeting point: 20:30 h. Ayre Astoria Palace Hotel (Plaza Rodrigo Botet, 5)**

### FRIDAY, 8

#### **Visit to the City of Arts and Sciences & boat trip on the Albufera lake**

If you come to Valencia a visit to the City of Arts and Sciences is a must. It is a scientific and cultural leisure complex, covering around two kilometres of the former riverbed of the River Turia. The work of Valencia's own Santiago Calatrava, this is an example of architecture at its most futuristic. The colossal structure houses an IMAX cinema (situated in the Hemisfèric), as well as Europe's largest aquarium – the Oceanogràfic, interactive educational exhibits in the Príncipe Felipe Science Museum and the avant-garde opera house - Palau de les Arts Reina Sofia. Furthermore, the impressive l'Assut de l'Or bridge and the Agora are all a delight for the senses.

Later, we will visit the Albufera lake, the largest lake in Spain and one of the most important wetland areas in the Iberian Peninsula. It is a place of great ecological interest with rare species of wading birds and a rich variety of wildlife. There is nothing more relaxing than a boat trip on the Albufera lake contemplating the red and amber tones of the setting sun dancing across the water.

**Meeting point bus: 17 h. Calle Poeta Querol, 7 (Salvatore Ferragamo Store)**

## WEDNESDAY, 6

8:30 - 9:00 **REGISTRATION**

9:00 - 9:30 **OPENING CEREMONY**

9:30 - 10:30 **KEYNOTE LECTURE. C. Gallegos.** Rheological aspects of dysphagia diagnosis and management

### FORMULATION AND PRODUCT DESIGN. Chair: J. Muñoz

10:30 - 10:45 **PD-01. M.T. Cidade, M. Cigl, V. Hamplova, A. Machado and A. Bubnov.** Design, mesomorphic properties and rheological characterization of a novel calamitic low molecular weight liquid crystal.

10:45 - 11:00 **PD-02. C. Bengoechea, A.A. Cuadri, A. Romero and A. Guerrero.** Soy protein-based superabsorbent biopolymer materials functionalized with different acylation agents.

11:00 - 11:30 **COFFEE BREAK**

11:30 - 12:15 **POSTER SESSION 1. Formulation and Product Design/Food Rheology**

### FORMULATION AND PRODUCT DESIGN. Chair: H. Ribeiro

12:15 - 12:30 **PD-03. E. Armero, G. Sanmartín and C. Collar.** Impact of heat moisture treatment on the physical profiles of blended matrices made of barley and wheat flour.

12:30 - 12:45 **PD-04. E. Cortés-Triviño, C. Valencia and J.M. Franco.** Formulation and rheological characterization of epoxidized lignin-based gel-like dispersions for lubricant applications

12:45 - 13:00 **PD-05. A.M. Borrero-López, C. Valencia and J.M. Franco.** Influence of processing conditions on the rheological behaviour of NCO-functionalized lignin-based gel-like dispersions.

13:00 - 13:15 **PD-06. A. Tenorio-Alfonso, M.C. Sánchez and J.M. Franco.** Assessment of the adhesion performance of cellulose acetate and castor oil-based adhesives on different substrates by probe-tack tests.

13:15 - 14.45 **LUNCH**

14.45 - 15.45 **BEST THESIS PRESENTATION**

## FOOD RHEOLOGY. Chair: G. Rasteiro

- 15:45 - 16:00 **FR-01. J. Smoot, L. G. Howarth and J. K. Whaley.** Mapping the impact of starch swelling behavior on rheology and food texture
- 16:00 - 16:15 **FR-02. P. Fradinho, I. Sousa and A. Raymundo.** Rice industry by-products in food emulsions
- 16:15 - 16:30 **FR-03. A. Dabija, G.G. Codină, M.C. Oroian and S. Mironeasa.** Effect of tomato skins powder addition on rheological and physicochemical characteristics of milk yoghurt.
- 16:30 - 17:00 **COFFEE BREAK**

## FOOD RHEOLOGY. Chair: A. Santamaría/ C. Gracia

- 17:00 - 17:30 **INVITED SPEAKER. I. Sousa.** The rheology as a tool to develop new food products.
- 17:30 - 17:45 **FR-04. A.P. Batista, I. Bursic, A. Miranda, S. Fragoso, P. Fradinho, A. Raymundo, I. Sousa.** Rheological characterization of *Spirulina* gluten-free cookie doughs.
- 17:45 - 18:00 **FR-05. J. Dias, P. Lage, N. Alvarenga, R.V. Duarte and J.A. Saraiva.** Impact of high pressure technology on the dynamic properties of filled chocolates.
- 18:00 - 18:15 **FR-06. N. Alvarenga, S. Santos, J. Dias, T. Brás, A.P.L. Martins and M.F. Duarte** Using the dynamic properties to follow the coagulation of ewe milk with *Cynara cardunculus*.
- 18:15 - 18:30 **FR-07. S. Ropciuc, A. Dabija, A.M. Sidor and M.A. Oroian.** Influence of fortification with vegetable and fruit powder on the rheological and physicochemical properties of yoghurt.
- 18:30 - 18:45 **FR-08. G.G. Codină, D. Zaharia, E. Todosi Sănduleac and A. Dabija.** Effect of inulin with different polymerisation degree on wheat flour dough rheological properties of 1250 type.
- 18:45 - 19:00 **FR-09. L. G. Howarth.** The Influence of starch rheology on dough behaviour for snacks
- 19:00 - 20:00 **GUIDED VISIT**
- 20:00 **WELCOME COCKTAIL**

## THURSDAY, 7

### SUSPENSIONS, COLLOIDS AND GRANULAR MATERIALS/ PHARMACEUTICALS AND COSMETICS. Chair: M. Nóbrega

- 9:00 - 9:15 SC-O1. M. G Rasteiro, C. Cotas and D. Asendrych. Rheology of fibre suspensions: experimental and modelling.
- 9:15 - 9:30 SC-O2. M. Felix, N.C. Isaurralde, J.A. López Osorio, C. Carrera and A. Guerrero. Emulsions stabilised with legume proteins. From interfacial to bulk rheology.
- 9:30 - 9:45 SC-O3. R. Soares Duarte, L. Campo-Deaño, R. A. Lima, F. J. Galindo-Rosales. Rheological characterization of concentrated suspensions of fumed silica for anti-impact applications.
- 9:45 - 10:00 SC-O4. J.A. Carmona, A. Caro, J. Santos, R. Llinares, P. Ramírez. Effect of surfactants on shear and microstructural properties of aqueous sepiolite gels.
- 10:00-11:00 KEYNOTE LECTURE. L. Sagis. Rheology of soft interface dominated materials: a multiscale approach.

11:00-11:30 **COFFEE BREAK**

11:30-12:15 **POSTER SESSION 2. Rheometry and Experimental Methods/Pharmaceutical and Cosmetics/Polymer and Biopolymers/ Suspensions, Colloids and Granular Materials**

### SUSPENSIONS, COLLOIDS & GRANULAR MATERIALS.

Chair: I. Sousa

- 12:15-12:30 SC-O5. K. Shahrivar, J. R. Morillas, E. Carreón-González, J. de Vicente. Field-induced aggregation in strongly confined magnetorheological fluids.
- 12:30-12:45 PhC-O1. B. Gregorí, A.P. Serro, J. Marto, R.G. Santos, J.M. Bordado, H.M. Ribeiro. The influence of polymer concentration on nail lacquers properties
- 12:45-13:00 PhC-O2. C. J Marto, B Chiari-Andréo, Vera Isaac, HM Ribeiro. Rheology and texturometry: Complementary tools to predict the water resistance performance of sunscreens.
- 13:00-13:15 PhC-O3. M.M. da Silva, R. Calado, J. Marto, A. Bettencourt, L.M.D. Gonçalves. Insights on nanoparticles mucoadhesiveness for ocular drug delivery: a rheological approach.

13:15-14:45 **LUNCH**

## MODELLING AND SIMULATION IN RHEOLOGY/ADVANCES IN NEW RHEOLOGICAL AREAS/RHEOMETRY AND EXPERIMENTAL METHODS.

Chair: P. Partal

- 14:45 - 15:00 **MS-O1. C. Fernandes, V. Vukčević, T. Uroić, L.L. Ferrás, O.S. Carneiro, R. Simões, H. Jasak and J.M. Nóbrega**  
A new coupled viscoelastic solver in OpenFOAM® framework.
- 15:00 - 15:15 **MS-O2. P. Troya, J. Ramirez and B.D. Olsen**  
Extremely slow reptation dynamics of rod-coil-rod triblock copolymers.
- 15:15 - 15:30 **AN-O1. R. Portela, J.M. Franco, P. Patrício, P. L. Almeida, R. G. Sobral and C. R. Leal.** Rotational and translational motion observed in *Escherichia coli* aggregates during shear.
- 15:30 - 15:45 **AN-O2. E. Ortigosa-Moya, R. Hidalgo-Alvarez and J. de Vicente.** Normal Stresses in magnetic-responsive shear thickening colloids.
- 15:45 – 16:00 **AN-O3. C. A. Gracia Fernández and A. Álvarez.** Three-dimensional rheological characterization of magneto rheological fluids trough OSP measurements.
- 16:00 - 16:15 **RE-O1. F. Meyer and J. P. Plog.** Following phase transitions with rheometry and simultaneous Raman-Spectroscopy.
- 16:15 - 16:30 **RE-O2. J. Laeuger, A. Braun and T. Masso.** New rheometric tools for complex materials.
- 16:30 - 17:00 ***COFFEE BREAK***
- RHEOMETRY AND EXPERIMENTAL METHODS. Chair: C. Leal**
- 17:00 - 17:30 **INVITED SPEAKER. J. Muñoz.** The role of rheology in the development of green emulsions.
- 17:30 - 17:45 **RE-O3. Y. Lefevre, P. Abgrall, P. Adamska, P. Bru and G. Meunier.** Microfluidic visual rheometer.
- 17:45 - 18:00 **RE-O4. J. R. Morillas, K. Shahrivar and J. de Vicente.** Micro-capillary flow behavior of magnetorheological fluids.
- 18:00 - 18:15 **RE-O5. P.F. Teixeira, F. Sutura, R. Scaffaro, L. Hilliou and J.A. Covas.** In-process material characterization at constant extrusion conditions: Application to clay/PLA bionanocomposites.
- 18:15 - 19:00 ***SPR Meeting (Salón de actos)***  
***GER Meeting (Aula 1.3)***
- 20:30 ***GALA DINNER***

## FRIDAY, 8

### POLYMERS AND BIOPOLYMERS. Chair: A. Guerrero

- 9:30 - 9:45 **PB-O1. A. Burgoa, R. Hernandez, A.M. Zaldua, A. Arrillaga and J.L. Vilas.** Morphology-rheology relationship on novel PA6-HNBR blends
- 9:45 - 10:00 **PB-O2. A. Zubarev.** Non-linear and hysteretic rheological properties of magneto-polymer composites
- 10:00 - 10:15 **PB-O3. M. Fernández, E. Garro and A. Santamaría.** A rheological study of epoxy resins mixed with ionic liquids and its implications in sustainable chemistry
- 10:15 - 10:30 **PB-O4. E.E. Herrera Valencia, M.L. Sánchez Villavicencio and F. Calderas García.** On the pulsating flow of a biological fluid: blood with cholesterol. Perturbation and analytical solutions.
- 10:30-11:00 **INVITED SPEAKER. A. Santamaría.** How to make friends with the help of rheology

11:00-11:30 **COFFEE BREAK**

### POLYMERS AND BIOPOLYMERS. Chair: T. Cidade

- 11:30 - 11:45 **PB-O5. M.T. López-López, A.B. Bonhome-Espinosa, J.D.G. Duran, V. Carriel, F. Campos and I.A. Rodriguez.** Rheology of magnetic biopolymer hydrogels.
- 11:45 - 12:00 **PB-O6. C. Gila Vilchez, M.T. López López, A.B. Bonhome Espinosa and J.D.G. López-Durán.** Magnetorheology of alginate ferrogels
- 12:00 - 12:15 **PB-O7. L. Sangroniz, J.L. Ruiz, M.M. Fernández, A. Santamaria and A.J. Müller** Morphology- rheology relationship in PET-PE-TiO<sub>2</sub> multiphasic systems: Analogies with recycled milk bottles.

12:15 - 13:00 **ROUND TABLE: RHEOLOGY AND INDUSTRY.**

**Chair: J.M. Franco.**

*Participants:* **M. Alonso** (RNB Cosméticos, SL, Valencia); **C. Gallegos** (Fresenius-Kabi Deutschland GmbH); **M. G. Rasteiro** (CIEPQP; Coimbra); **A. Raymundo** (ISA, Lisboa).

13:00 - 13:30 **CLOSING CEREMONY**

13:30 - 15:15 **LUNCH**

17:00 **THE CITY OF ARTS AND SCIENCES & ALBUFERA TRIP**



# ABSTRACTS ORAL COMMUNICATIONS

## Rheological aspects of dysphagia diagnosis and management

C. Gallegos

*I&D Centre Complex Formulations & Processing Technologies. Fresenius Kabi Deutschland GmbH.  
Daimlerstrasse 22. 61352 Bad Homburg (Germany)*

e-mail of the presenter: Crispulo.Gallegos-Montes@fresenius-kabi.com

Swallowing is defined as “the function of clearing food through the oral cavity, pharynx and esophagus into the stomach at an appropriate rate and speed”.

Dysphagia is a dysfunction of the transfer of the bolus from the mouth to the stomach, which may involve any of the stages of the above-mentioned normal swallowing sequence and may result in misdirection of transferred bolus. Thus, patients with structural or physiologic deficits in the mouth, pharynx, or esophagus may demonstrate signs and symptoms of dysphagia. From a pathological perspective, dysphagia may result from a variety of diseases or medical conditions or from treatment of diseases or medical conditions.

The rheological characterization of food boluses is highly relevant, as it is linked to the performance of the deglutition or swallowing process. The rheological properties of foods entering into the mouth are fundamentally a function of the food composition. However, once in the mouth, the rheological behavior is modified during the formation of the bolus, which is largely influenced by subjective sensorial perceptions. Thus, rheological properties play an important role in perceptions of food textures or consistencies.

Food bolus flow is a dynamic process that depends on the characteristics of the applied force. Thus, the bolus during the swallowing process is submitted to shear and extensional flows. However, the focus is usually centered on the measurement of shear viscosity. Likewise, structured food systems may exhibit solid-like behavior. In this case, more sophisticated rheological studies should be used to describe the rheological behavior of food boluses.

There are several guidelines from different dysphagia professional associations around the world concerning a “rheological” classification of fluids for dysphagia management. All of them are referring to viscosity as the only rheological property involved in diet modification for dietary management of dysphagia. In addition, only one of these guidelines proposes objective viscosity borders and ranges for thickened liquids or food boluses. In this case, the classification and ranges are based on shear viscosities measured at one single shear rate of  $50 \text{ s}^{-1}$  and at a temperature of  $25^\circ\text{C}$  (National Dysphagia Diet Task Force), without any scientific evidence or rationale given on the temperature and shear rate chosen for this scale. In fact, a wide range of shear rates ranging from  $5$  to  $1000 \text{ s}^{-1}$  are feasible.

It is quite clear that more research needs to be conducted to determine normative rheological values for the complex swallowing process and, consequently, for its application to dysphagia diagnosis and management.

In this sense, this presentation gathers up-to-date information on rheological aspects of the screening diagnosis of oropharyngeal dysphagia and on the nutritional management of dysphagic patients. More specifically, this lecture reviews the rheological aspects of swallowing and dysphagia (including shear and elongational flows) and its influence on the characteristics of the enteral nutrition for dysphagia management (ready-to-use oral nutritional supplements and thickening powders), with special focus on the real characteristics of the bolus after mixing with human saliva.

# Rheology of soft interface dominated materials: a multiscale approach

L. Sagis

Wageningen University, Food Physics Group, Bornse Weilanden 9, 6708 WG Wageningen, The Netherlands

I

e-mail of the presenter: Leonard.sagis@wur.nl

In emulsions and foams prepared from biomaterials, both the bulk phases and interfaces often have a complex microstructure. Such systems are in general subjected to fast and large deformations during production and processing, and as a result of their complex microstructure, their behavior is typically highly nonlinear under those conditions. When (mixtures of) surface active proteins, protein aggregates, polysaccharides, or (anisotropic) particles are present, these tend to assemble into two-dimensional gels, glasses, (liquid) crystalline phases, or two-dimensional segregated structures, after adsorption to the interface. Such two-dimensional structures impart significant surface rheological properties to an interface, that may even dominate the macroscopic dynamics of the system. When this occurs we refer to the material as a soft interface dominated materials (SIDM). The rheology of the interfaces in SIDMs, and the (two-way) coupling of that rheology with the bulk behavior is still poorly understood, particularly in the large deformation regime. To explore the macroscopic dynamics of SIDMs a multiscale approach is needed that links the structure of and interactions between stabilizers to the interfacial microstructure, links the interfacial structure to interfacial rheology, and finally, the interfacial rheology to macroscopic dynamics. In this talk I will primarily focus on some recent advances we have made in exploring the microscale of these systems, i.e. the interfacial microstructure and behavior. I will discuss some results on the nonlinear rheology of interfaces stabilized by oligosaccharide fatty acid esters, protein hydrogel particles, and modified cellulose nano-rods. We have determined the properties of these interfaces in large amplitude oscillatory surface shear (LAOSS), large amplitude oscillatory dilatation (LAOD), and large step dilatational deformations. The latter system we have also explored with MC and MD simulations.

## The Rheology as a tool to develop new food products

Isabel Sousa and Anabela Raymundo

*LEAF-Linking Landscape, Environment, Agriculture and Food, Instituto Superior de Agronomia, Universidade de Lisboa. Tapada da Ajuda, 1349-017 Lisboa (Portugal).*

e-mail: [isabelsousa@isa.ulisboa.pt](mailto:isabelsousa@isa.ulisboa.pt)

Innovation is recognised as the key driver of economic growth. Trends in food industry deal with a permanent need to develop new food products, adjusted to the consumer demands and, in the near future, to scarcity of food resources. Concepts of food as health and wellness promoters, “free-from” products, the use of alternative ingredients such as new protein sources, or the use of by-products in food formulations are current topics that act as driving forces for innovation.

Currently, food product development methodologies are generally based on the chemical and nutritional properties, complemented with a sensory validation, carried out in the final stages of the development process. However, the structure of food proved to be determinant of the food appeal and strongly impacts consumers’ acceptance. It is well known that products with the same chemical composition can present very different structures, resulting differently perceived texture and sensory properties. Therefore, the use of rheological tools to design new formulations and to optimise new industrial processes, from the earliest stages of the development phases, proves to be a promising methodology.

In the creative process, the food macromolecules (proteins and polysaccharides) are the major players for the creation of relevant food structures such as foams, emulsions and gels. The development of gluten-free or vegetarian products by using alternative proteins and polysaccharides, as well as the use of the food industry by-products as source of these structuring biopolymers, along with the structural implications of adding protein and/or fibre rich healthy ingredients (e.g. pea protein, microalgae, psyllium) are some of the examples where rheology tools can give a powerful insight and contribute to decision-making on product development stages.

The strategy to develop the food products will be presented as well as the use of small amplitude oscillatory measurements to access the features of the internal food structure promoted by these changes as well as steady shear testing for fluid foods. The impact of these modifications on the developed food product and its acceptance by the consumer will be discussed based on markets scaling.

The use of sensory and instrumental texture measurements, in different experimental modes and the possibility to correlate instrumental texture parameters, with sensory evaluation, will be considered as the strategy to bring the products characteristics closed to the consumer’s requirements.

**Keywords:** Rheology, food product development, texture, sensory analysis.

## The role of rheology in the development of green emulsions

J. Muñoz, M.C. García, L. A. Trujillo-Cayado, J. A. Carmona, J. Santos

*Universidad de Sevilla, Grupo de Reología Aplicada. Tecnología de Coloides. Facultad de Química. c/ P. García González, 1, 41012, Sevilla (Spain)*

e-mail of the presenter: [jmunoz@us.es](mailto:jmunoz@us.es)

Green emulsions are formulated and ideally prepared under the principles of the so-called sustainable development or green chemistry and find a great variety of applications. Green emulsions are increasingly used by the food industry insofar as there is an increasing tendency to reduce the number of synthetic additives and to increase the use of biomaterials and ingredients with functional properties. For similar reasons they are more and more used by the pharmaceutical and cosmetic industries. The chemical industry is also paying attention to the substitution of synthetic solvents by green solvents in water-based emulsions used as agrochemicals, paints, printing inks, fat removers and all-purpose cleaners. Green solvents are increasingly used since many synthetic solvents have been banned due to their carcinogenic or toxic properties and to their poor biodegradability. For this reason, scientists and engineers responsible for product development face the challenge to formulate emulsions containing new solvents, surfactants and additives obtained from renewable raw materials and exhibiting enhanced ecological properties.

This presentation highlights that rheology is a powerful tool for emulsion engineering if used cooperatively with different techniques, such as optical microscopy (transmission, polarising, phase contrast), confocal scanning laser microscopy (CSLM) and scanning electron microscopy (SEM, cryo-SEM), laser diffraction, and multiple light scattering.

A huge amount of emulsions must be formulated and processed such that they are classified as “flowable materials” showing submicron mean droplet sizes. For this reason, the scope of this presentation involves the use of formulations based on different green solvents, eco-label surfactants, copolymers, hydrocolloids and clays. In addition, the performance of different homogenizers will be analysed. The important issue of physical stability of relatively concentrated emulsions will also be addressed. Therefore, the role of rheology to detect and control destabilization by creaming as well as to understand oil flocculation, coalescence and Ostwald ripening will be assessed.

Given that the rheology of many “flowable” emulsions is controlled by the rheology of the continuous phase, different case studies will be shown. In this way, relevant examples of the rheology of polysaccharide solutions, weak gels, fluid (sheared) gels and suspensions of clays will be presented. This presentation will focus on the determination of the zero-shear viscosity, flow behaviour, apparent yield stress, linear and non-linear viscoelastic properties, using SAOS, LAOS and parallel superposition techniques.

**Keywords:** rheology, green emulsions, shear flow, viscoelasticity, emulsion stability

## How to make friends with the help of Rheology

Antxon Santamaría

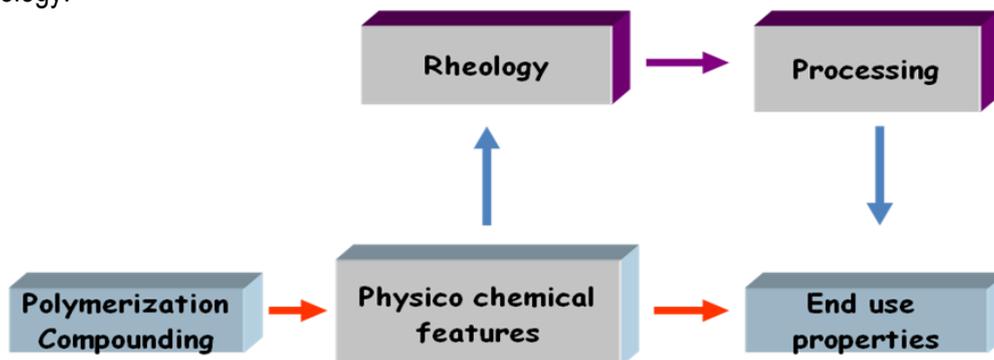
*Institute of Polymer Materials (POLYMAT) and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country (UPV/EHU), Paseo Manuel de Lardizabal 3, 20018 Donostia-San Sebastián (Spain).*

antxon.santamaria@ehu.es

The word rheology was coined by Eugene C. Bingham or Marcus Reiner, or by both at the same time, in Easton Pa. in 1928, in a meeting of engineers, chemist and physicists, which gave birth to the Society of Rheology. Rheology was well accepted from the very beginning, because the founders were able to explain the difference between this new branch of science and the already sound "Continuum Mechanics".

In those years, Hermann Staudinger was still fighting to defend that rubber, starch, cellulose and proteins were actually polymers, face to the majority of his colleagues. In fact, the most outstanding chemists of the 1920s resisted to accept the possibility that small molecules or monomers could link together covalently to form high-molecular weight compounds, named polymers.

The connection between rheology and polymers came rapidly, when Staudinger carried out viscosity measurements of rubber solutions to demonstrate the high molecular weight of polymers. Since then, the love between both newcomers of science was forever. The scheme shown below summarizes how rheology is located within the framework of polymer science and technology:



In this talk I describe how I have collaborated with rheologists and polymer people during several decades, using rheology as an instrument to solve problems related to characterization, processing and properties (and also as a tool to meet nice folks and make friends !)

# Design, mesomorphic properties and rheological characterization of a novel calamitic low molecular weight liquid crystal

M.T. Cidade<sup>1</sup>, M. Cigl<sup>2</sup>, V. Hamplova<sup>2</sup>, A. Machado<sup>1</sup> and A. Bubnov<sup>2</sup>

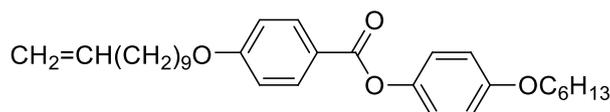
<sup>1</sup>CENIMAT/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

<sup>2</sup>Institute of Physics, The Czech Academy of Sciences, 182 21 Prague, Czech Republic

e-mail of the presenter: mtc@fct.unl.pt

Electrorheological (ER) fluids are smart materials that experience an abrupt increase of viscosity when subjected to an external electric field applied perpendicular to the flow field [1]. The reversible change in viscosity turns them suitable for applications in mechanical devices, like brakes, damping systems and clutches and electro-optic devices. Among the fluids capable of presenting ER effect are self-assembling materials, specifically the liquid crystalline materials with positive dielectric anisotropy.

In this work the design, synthesis and mesomorphic properties of a novel calamitic low molecular weight liquid crystal (denoted as UHQ6) are presented, along with its rheological characterization. On cooling from isotropic liquid, this material possesses the following mesophase sequence: the nematic phase, the orthogonal smectic A phase and a tilted smectic phase down to room temperatures. The chemical formula of UHQ6 material is presented below.



Small angle oscillatory shear (SAOS) measurements and steady state measurements were performed at 60°C and 83°C, in the nematic and smectic A phases, respectively, without and with an electric field (range within 0–2 kV mm<sup>-1</sup>) applied perpendicular to the flow direction. The increase of the viscosity values was found less than three times while increasing the electric field up to 2 kV/mm. It gives evidence that this specific LC material can be potentially appropriate for application in electro-optic devices.

**Keywords:** liquid crystal, smectic, nematic, rheology, ER effect

## References

[1] W.M. Winslow. Induced fibrillation of suspensions, J Appl Phys., **20**: 1137-1140 (1949).

## Soy protein-based superabsorbent biopolymer materials functionalized with different acylation agents

Bengoechea C.<sup>1</sup>, Cuadri A. A.<sup>2</sup>, Romero A.<sup>1</sup>, Guerrero A.<sup>1</sup>

<sup>1</sup> Universidad de Sevilla, Departamento de Ingeniería Química, c/ Prof. García González 1, 41012 Sevilla (Spain).

<sup>2</sup> Universidad de Huelva, Departamento de Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro2TecS), Campus de 'El Carmen', 21071 Huelva (Spain)

e-mail of the presenter: cbengoechea@us.es

As an alternative to acrylic superabsorbent polymers (SAP), this work studies the feasibility of obtaining natural-based SAP materials via soy protein (SPI) functionalization using different amounts of ethylenediaminetetraacetic dianhydride (EDTAD) or succinic anhydride (SA) as acylating agents.

After protein modification, blends containing 1:1 SPI/glycerol (unmodified SPI or acylated SPI) were mixed in a two-blade counter batch mixer. Temperature ramp DMA compression tests conducted on them point out the effect that a more hydrophilic protein character, as a consequence of the presence of a large amount of COO<sup>-</sup> groups, exerts on their rheological response. Thus, it was observed that the acylated blends require a maturation time of at least 24 h for getting higher elastic modulus in the low-intermediate testing temperature range (0-60 °C). On the other hand, the increase in tan  $\delta$  values for acylated SPI blends, over a broader temperature range, together with their higher sensibility to temperature, may be regarded as a favourable factor which facilitates their lab-scale injection molding. On the other hand, the acylated bioplastics samples processed by injection molding are less fragile than unmodified one, since the maximum strain before breaking rises.

Regarding their water uptake (WU) capacity, bioplastic samples are strongly enhanced for those prepared from acylated SPI (with values of up to 3650 wt.%) compared to the moderate value obtained for the reference sample (160 wt.%). Thus, all acylated bioplastics comply the WU requirements of SAP materials and could be re-used at least twice without losing their WU capacity. Interestingly, freeze-dried acylated samples (after 1 freeze-drying cycle) may be regarded as highly promising candidates for applications in which maintaining the dimensional stability during service is not crucial (e.g. in agriculture and horticulture). This research is part of a project financed by MINECO/FEDER, EU (CTQ2015-71164-P).

**Keywords:** superabsorbent polymers, acylation, bioplastics, hydrogels, water uptake capacity.

## Impact of heat moisture treatment on the physical profiles of blended matrices made of barley and wheat flours

Enrique Armero, Gemma Sanmartín, Concha Collar

*Cereals and Cereal-based Products. Food Science Department. Instituto de Agroquímica y Tecnología de Alimentos (CSIC). Avda. Catedrático Agustín Escardino, 7. 46980 Paterna (SPAIN).*

earmero@iata.csic.es

Heat moisture treatment (HMT) constitutes an environmentally friendly technique and a clean label alternative to chemical modification for altering the gelatinization and retrogradation properties of starches from different sources. HMT may positively impact on the structure restoration of diluted wheat matrices such as blends with non-gluten forming cereals like barley. Mixed breads obtained by 40 % replacement of wheat flour (WT) by barley flour (BL) exhibit superior nutritional quality than regular WT breads [1], but explicit impaired techno-functional performance compared to WT matrices.

The significance of HMT (15% moisture content, 1 h heating time at 120°C) on the physical profiles of binary dough and bread matrices (WT/BL, 60/40, w/w) was evaluated in doughs based on their pasting properties, forward extrusion and stress relaxation behaviours, and investigated in fresh breads by applying static deformation techniques (texture profile analysis and relaxation test), colour and volume measurements and sensory analysis. Instrumental (primary and secondary mechanical parameters, visco-metric parameters, Peleg model parameters of dough and bread crumb stress relaxation, specific volume and Hunter Lab color tristimuli parameters of breads) and sensory resulting characteristics were statistically tested for correlations. HMT of single hydrated flours significantly enhanced the viscoelastic profile during pasting and gelling, particularly for BL, in terms of promoted peak viscosity, holding strength and breakdown on cooking, and final viscosity and total setback on cooling, providing harder gels with greater initial force  $F_0$  during stress relaxation. Hydrated blends from both WT and BL HMT treated flours exhibited in general major viscoelastic changes and most elastic nature. Blended breads formulated with untreated WT and HMT BL flours explicit higher cohesiveness, hardness and resilience than any other tested binary bread matrix.

**Keywords:** Heat Moisture Treatment, blended breads, physical profile, wheat, barley

### References

[1] C. Collar, A. Angioloni. Nutritional and functional performance of barley flours in breadmaking: mixed breads vs wheat breads, *European Food Research and Technology*, 238: 459–469 (2014).

# Formulation and rheological characterization of epoxidized lignin-based gel-like dispersions for lubricant applications

E. Cortés-Triviño<sup>1</sup>, C. Valencia<sup>1,2</sup>, J.M. Franco<sup>1,2</sup>

<sup>1</sup> Department of Chemical Engineering, University of Huelva, Campus El Carmen, Campus ceiA3, 21071 Huelva, Spain.

<sup>2</sup> Pro2TecS-Chemical Product and Process Technology Centre, University of Huelva, 21071 Huelva, Spain.

esperanza.cortes@diq.uhu.es

Traditional thickening agents, including lithium, aluminium, sodium or calcium soaps, used in the lubricant industry are being replaced by natural materials that allow to reduce the impact over the environment [1]. Previously, some researches have used vegetables oils as lubricant base oil and chemically modified polymers as thickener [2], by obtaining lubricating performance with good rheological and thermal properties. In this way, the presence of numerous functional groups in the lignin chemical structure, its outstanding biodegradability and availability, makes this by-product a feasible candidate of chemicals and innovative materials [3] [4]. In this work, a simple protocol was applied to chemically modify an alkali lignin (AL) with polyethylene glycol diglycidyl ether (PEGDGE) in alkaline medium in order to use it as a reactive thickener in lubricating greases formulations. The influence of the lignin/PEGDGE weight ratio used in the functionalization reaction was studied and the epoxidized lignins obtained were characterized by means of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). Furthermore, these modified polymers were dispersed in castor oil (CO) and the rheological and tribological response of resulting epoxidized lignin gel-like dispersions in castor oil were investigated. According to rheological results, oleogels prepared with highly epoxidized lignins exhibited higher values of the linear viscoelastic functions. Furthermore, the thermo-rheological response provides a softening temperature of around 100°C, yielding a reasonable good thermal stability. In summary, epoxidized lignin confers suitable rheological and tribological properties to castor oil, resulting oleogels which can be potentially proposed as an alternative to traditional lubricating greases.

**Keywords:** epoxidized lignin, PEGDGE, rheology, lubricating greases.

## References

- [1] S. Boyde, Green lubricants. Environmental benefits and impacts of lubrication, *Green Chemistry*, **4**: 293-307 (2002).
- [2] R. Gallego, J. F. Arteaga, C. Valencia, and J. M. Franco, Thickening properties of several NCO-functionalized cellulose derivatives in castor oil, *Chemical Engineering Science*, **134**: 260–268 (2015).
- [3] G.-H. Delmas, B. Benjelloun-Mlayah, Y. Le Bigot, and M. Delmas, Biolignin™ based epoxy resins, *Journal of Applied Polymer Science*, **127**: 1863–1872 (2013).
- [4] J. Xin, M. Li, R. Li, M. P. Wolcott, and J. Zhang, Green Epoxy Resin System Based on Lignin and Tung Oil and Its Application in Epoxy Asphalt, *ACS Sustainable Chemistry & Engineering*, **4**: 2754–2761 (2016).

# Influence of processing conditions on the rheological behaviour of NCO-functionalized lignin-based gel-like dispersions

A.M. Borrero-López<sup>1</sup>, C. Valencia<sup>1,2</sup>, J.M. Franco<sup>1,2</sup>

<sup>1</sup> Departamento de Ingeniería Química. Campus de "El Carmen". Universidad de Huelva. 21071 Huelva. Spain. Campus de Excelencia Internacional Agroalimentario, ceiA3.

<sup>2</sup> Pro<sup>2</sup>TecS – Chemical Product and Process Technology Center. Universidad de Huelva. 21071 Huelva. Spain.

am.borrero@diq.uhu.es

Recently, the search of new materials which can mitigate climate change and resources extinction has changed industries focus on more environmentally aware attitudes. In the case of lubricant industries, this is increasingly yielding in the replacement of mineral oil into vegetable oil. However, still metallic soaps are used as gelling agents because of their high-grade functionality and microstructural performance [1]. Lignin, as the second most abundant biopolymer on earth, has been traditionally obtained as by-product in paper production and with no high-added valuable applications. However, its highly-branched aromatic structure and its interesting functional groups make it suitable for deeper research and use [2]. Diisocyanates, with -NCO groups in both extremes of the molecule, are capable of reacting with OH groups of different raw materials including lignin and vegetable oils yielding a highly entangled network, making feasible the oil confinement inside the structure for lubrication purpose [3]. In this work, the preparation protocol of totally renewable and eco-friendly oleogels based on lignin as thickener and castor oil as lubricant base oil was studied using different types of diisocyanates as crosslinkers. Two processes for oleogel formation are analysed; a previously developed two-step process [4] and a new simpler and more environmentally-careful direct process. Thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR) and rheological tests were performed to characterize these formulations. Results demonstrate crucial differences among oleogels depending on the diisocyanates chemical structure, as well as between the above mentioned processing protocols, achieving targeted rheological properties with lower lignin concentration when applying the direct process instead of the more selective two-step process.

**Keywords:** oleogel, lignin, diisocyanate, rheology, processing

## Bibliography

- [1] C. Roman, C. Valencia, and J. M. Franco, 'AFM and SEM Assessment of Lubricating Grease Microstructures: Influence of Sample Preparation Protocol, Frictional Working Conditions and Composition', *Tribol. Lett.*, vol. 63, no. 2, 2016.
- [2] A. Duval and M. Lawoko, 'A review on lignin-based polymeric, micro- and nano-structured materials', *React. Funct. Polym.*, vol. 85, pp. 78–96, 2014.
- [3] R. Gallego, J. F. Arteaga, C. Valencia, M. J. Díaz, and J. M. Franco, 'Gel-Like Dispersions of HMDI-Cross-Linked Lignocellulosic Materials in Castor Oil: Toward Completely Renewable Lubricating Grease Formulations', *ACS Sustain. Chem. Eng.*, vol. 3, no. 9, pp. 2130–2141, 2015.
- [4] R. Gallego, J. F. Arteaga, C. Valencia, and J. M. Franco, 'Chemical modification of methyl cellulose with HMDI to modulate the thickening properties in castor oil', *Cellulose*, vol. 20, no. 1, pp. 495–507, 2013.

# Assessment of the adhesion performance of cellulose acetate and castor oil-based adhesives on different substrates by probe-tack tests

A. Tenorio-Alfonso<sup>1</sup>, M.C. Sánchez<sup>1,2</sup>, J.M. Franco<sup>1,2</sup>

<sup>1</sup> Department of Chemical Engineering, University of Huelva, Campus El Carmen, Campus ceiA3, 21071, Huelva (Spain).

<sup>2</sup> Pro2TecS-Chemical Product and Process Technology Research Centre, University of Huelva, 21071, Huelva (Spain).

e-mail of the presenter: adrian.tenorio@diq.uhu.es

The employment of eco-friendlier and sustainable raw materials in the industrial production has become one of the main targets in the 21<sup>st</sup> century. Indeed, in the adhesive field, traditional adhesive formulations comprise the use of petro-based substances either in their composition or in their synthesis, whose hazard and toxicity have caused the current environmental awareness and stringent environmental regulations, leading to the replacement of those substances by new renewable raw materials. As a result of their high-quality adhesion performance, bio-based polyurethane adhesives have been recently developed [1]. Vegetable oil-based polyurethanes have proved to be a feasible alternative to traditional formulations, as can be found in previous studies [2]. In this work, aiming to completely remove the use of solvents in the polyurethane production, instead of a several-stage synthesis protocol previously applied [3], a single step reaction process was proposed inducing the reaction of cellulose acetate with 1,6-hexamethylene diisocyanate and castor oil at room conditions. The tackiness of this novel polyurethane-based adhesive was investigated by performing probe tack tests on different substrates (wood, stainless steel and aluminium). The objective of this study was to evaluate the influence of a range of parameters such as contact pressure, contact time and debonding rate over the immediate adhesion at different stages of curing. Tacking tests were coupled with complementary small-amplitude oscillatory torsional tests at different temperatures and standardized mechanical tests analysing shear (ASTM D906, D1002) and peeling (ASTM D903) strengths. Additionally, thermal behaviour and the chemical structure of this cellulose acetate-based adhesive was studied by means of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR).

**Keywords:** bio-adhesive, castor oil, cellulose acetate, polyurethane, probe-tack tests

## References

- [1] H. Liu, C. Li, X.S. Sun. Soy-oil-based waterborne polyurethane improved wet strength of soy protein adhesives on wood, *International Journal of Adhesion and Adhesives*, **73**: 66-74 (2017).
- [2] M.F. Valero, A. Gonzalez. Polyurethane adhesive system from castor oil modified by a transesterification reaction, *Journal of Elastomers and Plastics*, **44**: 433-442 (2012).
- [3] R. Gallego, J. Arteaga, C. Valencia, J. Franco. Chemical modification of methyl cellulose with HMDI to modulate the thickening properties in castor oil, *Cellulose*, **20**: 495-507 (2013).

## Mapping the impact of starch swelling behavior on rheology and food texture

James Smoot, Leslie G. Howarth, Judith K. Whaley

*Tate & Lyle, Innovation & Commercial Development, 5450 Prairie Stone Parkway, Hoffman Estates, IL 60192 (USA)*

Leslie.Howarth@TateandLyle.com

Starches are well-known thickening agents, and the complexities of such soft particle suspensions must be carefully considered during product development. Even in simple systems, textural properties can vary in surprising ways as the swelling of the starch and concentration-in-use change.

Physical and chemical treatments are applied to starch to control the swelling, as the swelling is reduced the particles become more rigid which gives them tolerance to shear which occurs during food processing. In the current work, we have modelled the effects of swelling volume and concentration on viscous and elastic properties. This has allowed us to create texture maps for thickened starch systems.

We have been able to overlay the texture maps, generated from instrument data, with sensory data to create comprehensive texture maps for starch dispersions having high predictive power for the effects of starch swelling, concentration and processing upon the textural and sensory attributes of the resulting food products.

## Rice industry by-products in food emulsions

Patrícia Fradinho, Isabel Sousa, Anabela Raymundo

LEAF-Linking Landscape, Environment, Agriculture and Food, Instituto Superior de Agronomia, Universidade de Lisboa. Tapada da Ajuda, 1349-017 Lisboa (Portugal).

e-mail of the presenter: pfradinho@isa.ulisboa.pt

Cereal industries generate high amounts of by-products with interesting food value. These products, such as broken grains and bran from rice milling, can be recovered and used in the production of added-value foods.

Several fundamental studies were conducted in order to incorporate rice four and bran in emulsions, multiphasic systems previously optimized by Raymundo *et al.* [1].

Due to their oil absorption capacity, *carolino* rice bran ( $5.13 \pm 0.05 \text{ g g}^{-1}$ ) and parboiled rice flour ( $1.96 \pm 0.08 \text{ g g}^{-1}$ ) were chosen. They also work as protein sources, with the purpose of stabilizing the emulsion. The emulsions' colour parameters ( $L^*$ ,  $a^*$ ,  $b^*$ ) were determined using a CR-400 colorimeter (Konica Minolta). Texture profile analysis of all emulsions was performed in a texturometer TA-XTplus (Stable Micro Systems) using a 10 mm cylindrical probe which penetrates the sample 15 mm, at  $1 \text{ mm.s}^{-1}$ . The evaluation of the internal structure of the emulsions was assessed by SAOS measurements, using a MARS III controlled-stress rheometer (Haake) coupled to a UTC-Peltier system for temperature control. A cone and plate sensor system with 35 mm diameter and  $2^\circ$  angle was used. All assays were performed at  $20^\circ\text{C}$ .

The amount of oil in the emulsions influences positively its texture properties, namely firmness, cohesiveness and adhesiveness, as observed in previous works [2]. Rice flour incorporation allows to maintain the texture characteristics of the emulsion, with the advantage of reducing the oil content, for similar texture characteristics, acting as fat mimetic.

Rheological measurements in the linear viscoelastic region show that  $G'$  is always higher than  $G''$ , which translates a predominance of the elastic component. It is evident that all the emulsions present a considerable degree of structuring, which will be compatible with high physical stability and thus a long shelf life.

All the emulsions show a shear-thinning behaviour: a Newtonian plateau followed by a region where the viscosity decreases with increasing shear rate. Flow equations were established, which are an important contribution to predict the emulsions behaviour in the final product.

There were no differences in viscosity neither in the colour parameters of the rice bran emulsions as a function of the amount of oil present in the formulation, nor of the incorporation of rice flour.

**Keywords:** emulsion, rice bran, flow behaviour, SAOS, texture

### References

- [1] A. Raymundo, L. Gouveia, A.P. Batista, J. Empis, I. Sousa, Fat mimetic capacity of *Chlorella vulgaris* biomass in oil-in-water food emulsions stabilized by pea protein, *Food Research International*, **38**: 961-965 (2005).
- [2] A. Raymundo, J. Franco, C. Gallegos, J. Empis, I. Sousa Effect of thermal denaturation of lupin protein on its emulsifying properties, *Nahrung*, **42** (3/4), S. 220-224 (1998).

**Acknowledgments:** This work was supported by COMPETE program: QREN – “Arroz +” project 38749/13, in co-promotion with two rice milling companies.

## Effect of tomato skins powder addition on rheological and physicochemical characteristics of milk yoghurt

Adriana Dabija<sup>1</sup>, Georgiana Gabriela Codină<sup>1</sup>, Mircea Adrian Oroian<sup>1</sup>, Silvia Mironeasa<sup>1</sup>

<sup>1</sup> *Stefan cel Mare University, University Street, 13, Suceava, 720229, Romania*

e-mail [silviam@fia.usv.ro](mailto:silviam@fia.usv.ro)

Tomato skins by-products contain nutrients and bioactive components which are essential requirements in the human diet. Milk supplementation with tomato skins powder can be improving nutritional properties of yogurt products, changing their technological quality. The aim of this study was to manufacture and determined the rheological and physicochemical characteristics of yoghurts with addition of tomato skins powder (TSP) at different levels (0.2–0.8%). Results showed that the acidity increased with an increase levels of TSP incorporated, while the pH value decreased leading to milk gelation. A pseudoplastic rheological behaviour described by the power-law model was found for all the yoghurt samples. The shear thinning behaviour is considerably influenced by the TPS addition. A noticeable increase in apparent viscosity was identifying up to 0.6% TSP addition, while the flow behaviour index decreased.

**Keywords:** yoghurt, tomato skins powder, rheological parameters

### Acknowledgment

This work was supported by a grant of the Romania National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-BG-2016-0089, within PNCDI III.

### References

- [1] Bhat Z.F., Bhat H. Milk and Dairy Products as Functional Foods: A Review. *International Journal of Dairy Science*, **6**, 1–12 , 2011
- [2] Del Valle M., Camara M., Torija M. E. Chemical characterization of tomato pomace. *Journal of the Science of Food and Agriculture*, **86**, 1232–1236, 2006
- [3] Siró I., Kapólna E., Kapólna E., Functional food. Product development, marketing and consumer acceptance -A review, *Appetite*, **51**, 456–467, 2008

## Rheological characterization of *Spirulina* gluten-free cookie doughs

A.P. Batista, I. Bursic, A. Miranda, S. Fragoso, P. Fradinho, A. Raymundo, I. Sousa

LEAF-Linking Landscape, Environment, Agriculture and Food. Instituto Superior de Agronomia. Universidade de Lisboa. Tapada da Ajuda. 1349-017 Lisboa. Portugal.

e-mail of the presenter: [paulabatista@isa.ulisboa.pt](mailto:paulabatista@isa.ulisboa.pt)

*Spirulina* (*Arthrospira platensis*) is a cyanobacteria widely used in human nutrition due to its nutritional properties - rich in proteins, gamma-linolenic acid (GLA), vitamins (e.g. B<sub>12</sub>) and phycobilliproteins. Besides this, the addition of *Spirulina* has been associated to both positive [1] and negative [2] structural effects in different food matrixes (pastas and gelled desserts, respectively). Therefore a thorough investigation is needed to assess the rheological and microstructural implications of *Spirulina* addition in food systems, namely its potential in the challenging design of gluten-free products.

The cookies were prepared with wheat flour and *Spirulina* biomass (up to 6% w/w) (as reference) as well as with rice flour (gluten-free) and *Spirulina*. The cookies were analysed in terms of dimensions (diameter, width, spread ratio), colour (L\*a\*b\*), a<sub>w</sub>, moisture, texture (bending and penetration tests) and the cookie doughs were analysed in terms of rheological linear viscoelastic behaviour (mechanical spectra). Selected samples were also analysed by Scanning Electron Microscopy.

From rheological tests it was observed a linear increase in the wheat cookie dough's viscoelastic moduli with *Spirulina* concentration increase (R<sup>2</sup>=0.97). Moreover, at 6% *Spirulina* incorporation it was possible to lower the flour content from 49 to 37% (w/w), while maintaining viscoelastic properties similar to the control wheat cookie dough. On the other hand, the addition of *Spirulina* to rice flour cookies clearly contributed to a more elastic dough, with positive impact in the cookies sensory properties. A linear increase in viscoelastic moduli with *Spirulina* concentration (R<sup>2</sup>=0.99) was also observed, with a much pronounced structuring effect even at 2% *Spirulina* addition (63% increase in G'<sub>1Hz</sub>, in relation to the control). The use of *Spirulina* biomass as functional ingredient in bakery gluten-free products is thus promising.

**Keywords:** *Spirulina*, Cookie dough, Texture, SAOS, Microstructure

**References:** [1] Fradique M, Batista AP, Nunes MC, Gouveia L, Bandarra NM, Raymundo A, Incorporation of *Chlorella vulgaris* and *Spirulina maxima* biomass in pasta products. Part1: preparation and evaluation, *Journal of the Science of Food and Agriculture*, **90**: 1656-1664 (2010). [2] Batista AP, Nunes MC, Fradinho P, Gouveia L, Sousa I, Raymundo A, Franco JM, Novel foods with microalgal ingredients – Effect of gel setting conditions on the linear viscoelasticity of *Spirulina* and *Haematococcus* gels, *Journal of Food Engineering*, **110**: 182-189 (2012).

**Acknowledgements:** The authors thank Prof. Mario Tredici Research Group from DISPAA–University of Florence (Italy) for providing *A. platensis* biomass and for all collaboration in this research project. This work was supported by national funds from Fundação para a Ciência e a Tecnologia (Portugal) through the research unit UID/AGR/04129/2013 (LEAF).

## Impact of high pressure technology on the dynamic properties of filled chocolates

J. Dias<sup>1</sup>, P. Lage<sup>1</sup>, N. Alvarenga<sup>1,2,3</sup>, R.V. Duarte<sup>4,5</sup>, J.A. Saraiva<sup>4,5</sup>

<sup>1</sup> Escola Superior Agrária - Instituto Politécnico de Beja, 7800-295, Beja (Portugal).

<sup>2</sup> LEAF, Instituto Superior de Agronomia - Universidade de Lisboa, Tapada da Ajuda 1349-017, Lisboa (Portugal).

<sup>3</sup> GeoBioTec Research Institute, Universidade Nova de Lisboa - Campus da Caparica 2829-516, Caparica (Portugal).

<sup>4</sup> QOPNA, Department of Chemistry, University of Aveiro, 3810-193 Aveiro (Portugal).

e-mail of the presenter: joao.dias@ipbeja.pt

The aim of this study was to evaluate the influence of the HHP (400MPa for 2.5min and 500MPa for 1min) and storage temperature (4°C and 20°C) on physicochemical, rheological and microbiological properties of filled chocolates during storage time. Small amplitude oscillatory measurements of chocolate fillings were performed using a controlled shear-strain rheometer (Malvern Kinexus lab+, England) connected to a refrigeration circuit with controlled temperature. The viscoelastic behaviour of the fillings was evaluated at 20 °C using a 4°/40 mm cone and plate geometry and gap distance of 1 mm. First, excess sample was trimmed with a thin plastic blade and the sample was allowed to rest for 5 min for temperature equilibrium. Later, the linear viscoelastic region (LVR) was evaluated by performing a strain sweep (0.001%–1000%) at a steady frequency of 1Hz. Finally, the dynamic frequency sweep was conducted applying a steady strain of 0.01%, within the LVR, from 0.01Hz to 100Hz. The results showed that the dynamic rheological parameters ( $G'$  and  $G''$ ) were not affected by the pressure or time of HHP treatment, but were affected by higher storage temperatures especially after 180d. The mechanical spectra of chocolate fillings stored at 4°C was the least affected, when compared with the chocolates stored at 20°C (0.1MPa/20°C, 400MPa/20°C and 500MPa/20°C).

**Keywords:** high pressure, chocolate fill, storage, SAOS

## Using the dynamic properties to follow the coagulation of ewe milk with *Cynara cardunculus*

N. Alvarenga<sup>1,2,3</sup>, S. Santos<sup>1</sup>, J. Dias<sup>1</sup>, T. Brás<sup>4,5</sup>, A.P.L. Martins<sup>6</sup> and M.F. Duarte<sup>4,7</sup>

<sup>1</sup> Escola Superior Agrária - Instituto Politécnico de Beja, 7800-295, Beja (Portugal).

<sup>2</sup> LEAF, Instituto Superior de Agronomia - Universidade de Lisboa, Tapada da Ajuda 1349-017, Lisboa (Portugal).

<sup>3</sup> GeoBioTec Research Institute, Universidade Nova de Lisboa - Campus da Caparica 2829-516, Caparica (Portugal).

<sup>4</sup> Centro de Biotecnologia Agrícola e Agro-Alimentar do Alentejo (CEBAL) / IPBeja 7801-908, Beja (Portugal).

<sup>5</sup> LAQV/REQUIMTE - FCT - Univ. Nova de Lisboa, Campus de Caparica 2829-516, Caparica (Portugal).

<sup>6</sup> UEISTSA - INIAV IP, Quinta do Marquês - Av. da República 2780-157, Oeiras (Portugal).

<sup>7</sup> ICAAM - Inst. de Ciênc. Agrárias e Ambientais Mediterrânicas, U. Évora, Pólo da Mitra, 7002-554 Évora (Portugal).

e-mail of the presenter: bartolomeu.alvarenga@ipbeja.pt

The objective of this study was to evaluate the dynamics of sheep milk coagulation with thistle flower extract (*Cynara cardunculus*) from three geographic origins using an optical NIR-based conventional methods (Optigraph) and using a strain controlled rheometer. The sweep time was performed in small amplitude oscillatory measurements using a controlled shear-strain rheometer (Malvern Kinexus lab+, England). The flower of three thistle samples from different locations were air dried, separated from the impurities and triturated with water in a blender. The filtrate obtained was used in the coagulation assays. The gelling dynamics was evaluated by means of a manufacturing surrogate test (2g flower/50mL H<sub>2</sub>O, using 0,25 mL extract/10 mL milk) on the Optigraph, and the rheometer (time sweep with a strain rate of 0.04% and the frequency 0.5 Hz) The graph of complex modulus  $G^*$  (Pa) vs time (s) was analysed to obtain different coagulation parameters, namely "coagulation time" parameters and "complex modulus" parameters (Fig.1). The data allowed to find some correlations between the study of the dynamics of coagulation by the Optigraph and using the rheometer. On the other hand, there was no influence of the thistle flower geographic origin on the coagulation dynamics.

**Keywords:** ewe milk, coagulation, *Cynara cardunculus*, time-sweeps, SAOS

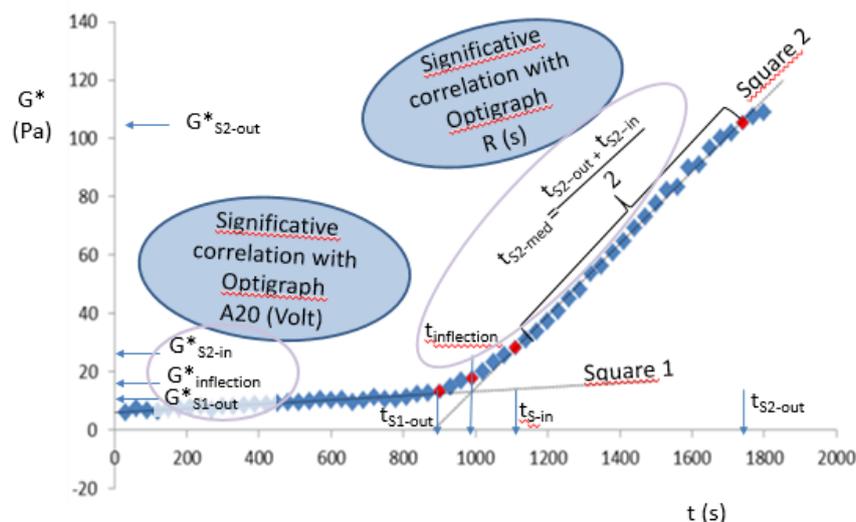


Figure 1. Correlations between optigraph parameters and sweep time graph parameters

**Acknowledgements:** The present work was supported by ValBioTecCynara (ALT20-03-0145-FEDER- 000038) – Economic valorization of Cardoon (*Cynara cardunculus*): study of natural variability and biotechnological applications), cofinanced by FEDER under the Alentejo 2020 Program.

## Influence of fortification with vegetable and fruit powder on the rheological and physicochemical properties of yoghurt

Sorina Ropciuc<sup>1</sup>, Adriana Dabija<sup>1</sup>, Anca Mihaela Sidor<sup>1</sup>, Mircea-Adrian Oroian<sup>1</sup>

<sup>1</sup> Stefan cel Mare University of Suceava, Faculty of Food Engineering, Suceava, Romania

[sorina.ropciuc@fia.usv.ro](mailto:sorina.ropciuc@fia.usv.ro)

Yogurt is a very popular dairy product in most countries, it is considered a healthy product and enjoys a positive reputation in the minds of consumers. The highest production or consumption of yogurt is in Mediterranean, Asian countries, and in central Europe. The aim of this study is to add vegetable powder (carrot and peas) and fruit (seabuckthorn and rosehip) rich in bioactive food principles and edible fibres in the yoghurt due to beneficial effects on human health. Fortifying yogurt with vegetable and fruit powder is of increasing interest to create functional foods with health benefits and improve their functionality. The addition of vegetable and fruit powder improves the physicochemical properties of natural yogurt as well as the rheological characteristics. The determinations describing the physicochemical properties of fortified yoghurt with vegetables and fruits are: pH, acidity, syneresis and color. Rheological characteristics were performed using the Haake Mars Modular Advanced Rheometers System, determining: viscoelastic properties, thixotropy and flow and viscosity curves. Fortified yoghurt can be useful for improving the syneresis effect, viscoelastic properties.

**Keywords:** vegetable and fruit powder, rheological properties, syneresis

### References

- [1] A. Aportela-Palacios, M. E., Sosa-Morales, and J. F., Vélez-Ruiz, Rheological and Physicochemical Behavior of Fortified Yogurt, with Fiber and Calcium, *Journal of Texture Studies* 36, 333-349, 2005
- [3] E., Arab-Tehrany, M., Jacquot, C., Gaiani, M., Imran, S., Desobry, and M., Linder, Beneficial Effects and Oxidative Stability of Omega-3 Long-Chain Polyunsaturated Fatty Acids, *Trends in Food Science & Technology*, 25, 24-33, 2012
- [4] Y., Morvarid, L., Nateghi, A., Elham, Effect of different concentration of fruit additives on some physicochemical properties of yoghurt during storage. *Annals of Biological Research*, 4(4), 244-249, 2013
- [5] Z. Tarakci, Influence of Kiwi Marmalade on the Rheology Characteristics, Color Values and Sensorial Acceptability of Fruit Yogurt, *Kafkas Üniversitesi Veteriner Fakültesi Dergisi*, Kafkas Univ Veteriner Fakül Dergisi 16 ,2, 173-178., 2010
- [6] M.A. Oroian, G. Gutt, Influence Of K-Carrageenan, Agar-Agar And Starch On The Rheological Properties Of Blueberries Yogurt, *Annals of DAAAM & Proceedings*, 1031-1032, 2011

## Effect of inulin with different polymerisation degree on wheat flour dough rheological properties of 1250 type

Georgiana Gabriela Codină<sup>1</sup>, Dumitru Zaharia<sup>2</sup>, Elena TODOSI SĂNDULEAC<sup>1</sup>, Adriana DABIJA<sup>1</sup>

<sup>1</sup> Ștefan cel Mare University, Faculty of Food Engineering, Str. Universității nr. 13, 720229, Suceava, Romania.

<sup>2</sup> S. C. Dizing S. R. L. Brusturi, Neamț, Romania.

e-mail of the presenter: codinageorgiana@yahoo.com; codina@fia.usv.ro

The aim of this study was to investigate the effect of inulin addition on wheat flour dough rheological properties. Inulin is a soluble fiber, a prebiotic not digested in the human digestive tract [1]. In this study two commercial inulin products were used namely native inulin and oligofructose extracted from chicory root were used. The inulin samples different between them by their polymerization degree and by their sugar free content were used in wheat flour dough at levels from 2.5% to 10%. The wheat flour type 1250 was of a strong one for bread making with a low deformation index. Also it presented a low alpha amylase activity due to its Falling Number value (363 s). Dough rheological properties were analyzed by using empirical and fundamental measurements. Like empirical ones was used the Rheofermentograph device which investigates dough rheological properties during fermentation (maximum height of gaseous production, total CO<sub>2</sub> volume production, volume of the gas retained in the dough at the end of the test, retention coefficient). Total CO<sub>2</sub> volume production decreases with the increase level of inulin addition. It seems that the inulin presence decreases the wheat flour dough expansion. Dough fundamental rheological properties were investigated by using a Haake dynamic rheometer in the linear viscoelastic range (frequency sweep and time cure tests) of the wheat flour dough. By inulin addition dough consistency lowered due to a decrease in water absorption. The most significant differences in elastic properties of wheat dough samples with inulin addition were observed between 30°C and 90°C to oscillatory temperature sweep test at constant frequency probably due to incompatibility between inulin and wheat flour starch and different kinetics of starch gelatinization [2].

**Keywords:** inulin, oligofructose, rheology, functional food

**Acknowledgment:** This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-BG-2016-0079, within PNCDI III.

### References

- [1] C. Morris, G.A. Morris, The effect of inulin and fructo-oligosaccharide supplementation on the textural, rheological and sensory properties of bread and their role in weight management: A review. *Food Chemistry*, **133**: 237–248 (2012).
- [2] D. Peressini, M. Foschia, F. Tubaro, A. Sensidoni, Impact of soluble dietary fibre on the characteristics of extruded snacks, *Food Hydrocolloids*, **43**: 73-81 (2015).

# The Influence of starch rheology on dough behavior for snacks

Leslie G. Howarth

*Tate & Lyle, Innovation & Commercial Development, 5450 Prairie Stone Parkway, Hoffman Estates, IL 60192 (USA)*

Leslie.Howarth@TateandLyle.com

The processing of fabricated potato crisps is a delicate art that is heavily reliant on the functionality of the starch combined with potato flakes to make the dough. Starch selection impacts dough characteristics, such as stickiness, sheetability, and expandability, which in turn impacts the uniformity, pillowing nature, crispness, crunchiness, hardness, and breakdown rate of final crisps. Combining deep insights of physical behavior of starch and dough with descriptive profiling for the crisps, one can select the suitable starch with key attributes that may have the biggest influence on the quality of the final product.

Rheology of starch at high solids is indicative of dough rheology. Moderately elastic doughs give good sheeting and high expansion. High expansion is correlated to crispy texture.



# Rheology of fibre suspensions: experimental and modelling

M. G Rasteiro<sup>1</sup>, C. Cotas<sup>1</sup>, D. Asendrych<sup>2</sup>

<sup>1</sup> Chemical Engineering Department – CIEPQPF, University of Coimbra, Coimbra (Portugal).

<sup>2</sup> Częstochowa University of Technology, Institute of Thermal Machinery, Częstochowa (Poland).

e-mail of the presenter: mgr@eq.uc.pt

An important issue in the pulp and paper industry is the pulp flow behaviour since it influences the properties of the final product. Stress-strain rate relationship is strongly non-Newtonian and the suspension flows with high resistance. Several structures can form between the fibres or fibres and additives, and the flow depends on the predominance of those structures, different regimes existing till shear stress surpasses the fluidization point [1]. Several approaches have been followed to characterize the rheological behaviour of fibre suspensions [1-3], since conventional rheometers are usually unreliable for these systems, especially for concentrated suspensions.

In this work an adapted Searle-type rotational plate rheometer with a gap size of 0.095 m [1,3], and possessing 3 chambers, was used. Two different pulps were tested (*eucalyptus* fibres and pine fibres), consistencies (w/w) between 1.50 and 3.50% having been used.

The objective of this work was to produce rheological information which could be used later in a flow model for pulp suspensions. Based on the experimental data apparent viscosity was correlated with shear rate and pulp consistency using a statistical 3D surface fit (Fig 1 - *eucalyptus* pulp). Apparent viscosity was expressed as a function of shear rate and consistency:

$$\mu = K' c^\alpha (\dot{\gamma})^{\beta c} \quad (1)$$

This surface fitting leads to the following values of the equation parameters: *eucalyptus*,  $K'=0.0085$  [Pa s<sup>1+β</sup>],  $\alpha=6.97$  and  $\beta=-0.26$  (correlation coefficient 0.98); pine  $K'=0.0754$  [Pa s<sup>1+β</sup>],  $\alpha=5.90$  and  $\beta=-0.28$  (correlation coefficient 0.94).

The rheometer used in this work allows visual inspection of the suspension guaranteeing that data is only acquired when no segregation is present.

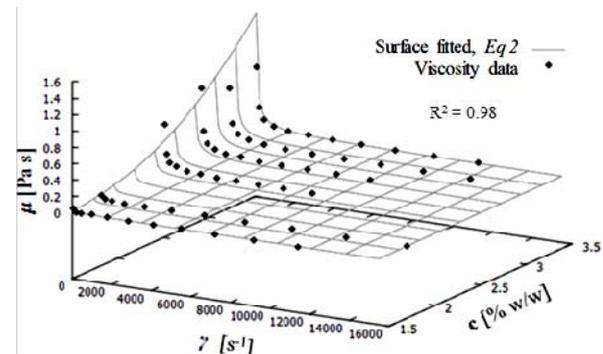


Fig 4 - Dependence of pulp apparent viscosity on shear rate and consistency – surface best fit (*Eucalyptus* fibres).

**Keywords:** Searl type rheometer; drag reduction; fibre suspensions

**References**

- [1] C. Ventura, A. Blanco, C. Negro, P. Ferreira, F. Garcia, M. Rasteiro, Modeling pulp fiber suspension rheology, *Tappi J.*, 6 (7), 17-23, 2007.
- [2] R. J. Kerekes, Rheology of fibre suspensions in papermaking: An overview of recent research, *Nord. Pulp Paper Res. J.*, 21 (5), 100 – 114, 2006.
- [3] A. Blanco, C. Negro, E. Fuente, J. Tijero, Rotor selection for a Searle-type device to study the rheology of paper pulp suspensions, *Chem. Eng. Process. - Process Intens.*, 46 (1), 37-44, 2007.

**Acknowledgements:** Financial support from PTDC/EQU-EQU/112388/2009 and Pest/C/EQB/UI0102/2013, FCT/MCTES (PIDDAC) co-financed by ERDF through COMPETE

# Emulsions stabilised with legume proteins. From interfacial to bulk rheology

Felix M.<sup>1</sup>, Isaurralde N.C.<sup>2</sup>, López Osorio J.A.<sup>3</sup>, Carrera C.<sup>1</sup>, Guerrero A<sup>1</sup>

<sup>1</sup> *Universidad de Sevilla, Departamento de Ingeniería Química, c/ Prof. García González 1, Sevilla (Spain).*

<sup>2</sup> *Universidad Nacional del Litoral (UNL) - Facultad de Ingeniería Química (FIQ) - Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE-CONICET). Argentina.*

<sup>3</sup> *Facultad de Ingeniería, Programa de Alimentos, Universidad de Caldas, calle 65 # 26-10, 275, Manizales, Caldas, Colombia.*

e-mail of the presenter: mfelix@us.es

Proteins are highly efficient in producing and stabilizing emulsions, by reducing interfacial tension that favours breakup of droplets and by forming viscoelastic interfacial films that helps to stabilize oil droplets. The dynamics of complex interfaces is generally dominated by interfacial rheology, which plays a key role to prevent destabilization. Dilatational rheology seems to be more relevant for short-term stability whereas interfacial shear is valuable for middle or long-term stability. Both viscoelastic responses often affect emulsion stability and bulk rheology.

Although not yet extensively investigated, the links between interfacial properties and bulk emulsion rheology seems to be highly promising. The objective of this work is to evaluate the relationship between interfacial and bulk rheology of O/W chickpea or fava protein-based emulsions and their contribution to emulsion microstructure and stability, as a function of protein concentration and pH.

Interfacial tension was measured as a function of time with a Wilhelmy plate fitted to a D502 tensiometer (Sigma). Interfacial SAOS rheology was studied by means of a double wall-ring geometry fitted to a DHR3 rheometer (TA Instruments). Dilatational rheology was measured with a pendant drop tensiometer (IT Concept).

Emulsions were prepared with a high-pressure homogenizer EmulsiFlex-C5 (Avestin). SAOS tests of emulsions were carried out with plate-plate geometry with the DHR3. Droplet size distribution was determined with a Mastersizer X (Malvern) and CLSM was performed with a LSM Duo (Zeiss). Backscattered light measurements were carried out with a Turbiscan (FormulAction) to study the destabilization mechanisms of emulsions.

Results confirm the relevance of both interfacial tension and viscoelastic measurements to select optimal conditions for emulsification. In addition, a good agreement between interfacial (shear) rheology, emulsion rheology, microstructural parameters and stability was found.

**Keywords:** Legume protein, Interfacial tension, Interfacial rheology, Emulsion rheology, Emulsion stability.

## Rheological characterization of concentrated suspensions of fumed silica for anti-impact applications

Rafael Soares Duarte<sup>1,2</sup>, Laura Campo-Deaño<sup>2</sup>, Rui A. Lima<sup>1</sup>, Francisco J. Galindo-Rosales<sup>2</sup>

<sup>1</sup> Escola de Engenharia da Universidade do Minho, Campus de Azurém, 4800-058 Guimarães (Portugal).

<sup>2</sup> CEFT, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, s/n, 4200-465 Porto (Portugal).

galindo@fe.up.pt

This study fits within the framework of the project CorkSTFluidics[1,2], which intend to develop ecofriendly energy absorbing composites based on microagglomerated cork pads reinforced with shear thickening fluids (STFs) by means of microfluidic patterns. Generally speaking, STFs are non-Newtonian fluids which viscosity increases whenever the applied shear rate/stress increases, with no need for the application of any external magnetic/electric field [3]. Traditionally, they have been rheologically characterized by *viscosity curves*, obtained through steady shear experiments. Nevertheless, this rheological information is insufficient to predict the flow behavior under complex dynamics loads like impact tests. In spite the amount of studies dealing with the dynamic and the extensional rheology of STFs has risen considerably [4,5] with the eclosion of new technological applications [2], there is still lack of information regarding the performance of this sort of fluids at the shortest time-response upon step-up applied shear rate, squeeze flow conditions or large amplitude oscillatory tests.

We consider concentrated suspensions (20% & 30% w/w) of fumed silica in polyethylene glycol (PEG) and polypropylene glycol (PPG), both with a molecular weight of 400 g/mol. The rheological characterization has been performed under steady shear (20s of shearing time) and at initial shear (20ms of shearing time) conditions. Additionally, the viscoelastic non-linearities of these fluids have also been studied through large amplitude oscillatory shear tests. Moreover, the evolution of the rheological properties with storing time and storing conditions have been determined within a period of 12 weeks. Finally, samples were undergone to low-velocity impact tests and their responses correlated with the rheological behaviour.

**Keywords:** Fumed silica, concentrated suspensions, shear thickening fluid, CorkSTFluidics

### References

- [1] F.J. Galindo-Rosales et al. CorkSTFluidics – A novel concept for the development of ecofriendly light-weight energy absorbing composites, *Materials & Design*, **82(5)**: 326-334 (2015).
- [2] F.J. Galindo-Rosales and L. Campo-Deaño, Composite layer material for dampening external load, obtaining process, and uses thereof, WO Patent App. PCT/IB2015/057399.
- [3] F.J. Galindo-Rosales, Complex fluids in energy dissipative systems, *Applied Sciences*, **6**: 206 (2016).
- [4] F.J. Galindo-Rosales et al., Shear-thickening behaviour of Aerosil R816 nanoparticles suspensions in polar organic liquids, *Rheologica Acta*, **48(6)**: 699-708 (2009).
- [5] M. Chellamuthu et al. Extensional rheology of shear thickening nano particle suspensions, *Soft Matter*, **5**: 2117-2124 (2009).

## Effect of surfactants on shear and microstructural properties of aqueous sepiolite gels

J.A. Carmona, A. Caro, J. Santos, R. LLinares, P. Ramírez

*Universidad de Sevilla, Grupo de Reología Aplicada. Tecnología de Coloides. Facultad de Química. C/P. García González, 1, 41012, Sevilla (Spain).*

e-mail of the presenter: pramirez@us.es

The rheological and microstructural properties of aqueous sepiolite gels have been studied. All the gels prepared exhibited very shear thinning flow behavior characterized by an apparent yield stress value that splits the flow curve into two parts; the first one with a gradual fall-off from a zero shear viscosity ( $\eta_0$ ) and a second one where the viscosity values drop several orders of magnitudes below the first part, eventually reaching a Newtonian plateau at high shear stresses. Furthermore, creep tests revealed an abrupt transition from a solid-like to a liquid-like regime that is related to a critical effective shear rate which must be reached before the material can flow steadily [1]. The influence of either cationic or anionic surfactant addition on the rheological and microstructural properties was also studied. Cetyl trimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were used as cationic and anionic surfactant, respectively. On the one hand, the viscoelastic properties, the apparent yield stress value and the zero shear viscosity of sepiolite gels increased with CTAB concentration above 5 mM. On the other hand, addition of SDS at concentrations above 5mM yielded a decrease in the gel-like behavior, apparent yield stress and also in the viscosity of the gels. Therefore, the rheological properties of these gels are likely related to electrostatic interactions between sepiolite gels and ionic surfactants. Scanning electron microscopy (SEM) images revealed that CTAB addition resulted in a more compact microstructure of gels, whereas a less compact structure was observed upon adding SDS. These results are in good agreement with the rheological behavior and confirm the importance of electrostatic interactions in both the microstructure and mechanical properties of sepiolite gels.

**Keywords:** Sepiolite, Clays, Yield stress, Scanning electron microscopy, Surfactants.

### References

[1] P. Coussot, H. Tabuteau, X. Chateau, L. Tocquer, G. Ovarlez. Aging and solid or liquid behaviour in pastes. *Journal of Rheology*, **50(6)**: 975-994. (2006).

# Field-induced Aggregation in Strongly Confined Magnetorheological Fluids

K. Shahrivar, J. R. Morillas, E. Carreón-González, J. de Vicente

*Biocolloid and Fluid Physics Group, Department of Applied Physics, Faculty of Sciences,  
University of Granada, C/ Fuentenueva s/n, 18071-Granada, Spain*

e-mail of the presenter: jvicente@ugr.es

Magnetorheological (MR) fluids are dispersions of magnetizable particles (usually carbonyl iron) in non-magnetic carrier fluids. In the absence of magnetic fields MR fluids typically behave as non-Brownian Hard Spheres suspensions. However, when an external magnetic field is applied the particles become magnetized and aggregate forming anisotropic structures oriented in the field direction. As a result of the formation of these structures, the MR fluids become strongly shear thinning and eventually, for appropriate particle volume fractions and field strengths, exhibit an apparent yield stress. MR fluids are currently used in a wide range of torque-transfer applications because of the fact that their rheological performance can be externally controlled [1-3].

Currently, there is a great interest in enhancing the rheological characteristics of MR fluids. For this, a deeper understanding of the physical mechanisms behind aggregates formation is required. In this presentation, we investigate the (irreversible) two-dimensional aggregation kinetics of dilute non-Brownian magnetic suspensions in rectangular microchannels using video-microscopy, image analysis, finite element methods and particle-level dynamic simulations. Especial emphasis is given to carbonyl iron suspensions that are of particular interest in the formulation of MR fluids. The results are compared to non-Brownian suspensions of magnetic latexes. We demonstrate that both suspensions follow a deterministic aggregation process. Furthermore, experimental and simulation aggregation curves can be collapsed in a master curve when using the appropriate scaling time ( $\propto \lambda^{-1} \phi_{2D}^{-2.5}$ ) as a function of only two dimensionless numbers: Lambda ratio ( $\lambda$ ) and particle surface fraction ( $\phi_{2D}$ ). Finally, some correlations between the microstructural aggregation states and bulk rheological performance are highlighted.

**Keywords:** Magnetorheology, Magnetic colloids, Colloidal Aggregation

## References

- [1] J. de Vicente, Líquidos Magnéticos, *Revista de Física (Real Sociedad Española de Física)*, **28(1)**: 28-31 (2014).
- [2] J. de Vicente, Magnetorheology: A Review, *e-rheo-iba*, **1**, 1-18 (2013).
- [3] J. de Vicente, D. J. Klingenberg, R. Hidalgo-Álvarez, Magnetorheological Fluids: A Review, *Soft Matter*, **7**: 3701-3710 (2011).

## The influence of polymer concentration on nail lacquers properties

B Gregorí<sup>1,2</sup>, AP Serro<sup>3</sup>, J Marto<sup>1</sup>, RG Santos<sup>2</sup>, JM Bordado<sup>2</sup>, HM Ribeiro<sup>1</sup>

1. *Research Institute for Medicine and Pharmaceutical Science (iMed.UL), Faculdade de Farmácia, Universidade de Lisboa, Portugal.*
2. *Centre for Natural Resources and the Environment (Ceren), Instituto Superior Técnico, Universidade de Lisboa, Portugal.*
3. *Centro de Investigação Interdisciplinar Egas Moniz (CiiEM), Instituto Superior de Ciências da Saúde Egas Moniz, Caparica, Portugal.*

e-mail of the presenter: hribeiro@campus.ul.pt

Currently, most common topical formulations (creams and lotions) present a low drug deliver to nail infection. Nail lacquers appear to increase drug delivery and simultaneously improve the effectiveness of treatment with increased patient compliance. These formulations leave a polymer film on the nail plate after solvent evaporation. The duration of the film residence in the nail constitutes an important property of a nail lacquer formulation.

In this study, the influence of polymer concentration on the properties of nail lacquer formulations was assessed. Polyurethane (PU) was the polymer selected for preparing 5 different nail lacquers formulations containing 1% of drug (terbinafine hydrochloride –TB- and ciclopirox) and different polymer concentrations (10%, 15%, 20% and 25%), while ethyl acetate, butyl acetate and ethanol were the solvents used.

Wettability (contact angle using drop method), adhesion (ISO 2409:2013), drying time, viscosity measurement (cone-plate Brookfield® viscometer, model DV-II + Pro) and scanning electron microscopy (SEM) were performed in order to achieve these aims.

The results obtained show that formulations with higher content of (25% and 20%) of polymer reveal lower values of wettability, which is in accordance with the adhesion determination. In fact, formulations containing 10% of PU presented the highest value of adhesion. The obtained drying times varies from 9 to 16 min: the higher the polymer concentration the longer the drying time. TB nail lacquers with 25%, 20%, 15% and 10% of PU showed  $17.03 \pm 0.07$ ,  $8.80 \pm 0.11$ ,  $4.70 \pm 0.06$  and  $2.62 \pm 0.04$  mPa.s viscosity values, respectively. The nail lacquers images obtained by SEM show homogeneous films covering the surface to the nail. Drugs (TB and ciclopirox) had no influence on film thickness and on the microstructure of PU based nail lacquers.

The concentration of the polymer influences the properties of the nail lacquers and in this study the formulations with lower PU concentrations presented better characteristics for the delivery of antifungal drugs.

**Keywords:** Nail lacquer, Polyurethanes, Morphology, Wettability, Viscosity

## Rheology and texturometry: Complementary tools to predict the water resistance performance of sunscreens

J Marto<sup>1</sup>, B Chiari-Andréo<sup>2,3</sup>, Vera Isaac<sup>2</sup>, HM Ribeiro<sup>1</sup>

<sup>1</sup> Research Institute for Medicine and Pharmaceutical Science (iMed.Ulisboa), Faculty of Pharmacy, Universidade de Lisboa, Lisboa, Portugal.

<sup>2</sup> Faculdade de Ciências Farmacêuticas, UNESP – Univ Estadual Paulista, DFM – Laboratório de Cosmetologia – LaCos, São Paulo, Brazil.

<sup>3</sup> Universidade de Araraquara – UNIARA, São Paulo, Brazil

e-mail of the presenter: jmmarto@ff.ulisboa.pt

Sunscreen products represent a trend of providing not only simple sun protection factor but also other additional benefits. Water resistance is a key parameter for today's sunscreens. Because a human *in vivo* test is time consuming and expensive, alternative methods have been tried using. In this study, we suggest to use the rheology and texturometry to screening and predict the result of water resistance of sunscreens. Thus, the rheological and mechanical behaviour was evaluated on three o/w sunscreens, differing only on type of physical UV filter (SA - 4% of anatase titanium dioxide (hydrophilic); SR - 4% of rutilo titanium dioxide (hydrophobic); P – without titanium dioxide). Sunscreens were characterized in terms of *in vitro* water resistance tests.

Rotational viscosity was determined using a C35 mm cone geometry, with an angle of 2°. Dynamic viscosity measurements were carried out between 1 and 1000 Pa on a logarithmic increment. Oscillation frequency sweep tests were performed at frequencies ranging between 0.01 and 1 Hz. Flow curves were generated by ramping the shear rate from 0 to 100 s<sup>-1</sup> in 120 seconds (ascent curve) and then from 100 to 0 s<sup>-1</sup> in 120 seconds (descent curve) and recording the shear stress throughout. The creep and recovery test was carried out with a shear stress of 1 Pa for emulsions, during 240 seconds. A Texture Analyzer TA.XT Plus was used to examine the texture properties of sunscreens, using an analytical probe (P/10, 10 mm Delrin). The *in vitro* sunscreen water resistance method was used as described elsewhere [1].

The SR formulation, with a higher thixotropy, showed higher water resistance retention (WRR) (88%) when compared with SA (59.7%). It was observed that G' increases with increase of WRR. This indicates that the structure of the emulsions become more robust. All formulations suffered deformation according to the compliance value (J). SR formulation presented lower Jo when compared with SA. The adhesiveness increased markedly for SR, what contributes to increase the skin adhesiveness and water resistance performance.

Thus, it seems that water resistance performance of the sunscreens depended on rheological and mechanical behaviour, the study of rheology and texturometry can help the development of simple, quick and cheap screening methods for this category of cosmetic products.

**Keywords:** Sunscreens, Rheology, Texturometry, Titanium dioxide, water resistant.

### References

[1] J. Marto, *et al.*, The green generation of sunscreens: Using coffee industrial sub-products. *Industrial Crops and Products*, 80:93-100 (2016).

## Insights on nanoparticles mucoadhesiveness for ocular drug delivery: a rheological approach

M.M. da Silva<sup>1</sup>, R. Calado<sup>1</sup>, J. Marto<sup>1,2</sup>, A. Bettencourt<sup>1</sup>, L.M.D. Gonçalves<sup>1</sup>

<sup>1</sup>Research Institute for Medicines (iMed.U LISBOA), Faculty of Pharmacy, Universidade de Lisboa, Av. Prof Gama Pinto, Lisboa (Portugal).

<sup>2</sup> LABORATÓRIO EDOL, Produtos Farmacêuticos S.A., Av. 25 de Abril, nº6, Linda-a-Velha (Portugal).

asimao@ff.ulisboa.pt

Pharmaceutical approaches based on nanotechnologies and the development of eye drops composed of mucoadhesive polymers are emerging strategies to seek for efficient treatment of ocular diseases. These innovative nanoparticulate systems aim to increase drugs bioavailability at the ocular surface. For the successful development of these systems the evaluation of mucoadhesiveness, that is the interactions between the ocular delivery system and mucins present at the eye, is of utmost importance. Rheological methods are among the most important tools for the evaluation of the mucoadhesion properties of ocular formulations.

In this context, the aim of the present work was to investigate the mucoadhesivity of a novel nanoparticle eye drop formulation containing an antibiotic (ceftazidime) intended to treat eye infections. Gel formulations comprise a polymer (hydroxypropyl)methyl cellulose (HPMC) 0.75% (w/v) in an isotonic solution incorporating chitosan/TPP-hyaluronic acid nanoparticles [1].

Viscosity measurements were conducted to assess the mucin interaction with the novel formulations. That is, the viscosity of the nanoparticles, and the gels incorporating the nanoparticles were characterized in contact with mucin at different mass ratios. Furthermore, the viscosity component due to biadhesion or rheological synergism parameter ( $\Delta\eta$ ) was obtained.

Results showed that at higher nanoparticles:mucin weight ratios a minimum in viscosity occurred which resulted in a negative rheological synergism. Also, the results highlighted the mucoadhesivity of the novel ocular formulation and its ability to interact with the ocular surface thus increasing the drug residence time in the eye.

Chitosan/TPP-hyaluronic acid nanoparticles gels are a promising platform for ocular drug delivery with enhanced mucoadhesive properties as demonstrated by viscosity measurements.

**Keywords:** mucoadhesion, nanoparticles, ocular, viscosity

### References

[1] A. Cadete, L. Figueiredo, R. Lopes, C.C.R., Calado, A.J. Almeida, L.M.D. Gonçalves Development and characterization of a new plasmid delivery system based on chitosan-sodium deoxycholate nanoparticles. *Eur J Pharm Sci*, **45**: 451–458 (2012).

## A new coupled viscoelastic solver in OpenFOAM® framework

C. Fernandes<sup>1</sup>, V. Vukčević<sup>2</sup>, T. Uroić<sup>2</sup>, L.L. Ferrás<sup>1</sup>, O.S. Carneiro<sup>1</sup>, R. Simões<sup>1</sup>, H. Jasak<sup>2,3</sup> and  
J.M. Nóbrega<sup>1</sup>

<sup>1</sup> Institute for Polymers and Composites/i3N, Univ. Minho, Campus de Azurém, 4800-058 Guimarães, (Portugal)

<sup>2</sup> Faculty of Mechanical Engineering and Naval Architecture, Ivana Lučića 5, 10000 Zagreb (Croatia)

<sup>3</sup> Wikki Ltd, 459 Southbank House, SE1 7SJ, London (United Kingdom)

e-mail of the presenter: mnobrega@dep.uminho.pt

Effective design approaches require the use of numerical modelling tools, to avoid long and high resource demanding experimental trial-and-error processes. The design tasks are even more difficult to undertake when dealing with complex rheology materials, as happens with the viscoelastic fluids, which present some counter intuitive phenomena. This framework has been motivating, during the last decades, the development of numerical modelling codes able to deal with viscoelastic fluids. The usual approaches employed, are based on segregated procedures, in which the mass, momentum and constitutive governing equations are solved iteratively and sequentially. This sequential process is quite sensitive and prone to divergence, thus is often reported to require high relaxation factors, to assure the achievement of a converged solution. Moreover, the segregated approach is also known to limit substantially the Deborah numbers that can be achieved on the numerical calculation.

This work reports the development of a coupled viscoelastic solver in OpenFOAM® computational library, in which the governing equations are solved simultaneously. The presented case studies clear evidence the advantages of the proposed approach, both in terms of calculation time and stability.

**Keywords:** computational rheology, viscoelastic, coupled solver, OpenFOAM.

# Extremely slow reptation dynamics of Rod-Coil-Rod Triblock Copolymers

Paola Troya<sup>1</sup>, Jorge Ramirez<sup>1,2</sup>, Bradley D. Olsen<sup>2</sup>

<sup>1</sup> Department of Chemical Engineering, Universidad Politécnica de Madrid (Spain)

<sup>2</sup> Department of Chemical Engineering, Massachusetts Institute of Technology (USA)

e-mail of the presenter: ap.troya@alumnos.upm.es

Rod-coil block copolymers have attracted a lot of interest in the last decade for their potential use in organic electronics [1] and biomaterial applications [2,3]. The equilibrium self-assembly of these materials has been thoroughly investigated [4,5], but a fundamental understanding of their dynamics is still not complete. Previous theoretical and experimental results suggest the appearance of new mechanisms of diffusion that slow down the dynamics of rod-coil diblock and triblock copolymers, with diffusivities that are smaller than both rod and coil homopolymers by over an order of magnitude in some cases [6,7]. As a result, a modified reptation theory has been introduced that attributes the slow dynamics of rod-coils to the mismatch between the curvatures of the entanglement tubes of the rod and coil blocks [8]. The present work extends the theoretical and simulation study to the case where both molecular ends are occupied by rods. In this new configuration, arm retraction is not and activated reptation is extremely difficult because any motion of the chain along its tube needs to drag both end rods along the flexible tube corresponding to the coil block. In addition, any new tube segment must be stiff, and therefore, in the absence of constraint release, the whole tube must have a very small curvature. New relaxation mechanisms emerge that result in even slower relaxation dynamics than in the case of similar rod-coil and coil-rod-coil block copolymers. A linear polymer that takes such a long time to disentangle is expected to also entangle at a very slow pace. From a technological point of view, a material with such slow reentanglement dynamics would be of interest in itself, because it would show a very low steady state viscosity. Knowledge of the mechanisms of motion and relaxation of these materials is of utmost importance for the prediction of their flow properties, their kinetics of self-assembly, and for the design of the right manufacturing processes.

**Keywords:** rigid polymers, coils, block copolymers, reptation

## References

- [1] R.A. Segalman, B. McCulloch, S. Kirmayer, J.J. Urban, *Macromolecules* **42**, 9205 (2009).
- [2] J.C.M. van Hest, *Polym. Rev.* **47**, 63 (2007).
- [3] W.D. Kohn, C.T. Mant, and R.S. Hodges, *J. Biol. Chem.* **272**, 2583 (1997).
- [4] P.F. Damasceno, M. Engel, and S.C. Glotzer, *Science* **337**, 453 (2012).
- [5] B.D. Olsen, M. Shah, V. Ganesan, R.A. Segalman, *Macromolecules* **41**, 6809 (2008).
- [6] M. Wang, A. Alexander-Katz and B.D. Olsen, *ACS Macro Lett.*, **1** (6), pp 676–680 (2012).
- [7] M. Wang, K. Timachova and B.D. Olsen, *Macromolecules*, **48** (9), pp 3121–3129 (2015).
- [8] M. Wang, A.E. Likhtman and B.D. Olsen, *J. Chem. Phys.* **143**, 184904 (2015)

## Rotational and translational motion observed in *Escherichia coli* aggregates during shear

R. Portela<sup>1</sup>, J.M. Franco<sup>2</sup>, P. Patrício<sup>3,4</sup>, P. L. Almeida<sup>3,5</sup>, R. G. Sobral<sup>1</sup> and C. R. Leal<sup>3,6</sup>

<sup>1</sup>UCIBIO@REQUIMTE, Departamento de Ciências da Vida, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

<sup>2</sup>Departamento de Ingeniería Química, Facultad de Ciencias Experimentales da Universidad de Huelva, Spain

<sup>3</sup>ISEL, Rua Conselheiro Emídio Navarro 1, P-1959-007 Lisboa, Portugal

<sup>4</sup>CEDOC, Faculdade de Ciências Médicas, Universidade Nova de Lisboa, 1169-056 Lisboa, Portugal

<sup>5</sup>CENIMAT/I3N, Faculdade Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

<sup>6</sup>Centro de Investigação em Agronomia, Alimentos, Ambiente e Paisagem, LEAF, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda 1349 - 017 Lisboa, Portugal

e-mail of the presenter: cleal@adf.isel.pt

Recently, the growth of an *Escherichia coli* culture was studied using real-time and in situ rheology and rheo-imaging measurements, allowing to characterize their rheological behavior during time [1]. In the *lag phase*, bacteria are adapting to the new environmental growth conditions, with a characteristic slow division rate. Accordingly, the viscosity shows a slow and constant increase with time. In the *exponential phase* the viscosity presents a dramatic increase, but exhibits several drops and recoveries. In the *late phase* of growth, the viscosity increase slows down, reaching an intermittent plateau of maximum viscosity, with several drops and recoveries. In this phase, the highest bacteria density is attained: bacteria still grow and divide, but at a lower rate; big and irregular bacteria aggregates are observed, which keep moving in suspension and no significant sedimentation is observed; the aggregates present translational motion in the shear flow direction and rotational motion in the vorticity direction; the aggregates become larger along time, due to the incorporation of smaller aggregates; due to the rotational motion, the aggregates become elongated along the rotational axis; apparently, the size of the aggregates does not influence the rotational motion, since almost all aggregates rotate with the same angular velocity, which is related to the applied shear rate. As a first approximation, and because an explicit individual motion of the cells within each aggregate is not observed, this behavior is interpreted in light of a simple rigid-body motion, in which shear rate and angular velocity are dependent.

**Keywords:** bacteria, aggregates, viscosity.

### References

[1] R. Portela, P. Patrício, P. L. Almeida, R. G. Sobral, J. M. Franco, and C. R. Leal, "Rotational tumbling of *Escherichia coli* aggregates under shear", *Phys. Rev. E* 94, 062402 (2016).

## Normal Stresses in Magnetic-responsive Shear Thickening Colloids

E. Ortigosa-Moya, R. Hidalgo-Alvarez, J. de Vicente

*Biocolloid and Fluid Physics Group, Department of Applied Physics, Faculty of Sciences,  
University of Granada, C/ Fuentenueva s/n, 18071-Granada, Spain*

e-mail of the presenter: eortigosa@ugr.es

Colloidal shear thickening is a stress controlled reversible phenomena typically occurring in stable colloids. It is currently understood using both lubrication-driven and friction-driven explanations. Interestingly, recent experiments suggest that First Normal-stress Differences elucidate the relative contributions from hydrodynamic lubrication and frictional contact forces in the shear-thickened state [1-2].

In the current work we study the role of interparticle attractive interactions in the onset of the shear thickening and in the First Normal-stress Differences. First, experiments are carried out in model shear-thickening colloids constituted by starch spheres suspended in water at a wide range of particle concentrations (from 30 to 42 vol%) to identify the Continuous and Discontinuous shear thickening transitions. Then, the starch suspensions are doped with iron microparticles (0.1 vol%) in order to make them magnetic field-responsive. Results demonstrate that the onset of the shear-thickened state can be externally controlled by the interparticle attractive interactions. Indeed, the shear thickening transition can be eventually suppressed superimposing sufficiently large magnetic fields.

**Keywords:** Shear-thickening, Starch, Magnetorheology, Magnetic colloids

### References

- [1] X. Cheng, J. H. McCoy, J. N. Israelachvili, I. Cohen, Imaging the Microscopic Structure of Shear Thinning and Thickening Colloidal Suspensions, *Science*, **333**: 1276 (2011).
- [2] M. Wyart, M. E. Cates, Discontinuous Shear Thickening Without Inertia in Dense Non-brownian Suspensions, *Phys. Rev. Lett.*, **112**: 098302 (2014).

## Three-dimensional Rheological Characterization of Magneto Rheological fluids through OSP Measurements

Carlos A. Gracia Fernández<sup>1</sup>, Ana Alvarez<sup>2</sup>

<sup>1</sup> TA Instruments-Waters Crommatografía, Ronda Can Fatjó, Cerdanyola del Vallés (Spain).

<sup>2</sup> University of A Coruña, EPS Avda, Mendizábal s/n, 15403 Ferrol (Spain).

e-mail of the presenter. cgracia@tainstruments.com

Typically, the standard measurements of Magnetorheological fluids apply vertical magnetic fields versus the applied shear.

In the present work, it will be performed oscillatory measurement in several directions versus the applied magnetic field. The main target is, from a practical point of view, to establish the relationship between the rheological properties and the magnetic field applied not only in the perpendicular direction but also in the other 2 spatial directions.

In order to get that target, an orthogonal superposition geometry has been built made off plastic based in the Standard Double Gap Couette geometry. This geometry allows us to perform several kinds of stresses:  $\sigma_{12}$ ,  $\sigma_{32}$ ,  $\sigma_{23}$  and therefore, not only  $G_{12}$  will be measured but also  $G_{32}$ , and  $G_{23}$ .

A solenoid is built surrounding the Plastic OSP geometry what provides the magnetic field intensity required.

The MRfluid used in the present work is an standard Iron Suspension provided by Lord Company.

**Keywords:** MRfluids, Orthogonal Superposition

### References

- [1] C. Gracia-Fernández, S. Gómez-Barreiro, Aadil Elmoumni, A. Álvarez, J. López-Beceiro, R. Artiaga: *Simultaneous application of electro and orthogonal superposition rheology on a starch/silicone oil suspension*. Journal of Rheology 01/2016; 60(1), DOI:10.1122/1.4937930

## Following Phase Transitions with Rheometry and Simultaneous Raman-Spectroscopy

Fabian Meyer and Jan P. Plog

*Thermo Fisher Scientific, Dieselstr.4, Karlsruhe (Germany).*

e-mail of the presenter: [fabian.meyer@thermofisher.com](mailto:fabian.meyer@thermofisher.com)

The use of a coupled rheometer and Raman spectrometer for obtaining comprehensive insight into a materials behavior is presented.

Rheology is the study of flow and deformation of matter. During a rheological measurement the response of a material to a mechanical excitation (stress or strain) can be measured using a rotational rheometer. The obtained data represents the overall response of the material which is exposed to the shear field in the measuring geometry. The mechanical properties are directly related to a materials microscopic or molecular structure and its changes. However, rheological measurements alone do not provide any information about the structure and the changes that occur on the microscopic and/or molecular level.

Raman spectroscopy has shown its ability as a powerful, effective and non-invasive method for chemical analysis. Coupling a rheometer with a Raman spectrometer provides direct information about molecular reaction kinetics and mechanical properties. This is extremely useful for studying phase transition behavior such as the crystallization behavior of polymer melts during processing. It can also provide insight for *in-situ* characterization and monitoring, which can be challenging when working with on-line techniques as only relative flow fields are characterized. Finally, the coupling gives the researcher the advantage of maximizing and synchronizing the information gathered from a single measurement as well as enabling transient information on their materials during fast processing conditions.

In this contribution we present results obtained with the new combination of a commercially available rotational rheometer with a Raman spectrometer. Details of this unique set-up as well as selected results will be presented.

**Keywords:** rheometry, Raman spectroscopy, polymers, crystallization.

### References

[1] A.P. Kotula, M. Meyer, F. De Vito, J. Plog, A.R. Hight Walker, K.B. Migler, The rheo-Raman microscope: Simultaneous chemical, conformational, mechanical, and microstructural measures of soft materials, *Review of Scientific Instruments*, **87(10)**, (2006).

## New rheometric tools for complex materials

Dr. Joerg Laeuger, Dr. Andre Braun, Teresa Masso

*Anton Paar Germany GmbH, Ostfildern, Germany*

There is a broad range of standard rheological tests which can be used to characterize the rheological behaviour of complex materials. Nevertheless there are still limitations, or parameters which haven't been considered extensively until now. Aim of the contribution is to highlight several new tools which can be of interest for advanced rheological testing and which can help to get profound knowledge of the materials properties.

A rheometer with two drives located on opposite sides of the sample opens new testing opportunities. Using such a setup, combined with a new developed extensional fixture, measurements towards small tensile stresses are possible, since the torque detection is not affected by any mechanical gears or bearings.

A main limitation for characterizing polymer melts and concentrated polymer solutions at large deformations or high shear rates, is known as edge fracture. To limit the impact of edge fracture a cone partitioned plate (CPP) has been recommended [1,2]. By employing a two motor rheometer in a separate motor transducer (SMT) configuration and a newly designed CCP geometry it is possible to measure towards larger strains and strain rates compared to cone-and-plate geometries.

The combination of microscopy with rheological measurements is of interest in order to correlate microstructural properties with the macroscopic rheological behaviour. For such tests rheometers with two drive units working in counter-rotating mode can be of advantage due to the possibility to visualize microstructures kept in the stagnation plane.

A new experimental method for studying the mechano-optical rheology of polymeric liquids and soft matter materials is based on a combination of rotational rheology and a recently developed optical technique - shear-induced polarized light imaging (SIPLI) [3]. The method provides a unique opportunity to monitor a complete sample view during rheological measurements in plate-plate and cone-and-plate geometry. Simultaneous SIPLI and the rheology of the oriented lamellar phase of block copolymers and liquid crystals as well as a direct relation between the shish formation and the polymer melt viscosity upturn during flow-induced crystallization of semi-crystalline polymers are presented. Moreover SIPLI can be used for quantitative birefringence measurements.

While it is already known that ambient condition can have an impact on the rheological properties of materials mostly only the impact of temperature is taken into account during rheological testing. Nevertheless, for some materials also relative humidity of the ambient air can influence the rheological properties. Hence using special accessories to control temperature and relative humidity separately during rheological testing can be of advantage. The presentation will highlight some examples where setting temperature and relative humidity helps to get a better understanding on the materials properties at processing and storage conditions.

### References

- [1]. J.Meissner, R.W. Garbella, J. Hostettler, *J. Rheol.*, **1989**, *33*, 843.
- [2]. T. Schweizer, *J. Rheol.*, **2003**, *47*, 1071.
- [3]. O.O. Mykhaylyk, et al., *J. Polym. Sci. Pol. Phys.*, **2016**, *54*, 215

## Microfluidic Visual Rheometer

Yoann Lefeuvre, Patrick Abgrall, Patrycja Adamska, Pascal Bru, Gérard Meunier

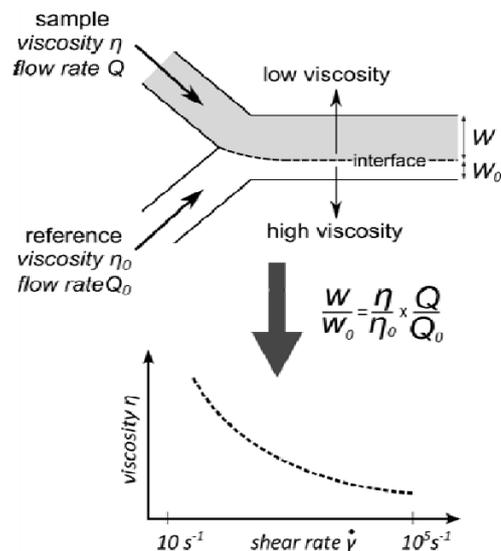
<sup>1</sup> Formulation, 10 impasse Borde Basse, 31240, L'Union (France).

lefeuvre@formulation.com

Rheological analysis is made fast and easy with a novel instrument based on a simple microfluidic flow comparator. Using only tiny amount of samples, the technology allows flow viscosity measurements of liquid products from water-like inks to thick cosmetic formulations, under a wide range of shear rates (including high values up to 105 s<sup>-1</sup>). Additionally, the user-friendly visual principle makes possible routine optical control of both samples and easily replaceable flow cells to assess measurement quality.

### Measurement principle

A sample and a viscosity standard are pushed together through a microfluidic comparator (Y-junction) at controlled flow rates set by two syringe pumps. As a result, a laminar co-flow can be observed. Images of the resulting interface are acquired via an integrated optical system and the position is measured relatively to the channel wall positions. The position of the interface is simply related to the viscosity and the flow rate ratio between the sample and the reference. Using dedicated algorithms, sample viscosity is automatically extracted over a controlled range of shear rates and temperatures.



Measuring the viscosity with microfluidics gives many benefits to the technology. Because of the highly confined conditions, high shear rates can be reached with sample volumes at milliliter range. In addition, constant comparison to a reference solution and working at flow render the measurement calibration free and fully automatic (no need to resample between repetition, automated shear rate and temperature screening). Image based acquisition gives to the user possibility to directly supervise the quality and thus accessing precise and repeatable (1%) measurements.

### Applications

Fluidicam was designed as a versatile rheometer able to measure virtually any flowing fluid. Its high accuracy even at low viscosities and high shear is a very good fit for inkjet and sprayable formulations, or to mimic end-user conditions for lubricants (mechanics, cutting, wire drawing). Viscosity measurement range is simply adjusted by changing the reference liquid, making also Fluidicam a very suitable technique for much thicker, pasty fluids in cosmetics or food. Flow characterization of costly or rare fluids (pharmaceutical products, blood, synovia) is made possible owing to its low volume consumption.

Keywords: microfluidic Rheometer, high shear rate, high sensibility viscosity measurement.

## Micro-capillary Flow Behavior of Magnetorheological Fluids

J. R. Morillas, K. Shahrivar, J. de Vicente

*Biocolloid and Fluid Physics Group, Department of Applied Physics, Faculty of Sciences,  
University of Granada, C/ Fuentenueva s/n, 18071-Granada, Spain*

e-mail of the presenter: jmorillas@ugr.es

Magnetorheological (MR) fluids are non-Brownian suspensions of magnetisable particles that exhibit a “liquid-to-solid” transition upon the application of external magnetic fields. In the absence of magnetic fields, MR fluids behave as regular Newtonian fluids [1]. However, in the presence of sufficiently large magnetic fields a plastic behaviour is typically described. Recently, a Casson-like Universal Master Curve has been successfully proposed for the description of their bulk rheological properties [2,3].

In this communication we validate the Universal Master Curve against steady shear data in strongly confined microfluidic flows. Stress-controlled experiments were carried out in glass microchannels (100  $\mu\text{m}$  width) and pressure drop  $\Delta p$  versus flow rate  $Q$  curves were obtained under magnetic fields in the linear magnetization regime (up to approx. 100 kA/m). With this, the viscosity curves were computed using the Weissenberg-Rabinowitsch-Mooney equation. Experimental results were also compared with Computational Fluid Dynamics Simulations.

**Keywords:** Magnetorheology, Magnetic colloids, Microchannels, Non-optical microrheology

### References

- [1] J. de Vicente, Magnetorheology: A Review, *e-rheo-iba*, **1**, 1-18 (2013).
- [2] J. A. Ruiz-López, J. C. Fernández-Toledano, R. Hidalgo-Alvarez, J. de Vicente, Testing the Mean Magnetization Approximation, Dimensionless and Scaling Numbers in Magnetorheology, *Soft Matter*, **12**: 1468-1476 (2016).
- [3] J. A. Ruiz-López, J. C. Fernández-Toledano, D. J. Klingenberg, R. Hidalgo-Alvarez, J. de Vicente, Model Magnetorheology: a Direct Comparative Study between Theories, Particle-level Simulations and Experiments, in Steady and Dynamic Oscillatory Shear, *Journal of Rheology*, **60(1)**: 61-74 (2016).

## In-process material characterization at constant extrusion conditions: application to clay/PLA bionanocomposites

P.F. Teixeira<sup>1</sup>, F. Sutura<sup>2</sup>, R. Scaffaro<sup>2</sup>, L. Hilliou<sup>1</sup>, J.A. Covas<sup>1</sup>

<sup>1</sup> University of Minho; IPC/I3N, Campus de Azurém 4800-058, Guimarães (Portugal).

<sup>2</sup> University of Palermo, Viale delle Scienze 90128 Palermo (Italy).

e-mail of the presenter: p.teixeira@dep.uminho.pt

Recently, the authors developed a prototype modular small-scale single / twin-screw extrusion system, with outputs in the range of grams/hour, coupled to a rheo-optical slit die. This experimental set-up is adequate to measure shear viscosity and normal-stress differences and perform optical measurements [1-4]. As with most similar attempts, the generation of a range of shear rates implied operating the extruder with varying screw speeds or feed rates. However, these variations change the thermomechanical history of the material experienced inside the machine. Henceforth, material characteristics at the die inlet may change. This may jeopardize the validity of the measurements, since a different material might be generated for each shear rate of the flow curve. To circumvent this problem, the authors adopted a design concept that has been seldom utilized, consisting of a die with two perpendicular channels, each fitted with an output control valve at its inlet, the total pressure drop remaining constant. While one of the channels can be utilized for conventional extrusion, the other has a slit configuration and adequate for rheo-optical characterization. This solution is validated and used for the specific study of the interplay between process parameters, process-induced structure and rheology of a clay/PLA biodegradable nanocomposite.

**Keywords:** extrusion, slit die, rheo-optics, bionanocomposites

### References

- [1] P.F. Teixeira, L. Hilliou, J.A. Covas, J.M. Maia, Assessing the practical utility of the hole-pressure method for the in-line rheological characterization of polymer melts, *Rheol Acta*, **52**: 661-672 (2013).
- [2] P.F. Teixeira, J.M. Maia, J.A. Covas, L. Hilliou, In-line particle size assessment of polymer suspensions during processing, *Polym Test*, **37**: 68-77 (2014).
- [3] P.F. Teixeira, S.N. Fernandes, J. Canejo, M.H. Godinho, J.A. Covas, C. Leal, L. Hilliou, Rheo-optical characterization of liquid crystalline acetoxypolypropylcellulose melt undergoing large shear flow and relaxation after flow cessation, *Polymer*, **71**: 102-112 (2015).
- [4] P.F. Teixeira, J.M. Maia, J.A. Covas, L. Hilliou, A small-scale experimental extrusion set-up for exploring relationships between process-induced structures and characteristics of multiphase polymer systems. *Macromol Mater Eng*, **12**: 1278-1289 (2015).

## Morphology-rheology relationship on novel PA6-HNBR blends

A. Burgoa<sup>1</sup>, R. Hernandez<sup>1</sup>, A.M. Zaldua<sup>1</sup>, A. Arrillaga<sup>1</sup>, J.L. Vilas<sup>2</sup>

<sup>1</sup> Leartiker Research and technology, Xemein Etorbidea, 12-A, Markina-Xemein (Spain).

<sup>2</sup> Departamento de Química Física, Facultad de Ciencia y Tecnología, Campus de Leioa, Universidad del País Vasco UPV/EHU (Spain)

e-mail of the presenter: aburgoa@leartiker.com

The use of thermoplastic elastomers has been increasing in the last two decades, since the introduction of the first Santoprene® grades in the late 80's of the XX century. Since that time a high amount of different materials have appeared in the market, from TPV's (based in the well-known dynamic vulcanisation technique) to physical blends and alloys of elastomers with thermoplastic matrixes of diverse natures.

Now at day's most of the thermoplastic elastomers available in the market are blends of Polyolefines (TPOs) or SEBS triblock copolymers with Polypropylene or derivatives. These TPEs have limited resistance to fuels and temperature due to the low melting temperature of the thermoplastic matrix.

The objective of this work is the development of novel TPEs based in a high temperature resistant matrix, Polyamide 6 (Durethan B 30 S), with an elastomer phase with high resistance to fluids and temperature, based in HNBR (Terban AT 3904 VP). Due to the low compatibility of these two materials a third component, HXNBR (Terban XT KA 8889 VP), has been added to the blend in order to obtain better adhesion among the phases.

The preparation of the blends has been done in two steps, first a two roll mill blender has been used to produce the elastomeric compound in proportions of HNBR/HXNBR 70/30, 50/50 and 30/70. Later the compounded materials, as well as the pure HNBR and HXNBR have been blended in a Brabender DSE 20/40 corrotating twin screw extruder at 240°C with the Polyamide 6. A particular composition of 60 rubber/40 plastic was selected for the present investigation.

The Rheological properties of the blends have been characterised using a Rosand RH7 twin bore capillary rheometer and a Thermo Haake Mars III oscillatory rheometer and the morphology has been studied using a Nikon Eclipse 80i optical microscope equipped with a Linkam temperature controlled stage and by scanning electron microscopy. The rheological properties and morphology of the blends have been studied.

**Keywords:** TPE, Blend, PA6, rheology, morphology

### References

- [1] Banerjee, Shib Shankar, and Anil K. Bhowmick. HIGH-TEMPERATURE THERMOPLASTIC ELASTOMERS FROM RUBBER-PLASTIC BLENDS: A STATE-OF-THE-ART REVIEW, *Rubber Chemistry and Technology*, **volume 90**: page 1-36 (2017).
- [2] Chowdhury, Rajesh, M. S. Banerji, and K. Shivakumar. Polymer blends of carboxylated butadiene-acrylonitrile copolymer (nitrile rubber) and polyamide 6 developed in twin screw extrusion. *Journal of applied polymer science*, **volume 104**: page 372-377 (2007).

## Non-linear and Hysteretic rheological properties of magneto-polymer composites

Andrey Zubarev

*Ural Federal University Institution, Ekaterinburg (Russia)*

e-mail of the presenter: A.J.Zubarev@urfu.ru

Composites of micronized magnetic particles in polymer matrices present new kind of smart magnetically controlled soft materials, usually named as ferrogels, ferroelasts, magnetically active elastomers, etc. These systems attract considerable interest of researches and engineers due to rich set of physical properties valuable for many industrial and bio-medical applications.

Many experiments with these composites demonstrate strong non-linear dependence of elastic stress on deformation, even in the range of deformations, corresponding to the linear elasticity of the pure polymer matrix. Moreover, hysteretic dependences of magnetization, magnetostriction and the stress - deformation dependences many times have been detected experimentally. Application of these materials in high technologies requires understanding of the physical cause of the non-linear phenomena and development of theoretical models for their accurate quantitative description.

We present theoretical model of the non-linear and hysteretic effects, based on the conception of formation, by the particles, of the chain-like aggregates in the polymer matrix. Unification of the particles in the chains because of magnetic interaction between them; rupture of the chains under the elastic forces in the polymer matrix, as well as effect of the chains on the macroscopic properties of the composites are considered. Theoretical results quantitatively reproduce the experimental ones and can serve as a basement for the study of non-linear viscoelastic and other complicated rheological phenomena in these materials.

# A rheological study of epoxy resins mixed with ionic liquids and its implications in sustainable chemistry

Mercedes Fernández, Eneritz Garro, Antxon Santamaría

*Institute of Polymer Materials (POLYMAT) and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country (UPV/EHU), Paseo Manuel de Lardizabal 3, 20018 Donostia-San Sebastián (Spain).*

e-mail of the presenter: mercedes.fernandez@ehu.es

Epoxy resins are the most important thermosetting polymers, because they possess a set of properties which make them apt for many applications in different industrial sectors. However, epoxy resins have a weak point from an environmental point of view, which concerns the use of volatile and toxic chemical agents, such as amines, to carry out the curing (crosslinking) process. On the other hand, ionic liquids (IL) have gained ground in recent years as “green solvents”, because of their high thermal stability, low volatility and recyclability, among other advantages.

In recent years the use of ionic liquids as catalysts and curing aids of epoxy resins has been reported in the literature (1), but, notwithstanding the practical relevance of the subject, the origin of the interactions between both substances remains unclear. The use of rheological measurements to gain insight into epoxy-IL interactions has not been considered, so far.

In this oral communication a rheological study of epoxy-IL systems is carried out, using hydrophobic and hydrophilic ionic liquids and considering the following aspects: a) Analysis of the terminal viscoelastic zone of epoxy-IL mixtures in the liquid state, using SAOS flow b) Time scans under isothermal conditions by SAOS experiments, to investigate the reduction of curing time, temperature and amine content, when ILs are added c) Dynamic mechanical thermal analysis (DMTA) and dielectric tests to evaluate the mechanical and electrical properties of the cured samples and correlate the results with the confinement or phase separation of the ionic liquid in the epoxy network.

**Keywords:** epoxy, ionic liquids, SAOS, DMTA, sustainability

## References

[1] T.K.L. Nguyen, S. Livi, B.G. Soares, S. Pruvost, J. Duchet-Rumeau, J.F. Gérard, Ionic liquids: A New Route for the Design of Epoxy Networks, *ACS Sustainable Chemistry and Engineering* 4, 481-490 (2016).

## The role of extensional viscosity on the tacking performance of biobased adhesives

Latchmi C. Raghunanan<sup>1</sup>, Alberto Romero<sup>2</sup>, Cecilio Carrera<sup>2</sup>, Inmaculada Martínez<sup>1</sup>, Concepción Valencia<sup>1</sup> María C. Sánchez<sup>1</sup>, and José M. Franco<sup>1</sup>

<sup>1</sup> *Departamento de Ingeniería Química, Facultad de Ciencias Experimentales, Universidad de Huelva, Campus de El Carmen, Huelva 21071, Spain.*

<sup>2</sup> *Departamento de Ingeniería Química, Facultad de Química, Universidad de Sevilla, c/ Profesor García González, s/n, 41001 Sevilla*

latchmi.raghunanan@diq.uhu.es

Previously synthesized biobased polyurethane adhesives have demonstrated surprising adhesion properties in a wide range of substrates, including, but not limited to, wood, stainless steel, aluminium and glass. As part of ongoing research aimed at understanding the fundamental mechanisms of adhesion with these varied substrates, we are attempting to relate the rheology of the adhesives with their adhesive properties. Our immediate goal is to isolate the contribution of the flow properties of the adhesives from their tacking performance with the different substrates, thereby quantifying the true interfacial interactions between the adhesive and the substrate surface(s). The tacking performance between the adhesives and the different substrate surfaces will be obtained from tacking experiments using the Universal Testing Machine, and the rheological properties of the adhesives will be obtained from extensional flow experiments using the CaBER capillary extensional rheometer.

**Keywords:** polyurethane; adhesive; extensional viscosity; tack; biobased.

## Rheology of magnetic biopolymer hydrogels

Modesto T Lopez-Lopez<sup>1</sup>, Ana B Bonhome-Espinosa<sup>1</sup>, Juan DG Duran<sup>1</sup>, Victor Carriel,<sup>2</sup>

Fernando Campos,<sup>2</sup> Ismael A. Rodriguez<sup>2</sup>

<sup>1</sup> *Departamento de Física Aplicada, Universidad de Granada, Campus de Fuentenueva 18071 Granada (Spain).*

<sup>2</sup> *Departamento de Histología, Facultad de Medicina, Universidad de Granada, 18071 Granada (Spain).*

e-mail of the presenter: modesto@ugr.es

Hydrogels are 3-D networks of polymer chains in which water is the dispersion medium. These soft materials have found extensive applications in biomedicine due to their resemblance to living tissues [1]. Furthermore, hydrogels can be endowed with exceptional properties by addition of synthetic materials. For example, the inclusion of magnetic particles into biopolymer hydrogels enables the generation of biomaterials with unique magnetic field-sensitive properties [2-3].

In this work we review our recent progress in the field of the rheological characterization of magnetic hydrogels consisting of biopolymer networks of human fibrin with embedded magnetic nanoparticles, swollen by a water-based solution. Interestingly, our magnetic hydrogels presented superior rheological properties than nonmagnetic hydrogels. To be precise, the rigidity modulus, as well as the viscoelastic moduli, increased with magnetic nanoparticle content much more intensely than what is predicted by the classical theories of composite materials. This finding correlated well with electron microscopy observations, which revealed that magnetic hydrogels presented some cluster-like knots that were connected by several polymer threads. By contrast, nonmagnetic hydrogels presented a homogeneous net-like structure with only individual connections between pairs of fibrin fibres. We also investigated our magnetic hydrogels under the presence of applied magnetic fields, and found that they presented reversibly tuneable rheological properties, which constitutes a unique advantage with respect to other biomaterials. Finally, we studied the cross-linking kinetic by rheological measurements, and found that the gel point of the hydrogels was reached faster in the presence of magnetic nanoparticles. From all this, we can conclude that nanoparticles favour the cross-linking process, serving as nucleation sites for the attachment of the polymer.

**Acknowledgments:** FIS2013-41821-R (MINECO; co-funded by ERDF, EU).

**Keywords:** hydrogel, polymer, magnetic nanoparticle, cross-linking, rheology.

### References

- [1] E. Caló, V.V. Khutoryanskiy, Biomedical applications of hydrogels: A review of patents and commercial products, *European Polymer Journal*, **65**: 252–267 (2015).
- [2] M.T. Lopez-Lopez, G. Scionti, A.C. Oliveira, J.D.G. Duran, A. Campos, M. Alaminos, I.A. Rodriguez, Generation and characterization of novel magnetic field-responsive biomaterials, *PLoS ONE*, **10**: e0133878 (2015).
- [3] L. Rodriguez-Arco, I.A. Rodriguez, V. Carriel, A.B. Bonhome-Espinosa, F. Campos, P. Kuzhir, J.D.G. Duran, M.T. Lopez-Lopez, Biocompatible magnetic core-shell nanocomposites for engineered magnetic tissues, *Nanoscale*, **8**: 8138-8150 (2016).

## Magnetorheology of alginate ferrogels

Cristina Gila Vílchez<sup>1</sup>, Modesto T. López López<sup>1</sup>, Ana B. Bonhome Espinosa<sup>1</sup>, Juan D. García López-Durán<sup>1</sup>

<sup>1</sup> Department of Applied Physics, University of Granada, Avda. Fuentenueva s/n, 18017, Granada (Spain).

e-mail of the presenter: gila@ugr.es

Hydrogels are being widely studied due to their properties such as high water content, softness, flexibility and biocompatibility. Thus, they have found extensive applications as biomaterials [1]. The mechanical properties of these materials can also be controlled by an external magnetic field when magnetizable microparticles are embedded in the polymer network, obtaining magnetic-field sensitive gels called ferrogels [2]. This smart property might be used, for example, to match the mechanical properties of magnetic scaffolds to those of potential target tissues in tissue engineering applications, or in technological applications as magneto-controlled dampers, vibration and shock absorbers [3, 4]. This work focuses on the rheology of alginate hydrogels with silica-covered iron particles (Fe-CC) embedded into them. Their rheological properties have been measured in a range of different magnetic field intensities (H), finding that the storage modulus  $G'$  and the loss modulus  $G''$  increase as H is increased, as well as with the Fe-CC concentration. In particular, these ferrogels presented superior mechanical properties as compared with nonmagnetic hydrogels, being in all cases more elastic than viscous. The limit of the linear viscoelastic region (LVR) has been also determined, concluding that the LVR of the hydrogel is narrowed both by the increase in the particle concentration and in the field intensity. An optimum Fe-CC concentration has been identified, above which the hydrogels are more fragile and break at the highest H values tested. Below such Fe-CC optimum, the effect of the field on  $G'$  and  $G''$  is not as pronounced as at larger concentrations. Furthermore, in that Fe-CC optimum, a power law dependence was found between  $G'$  and H. In summary, the mechanical versatility of these ferrogels makes them attractive candidates for further development in biomedical and technological applications.

**Keywords:** Hydrogels, Rheology, Magnetorheology, Ferrogel.

### References

- [1] E. Caló, V. V. Khutoryanskiy, Biomedical applications of hydrogels: A review of patents and commercial products, *European Polymer Journal*, **65**: 252 – 267 (2015).
- [2] M. T. López-López, G. Scionti, A. C. Oliveira, J. D. G. Durán, A. Campos, M. Alaminos, I. A. Rodríguez, Generation and Characterization of Novel Magnetic Field-Responsive Biomaterials, *PLoS ONE*, **10**(7): e0133878 (2015).
- [3] M. T. López-López, I. A. Rodríguez, L. Rodríguez-Arco, V. Carriel, A. B. Bonhome-Espinosa, F. Campos, A. Zubarev, J. D. G. Durán, Synthesis, characterization and in vivo evaluation of biocompatible ferrogels, *Journal of Magnetism and Magnetic Materials*, (2016).
- [4] M. T. López-López, J. D. G. Durán, L. Y. Iskakova, A. Y. Zubarev, Mechanics of Magnetopolymer Composites: A Review, *Journal of Nanofluids*, **5**: 479 – 495 (2016).

## Morphology- rheology relationship in PET-PE-TiO<sub>2</sub> multiphasic systems: Analogies with recycled milk bottles

Leire Sangroniz<sup>1</sup>, José Luis Ruiz<sup>1</sup>, María Mercedes Fernández<sup>1</sup>, Antxon Santamaria<sup>1</sup>, Alejandro J. Müller<sup>1-2</sup>

<sup>1</sup>POLYMAT and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel de Lardizabal 3, 20018 Donostia-San Sebastián, Spain

<sup>2</sup> IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

leire.sangroniz@ehu.es

In the last few years, it has been shown that it is possible to compatibilize immiscible polymer blends adding fillers [1]. For blends with droplet matrix morphology, the addition of fillers can reduce the dispersed phase size. The presence of fillers also modifies the rheological properties of the blends. In this contribution, the addition of titanium dioxide (TiO<sub>2</sub>) to polyethylene terephthalate / low density polyethylene immiscible blends is studied, focusing on the rheological properties of the blends in continuous flow. This blend is interesting from a technological point of view, since in the last years PET bottles filled with TiO<sub>2</sub> have been introduced in the market for milk packaging. Taking into account that PET filled with TiO<sub>2</sub> is not compatible with actual PET recycling processes, an alternative solution is to recycle milk bottles with the bottle caps, usually made from polyolefins, which leads to PET/polyolefins immiscible blends with TiO<sub>2</sub> particles.

The morphological analysis revealed that for PET/LDPE blends the titanium dioxide is located preferentially at the interface. The size of the dispersed phase is reduced, which can be attributed to the barrier effect of the particles located at the interface, preventing the coalescence of the droplets, to the changes in the viscosity of the phases or to the reduction of the interfacial tension [2]. Regarding to the rheological properties, the results showed that some of the blends exhibit a viscoplastic behaviour. According to our analysis the requirements to obtain a viscoplastic behaviour are the following: a) emulsion like structure, b) the presence of TiO<sub>2</sub> particles and c) optimum size of the LDPE dispersed phase. Interestingly, the yield stress seems to be inversely proportional to the size of the LDPE droplets. Continuous flow experiments were complemented with small amplitude oscillatory shear experiments, demonstrating the effect of the morphology on the dynamic viscoelastic results in the terminal or flow region, in particular when a viscoplastic behaviour occurred.

**Keywords:** immiscible blends, nanoparticles, morphology, viscoplasticity

### References

- [1] F. Laoutid, M. Estrada, R.M. Michell, L. Bonnaud, A.J. Müller, P. Dubois, The Influence of nanosilica on the nucleation, crystallization and tensile properties of PP-PC and PP-PA blends, *Polymer*, **54**: 3982-3993 (2013).
- [2] A. Taguet, P. Cassagnau, J.M. Lopez-Cuesta, Structuration, selective dispersion and compatibilizing effect of (nano)fillers in polymer blends, *Progress in Polymer Science*, **39**: 1526-1563 (2014).



# LIST OF POSTERS PRESENTED

## POSTER SESSION 1. *Wednesday, 6 (Room 0.1)*

### FORMULATION AND PRODUCT DESIGN

- PD-P1. **A. Ares-Pernas, X. García-Fonte and M.J. Abad.** Improving thermal conductivity of alumina whisker composites by controlling the rheology and the whiskers selective location in PE/PA6 immiscible blends.
- PD-P2. **V. Perez-Puyana, I. Carreño-Carmona, L. Cabrera-Correa and A. Romero.** Study of collagen and chitosan-based 3D matrices as potential scaffolds in tissue engineering.
- PD-P3. **V. Perez-Puyana, L. Cabrera-Correa, I. Carreño-Carmona and A. Romero.** Development of collagen and chitosan-based membranes by electrospinning as potential scaffolds in regenerative medicine.
- PD-P4. **M. Jiménez-Rosado, S. Gamero-Roldán, F. Cordobés, M. Ruiz and A. Guerrero.** Development of protein-based absorbent matrices containing zinc as micronutrient for horticulture.
- PD-P5. **J. M. Aguilar, E. Álvarez, B. Sánchez, M.L. López-Castejón and F. Cordobés.** Assessment of alginate/soy protein-based porous matrices.
- PD-P6. **A. Tenorio-Alfonso, M.C. Sánchez and J.M. Franco.** Rheology and bonding performance of bioadhesives based on MDI-modified cellulose acetate and castor oil.
- PD-P7. **M. Espert, J. Borreani, I. Hernando, A. Quiles, A. Salvador and T. Sanz.** Effect of cellulose ether chemical substitution on structure of O/W emulsions during in vitro digestion.
- PD-P8. **A.A. Cuadri, F.J. Navarro, F.J. Martínez-Boza and P. Partal.** Thermo-rheological properties of polypropylene modified bitumens for paving and roofing applications.
- PD-P9. **F.J. Ortega, M. García-Morales, F. J. Navarro and M. Jasso.** Rheological properties of a model bitumen rejuvenated by DSA (dodecyl succinic anhydride).
- PD-P10. **M.A. Silva Espinoza, E. Algarra Alexandre, M. Uscanga Ramos M.M. Camacho Vidal, N. Martínez Navarrete.** Orange juice obtained from powdered freeze-dried fruit puree powder particle size and juice viscosity relationship.
- PD-P11. **M. Uscanga, M.A. Silva, M.M. Camacho and N. Martínez-Navarrete.** Viscosity of the juice obtained after the rehydration of a freeze-dried orange puree as affected by the initial water content.
- PD-P12. **A. Mejía, M.A. Martín-Alfonso, F.J. Navarro, P. Partal and F.J. Martínez-Boza.** Rheological design of sustainable fluids enhanced with nanoparticles.
- PD-P13. **L.A. Trujillo-Cayado, J.M. Franco, C. Valencia, M.C. Alfaro and J. Muñoz.** Influence of the homogenization pressure on the rheology of biopolymer-stabilized emulsions formulated with thyme oil.

- PD-P14. **L.A. Trujillo-Cayado, M.C. García, J. Santos, J.A. Carmona and M.C. Alfaro.** Effect of eco-friendly surfactant concentration on physical stability and rheological properties of green emulsions.
- PD-P15. **J. J. Ojeda-Flores and Juan F. Miravet.** Molecular gels & surfactants. NMR & rheological studies.
- PD-P16. **A.N. Gâtlan, A. Dabija, M.A. Oroian, G. Gutt, E. T. Sânduleac.** Optimization of seabuckthorn fruit powder yogurt formulation using rheological analysis.

## FOOD RHEOLOGY

- FR-P1. **C. A. Tovar, J. Borderias and B. Herranz.** Effect of high pressure processing on the rheological properties of 5% glucomannan gels at several pHs.
- FR-P2. **M.D. Alvarez, B. Herranz, I. Fernández-Jalao, C. Sánchez-Moreno and B. De Ancos.** Release of flavonols in simulated in vitro gastrointestinal digestion and its relationship with viscosity in onion and apple products and commercial quercetin supplement.
- FR-P3. **L. Piñeiro, I. Franco and C.A. Tovar.** Rheological and biochemical study of afuega'l pitu cheese (PDO).
- FR-P4. **A. Gomez Gomez, A. Chatzifragkou, P. Tosi and J. Rodriguez Garcia.** Dough mechanical properties: protein composition and salt concentration.
- FR-P5. **J. Rubio-Merino, F.J. Rubio-Hernández and A.I. Gómez-Merino.** Rheological behaviour of fruit and milk-based smoothies.
- FR-P6. **A. Bettencourt, C. Marques and L. Pinheiro.** The effect of cooking procedures on the rheological properties of olive oils.
- FR-P7. **R. Moreira, F. Chenlo, C. Silva and M.D. Torres.** Rheology of aqueous methylcellulose/tragacanth gum dispersions.
- FR-P8. **O. Carvalho, P. Fradinho, A. Raymundo and I. Sousa.** Hermetic storage of paddy rice: the impact of moisture on the rheology of the pastes.
- FR-P9. **R. Moreira, F. Chenlo, C. Silva and M.D. Torres.** Influence of sugars on the apparent viscosity enhancement of aqueous tragacanth gum dispersions.
- FR-P10. **R. Moreira, J. Sineiro, F. Chenlo, S. Arufe, H. Chiron and G. Della Valle.** Rheological properties of wheat flour dough enriched with fucus vesiculosus brown seaweed powder.
- FR-P11. **R. Moreira, J. Sineiro, F. Chenlo, S. Arufe and M.D. Torres.** Seaweed-enriched gluten-free chestnut doughs: effect of bifurcaria bifurcata addition on rheological behaviour.
- FR-P12. **E. Flores Huicochea, R. Rendón Villalobos and L.A. Cruz Amador.** Flow curve of biopolymer of chia (*Salvia hispanica L.*) with monovalent ions.
- FR-P13. **L. Pinheiro, J. Gonçalves, C. Faustino.** Viscosity profile of selected monofloral portuguese honeys.

- FR-P14. **P. Fradinho, J. Loureiro, A. Raymundo and I. Sousa.** Effect of by-products from rice industry in rheological properties of gluten-free baking doughs.
- FR-P15. **A. Raymundo, A. Morais, P. Fradinho and I. Sousa.** Rheological evaluation of gelled structures of rice flour for the production of different food products.
- FR-P16. **P. Fradinho, I. Sousa and A. Raymundo.** Psyllium husk' rheological properties for application in gluten-free pasta.
- FR-P17. **C. Arancibia, S. Fiszman and A. Tárrega.** Flow behaviour and viscoelasticity of nanoemulsions with different thickening agents.
- FR-P18. **A.P. Batista, S. Ramos, B. Archer de Carvalho, I. Sousa, A. Raymundo.** Developing innovative cheese products with *Chlorella*.
- FR-P19. **M. Espert, A. Salvador, M.J. Hernandez and T. Sanz.** In vitro stomach incubation in a rheometer.
- FR-P20. **C. Macedo, C. Nunes, A. Lima, R. Ferreira, I. Sousa and A. Raymundo.** Rheological evaluation of bread dough grown from fermented whey.
- FR-P21. **J. Rubio-Merino, E. Amate-Ruiz, A.I. Gómez-Merino, F.J. Rubio-Hernández, J.L. Arjona-Escudero and I.M. Santos-Ráez.** A comparative study of flaxseed/chia-quinoa dough: thixotropic and viscoelastic behaviour.
- FR-P22. **M.L. Quispe, S.C. Velezmoro, D.F. Vargas and I. Betalleluz-Pallardel.** Rheological and textural behaviour of fresh and frozen mashed potatoes of native yellow potatoes (*Solanum Goniocalyx*).
- FR-P23. **M. Espert, T. Sanz, M.J. Hernandez and A. Salvador.** Effect of pH and temperature in hydrocolloids and hydrocolloids based emulsions.
- FR-P24. **B. Józwiak, M. Orczykowska and M. Dziubiński.** Rheological properties of kuzu starch-galactomannan pastes.
- FR-P25. **A. Dabija, M.A. Oroian, A.M. Sidor, G.G. Codină.** Rheological characterization of yogurt with different types of fibres.
- FR-P26. **S. Benkadri, T. Sanz, A. Salvador and M. N. Zidoune.** Effect of xanthan gum on the rheological properties of toddler gluten-free biscuit dough and final biscuit quality.
- FR-P27. **M. Villanueva, S. Pérez-Quirce and F. Ronda.** Effects of acidification and exogenous proteins on rheological properties of gluten-free starch-based doughs.
- FR-P28. **J. Harasym, M. Villanueva and F. Ronda.** Effect of partial substitution of rice flour with buckwheat flour on gluten-free bread quality and rheology of dough.
- FR-P29. **S. Perez-Quirce, A. Vela, P. A. Caballero and F. Ronda.** Enrichment of gluten-free rice-based doughs with yeast and fungi (1-3)(1-6)- $\beta$ -glucans extracts.

## POSTER SESSION 2. *Thursday 7 (Room 0.1)*

### SUSPENSIONS, COLLOIDS AND GRANULAR MATERIALS

- SC-P1.** J.L. Arjona-Escudero, I.M. Santos-Ráez, A.I. Gómez-Merino and F.J. Rubio-Hernández. Rheological study of the aggregation state of alumina nanofluids.
- SC-P2.** I.M. Santos-Ráez, J.L. Arjona-Escudero, A.I. Gómez-Merino and F.J. Rubio-Hernández. Gibbs free energy of activation for viscous flow in alumina suspensions.
- SC-P3.** P. Ramírez, L. A. Trujillo<sup>1</sup>, J.A. Carmona, M.J. Martín and M.C. García. Interfacial rheology and emulsifying properties of bio-based surfactants obtained from coconut oil.
- SC-P4.** O. Shtyka, L. Przybysz, M. Błaszczuk and J. Sęk. Emulsions structure and viscosity changes during process of hydrophilic/oleophilic granular structures imbibition.
- SC-P5.** L. G. Baltazar, F.M.A. Henriques, D. Miguel and M.T. Cidade. Effects of hydrophobic additives on the rheology of hydraulic grouts.
- SC-P6.** M. F. Naccache, W. Lopez, P. R. De Souza Mendes, A. Alvarez and A. Abdu. Flow dynamics of air bubbles rising in yield stress fluids.

### PHARMACEUTICAL AND COSMETICS

- PhC-P1.** A. Nunes, J. Marto, J. Sotomayor and H.M. Ribeiro. The impact of thickeners and surfactants on the rheology of hair cleansing products.
- PhC-P2.** J. Marto, P. Prazeres, P. Pinto and H.M. Ribeiro. Sustainable exfoliators: the influence of quercus suber bark particle size on rheological properties and on in vivo efficacy.
- PhC-P3.** M. Pleguezuelos-Villa, A. Nácher, S. Mir-Palomo, M. J. Hernández, O. Vila Buso, V. Alonso Usero, A. Torrens and O. Díez-Sales. A preformulation study of hydrogels through a double crosslinking strategy.
- PhC-P4.** M. Pleguezuelos-Villa, A. Nácher, O. Díez-Sales, M. Merino-Sanjuán, D. Peris-González, M. J. Hernández and V. Merino. Rheological parameters on microstructure of topical formulations assessment.
- PhC-P5.** J.A. Picó, J. Peris, A. Sánchez, M.J. Hernández, A. Nacher and O. Díez-Sales. A comparative rheological study of several dentifrices trademarks.
- PhC-P6.** J.A. Picó, J. Peris, A. Sánchez, M.J. Hernández, A. Nacher and O. Díez-Sales. Influence of hydrated silica on rheological properties of base formulations for toothpastes.
- PhC-P7.** S. Bayarri S, J.L. Gómez J.L. and M. Alonso. Rheological properties and particle size distribution of face creams.
- PhC-P8.** M. Reis Jr, J. Reis, J. Santos, A. Almeida and V. Isaac. Photoprotective rheology: guarantee of effectiveness and safety of photoprotection.

### ADVANCES IN NEW RHEOLOGICAL AREAS

- AN-P1.** M. I. Calafel, R. H. Aguirresarobe, A. Santamaria, N. Sadaba, M. Boix, B. Pascual and I. Conde. Crucial viscoelastic features for polymer 3D printing.
- AN-P2.** R. E. D. Rudge, M. Workamp, P. de Visser, E. Scholten and J. A. Dijkman. Flowing from rheology to tribology.

## RHEOMETRY AND EXPERIMENTAL METHODS

- RE-P1. **A. Yuliestyan, A.A. Cuadri, M. García-Morales and P. Partal.** Low temperature rheological performance of modified bituminous binders.
- RE-P2. **C. Roman, C. Valencia and J. M. Franco.** On the shear-induced structural degradation of lithium and calcium lubricating greases.
- RE-P3. **M.C. García, S. Sánchez, J. Santos, M.C. Alfaro and J. Muñoz.** Remediating slip effects in the shear flow of gellan sheared gels.
- RE-P4. **C. A. Gracia Fernández and M. T. López-López.** Shear and axial measurements on magnetorheological fluids.
- RE-P5. **R. P. O. Campos, R. A. Lima and L. Campo-Deaño.** Blood analogue fluid flows in complex geometries.

## POLYMERS AND BIOPOLYMERS

- PB-P1. **I. Stanciu.** Viscosity index improvers for multi-grade oil of copolymers polyethylene-propylene and hydrogenated poly (isoprene-co-styrene).
- PB-P2. **C. Roman, M. García-Morales and T. McNally.** Can MWCNTS localize in the least favorable phase in a binary immiscible polymer blend?
- PB-P3. **L. Sangroniz, A.Sangroniz, M. Iriarte, A. Etxeberria and A. Santamaria.** Improving the properties of biodegradable poly(butylene adipate-co-terephthalate) for packaging: from processing to application.
- PB-P4. **M.L. López-Castejón, C. Carrera, M. Ruiz, J. Fuente and C. Bengoechea.** Relationship between interfacial and emulsifying characteristics of a quinoa protein concentrate.
- PB-P5. **S. Gamero, M. Jiménez, J. Fuente and C. Bengoechea.** Effect of the addition of cellulosic fibers on the physico-chemical properties of soy protein bioplastics.
- PB-P6. **M.Felix, I. Martínez, J.M. Aguilar and A. Guerrero.** Soy-based nanocomposites materials: a comparison between injection moulding and extrusion.
- PB-P7. **J.E. Martín Alfonso, C. Valencia and J.M. Franco.** Linear viscoelasticity of aqueous dispersions containing blends of tragacanth and locust bean gum polysaccharides.
- PB-P8. **I. Díaz, I. Martínez and P. Partal.** Thermo-rheological behaviour and microstructure of egg white-based biocomposites.
- PB-P9. **M.C. García, J.A. Carmona, M.J. Martín, J. Santos and M.C. Alfaro.** Rheological properties of aqueous solutions of diutan gum.
- PB-P10. **J.A. Carmona, L.A. Trujillo-Cayado, M.C. García, N. Calero and P.Ramírez.** Shear rheology of welan gum solutions.
- PB-P11. **P. Ziolkowski, P. Owczarz and M.Dziubiński.** Investigation of sol-gel phase transitions of colloidal chitosan solutions conducted by rheometric and light scattering technics.

# ABSTRACTS POSTER COMMUNICATIONS

# Improving thermal conductivity of alumina whisker composites by controlling the rheology and the whiskers selective location in PE/PA6 immiscible blends

Ana Ares-Pernas, Xoán García-Fonte, María José Abad

<sup>1</sup> *Universidade da Coruña, Grupo de Polímeros, Centro de Investigacións Tecnolóxicas, Campus de Ferrol, 15471 Ferrol, Spain*

aares@udc.es

For some electronic applications high thermal conductivity and high electrical resistivity, composites are desired. In the literature there are several attempts to achieve this goal, introducing electrically insulating fillers with high thermal conductivity, using hybrid thermal conductive fillers to reduce the filler content, etc... Moreover, in the most recent studies is pointed out that this outcome can be achieved by controlling the selectively location of fillers in a phase of the polymer blend [1].

In these work, alumina whiskers composites were melt-mixing by extrusion dispersing different amounts of electrically insulating filler, in different ratios of PE/PA6 blends. The mixing strategy, the ratio of PE/PA6 and the filler amount were well-designed with the aim to control rheology changes that it can affect the composites morphology and consequently the electrical and thermal properties [2].

The rheology characterization of designed composites was performed by small amplitude oscillatory shear experiments. With the aim to analyze the influence of PE/PA6 ratio in the rheological properties coalescence experiments were realized too. Relationships with morphology were established appropriately by electronic microscopy [3]. Using the laser flash technique, the thermal diffusivity and thermal conductivity of composites were controlled.

The ultimate aim is optimize the thermal conductivity of composites using the minor amount of filler in an immiscible polymer blend with a controlled morphology, which favours the formation of thermal conductive paths.

## References

- [1] J-P. Cao, J. Zhao, X. Zhao, F. You, H. Yu, G-H. Hu, Z-M. Dang, High thermal conductivity and high electrical resistivity of poly(vinylidene fluoride)/polystyrene blends by controlling the localization of hybrid fillers, *Composites Science and Technology*, 89: 142 – 148 (2013).
- [2] S. Zhou, W. Luo, H. Zou, M. Liang, S. Li, Enhanced thermal conductivity of PA6/PP immiscible blends with high loadings of graphite, *Journal of Composite Materials*, 50 (3): 327-337 (2016).
- [3] M. Kong, Y. Huang, Y. Lv, S. Wang, Q. Yang, G. Li, Flow induced morphological instability in nanosilica-filled polyamide 6/polystyrene blends, *Polymer*, 55: 4348-4357 (2014).

## Study of collagen and chitosan-based 3D matrices as potential scaffolds in Tissue Engineering

V. Perez-Puyana, I. Carreño-Carmona, L. Cabrera-Correa, A. Romero

*Departamento de Ingeniería Química, Facultad de Química, Universidad de Sevilla, C/ Profesor García González, 41012 Sevilla (Spain).*

e-mail of the presenter: alromero@us.es

Tissue Engineering is based on three main elements: cells, growth factors and scaffolds. A scaffold is a three-dimensional porous structure which should give a certain mechanical support for an optimal cell growth. Furthermore, this mechanical support must be maintained until the tissue formed has enough mechanical integrity and, even, the cells that make up the formed tissue must express the suitable genes in order to maintain the specific function of the tissues [1]. For that reason, the knowledge provided by Biomaterials Engineering gives the base for the development of porous 3D matrices which could act as scaffolds in Tissue Engineering.

There are several techniques to develop scaffolds. Among them, one of the most commonly used techniques consists of a freeze-drying process driven to hydrogels previously elaborated. The mechanical resistance of the scaffolds produced could be enhanced by a later heating treatment at 105°C or by the addition of a crosslinking agent. In addition, an exhaustive characterization is subjected to the scaffolds by analyzing their mechanical and structural properties. It is important to use biopolymers as collagen or chitosan as raw material because they provide biocompatibility, which is essential. Indeed, the main objective of this study is the development and characterization of collagen and chitosan scaffolds studying the influence of the conditions used (i.e. pH or the addition of a crosslinking agent like glutaraldehyde).

An increase in the polymer concentration (either collagen or chitosan) produces scaffolds with higher mechanical properties. Furthermore, scaffolds with a 50/50 collagen/chitosan ratio were produced in order to study the influence of the processing conditions on the structure and properties of the scaffolds fabricated, revealing that the conditions absolutely influence the final properties of the scaffolds.

**Keywords:** Chitosan, Collagen, Freeze-Drying, Mechanical Properties, Scaffolds

### Acknowledgements

This work is part of a research project sponsored “Ministerio de Economía y Competitividad” from Spanish Government (Ref. CTQ2015-71164-P, MINECO/FEDER, EU). The authors gratefully acknowledge their financial support. The authors also acknowledge the University of Seville for the VPPI-US grant.

### References

[1] S. Jana, B.J. Tefft, D.B. Spoon, R.D. Simari. Scaffolds for Tissue Engineering of cardiac valves, *Acta Biomaterialia*, **10(7)**: 2877-2893 (2014).

## Development of collagen and chitosan-based membranes by electrospinning as potential scaffolds in Regenerative Medicine

V. Perez-Puyana, L. Cabrera-Correa, I. Carreño-Carmona, A. Romero

*Departamento de Ingeniería Química, Facultad de Química, Universidad de Sevilla, C/ Profesor García González, 41012 Sevilla (Spain).*

e-mail of the presenter: alromero@us.es

Membranes formed by nanometric-size fibers present interesting characteristics such as a high specific surface with functionality and a greater mechanical behaviour. These properties make nanofiber materials excellent candidates in many applications: chemical, electronic, or biomedical. Considering the biomedical applications, these materials could be used as potential scaffolds for Regenerative Medicine. These membranes are processed by electrospinning, which is an innovative process that allows the continuous production of fibers with diameters in a range between 3 nm and 1  $\mu\text{m}$  [1]. It is based in the elongation of a viscoelastic solution to form a filament. The solution is projected from a syringe into a collector due to a voltage applied and the membrane is formed on the surface of the collector.

The stability of the three-dimensional structure of biopolymers (proteins and polysaccharides) does not allow the optimal formation of the continuous filament. For that reason, synthetic polymers are commonly incorporated. Thus, the aim of this study is to optimize the electrospinning process of fish collagen and chitosan systems, evaluating the incorporation of a water-soluble polymer, POE. The electrospinning process was not achieved for the systems with collagen and/or chitosan, so the synthetic polymer (POE) was included in the formulation. Systems with different POE, POE/collagen and POE/chitosan concentrations were elaborated and studied. A concentration of 3.5% POE was selected as the optimal concentration due to the properties exhibited by the solutions and fibers obtained. An increase in POE concentration leads to solutions with a higher viscosity and, consequently, worse fiber distributions.

**Keywords:** Collagen, Chitosan, POE, Electrospinning, SEM.

### Acknowledgements

This work is part of a research project sponsored "Ministerio de Economía y Competitividad" from Spanish Government (Ref. CTQ2015-71164-P, MINECO/FEDER, EU). The authors gratefully acknowledge their financial support. The authors also acknowledge the University of Seville for the VPPI-US grant.

### References

[1] S. Agarwal, A. Greiner, J.H. Wendorff. Electrospinning of Manmade and Biopolymer Nanofibers-Progress in Techniques, Materials and Applications, *Advanced Functional Materials*, **19(18)**: 2863-2879 (2009).

## Development of protein-based absorbent matrices containing zinc as micronutrient for horticulture

Jiménez-Rosado M.<sup>1</sup>, Gamero-Roldán S.<sup>1</sup>, Cordobés F.<sup>2</sup>, Ruiz M.<sup>1</sup> Guerrero A.<sup>2</sup>

<sup>1</sup> Universidad de Sevilla, Escuela Politécnica Superior, C/Virgen de África n°7, Sevilla (Spain).

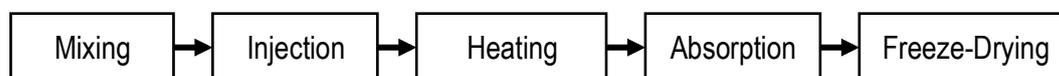
<sup>2</sup> Universidad de Sevilla, Facultad de Química, C/Profesor García González n°1, Sevilla (Spain).

e-mail of the presenter: fcordobe@us.es

Superabsorbent biopolymers (SAB) are a good example of new type of materials, being based on renewable natural components with a reasonable low cost. The aim of this work is to evaluate the potential application of protein-based absorbent materials in horticulture. Due to technological, economic and environmental benefits, these biopolymer matrices are highly attractive for the incorporation and subsequent release of micronutrients that are essential for the development and health of plants, thus avoiding the typical excesses of conventional fertilizers.

Two different procedures are assessed to introduce the selected nutrient (zinc) in a soy protein-based matrix, evaluating the mechanical properties, water uptake capacity and loading level of zinc into the matrix.

The processing stages for the preparation of SAB materials are as follows:



The nutrient is incorporated either into the absorption or mixing stages. Depending on the selected process, different water uptake capacity and rheological properties are obtained. SAB loaded with up to 25 wt% zinc sulfate may be prepared by immersion in a saturated solution of zinc sulfate and absorption followed by freeze-drying. These samples show both low rheological consistency and water absorption capacity. On the other hand, samples loaded with up to 15 wt% zinc carbonate may be obtained by introducing the nutrient into the mixing stage. Despite this lower loading level, related to an excessive rheological consistency of the blends that may impair injection moulding, this procedure leads to injected matrices with enhanced mechanical properties and water absorption capacity. In any case, this zinc content may be regarded as sufficient for the plant requirements. Besides, the overall process seems to gather more adequate conditions for their industrial application when this latter procedure is carried out. This research is part of a project financed by MINECO/FEDER, EU (CTQ2015-71164-P).

**Keywords:** biopolymers, superabsorbent, micronutrients, horticulture.

## Assessment of alginate/soy protein-based porous matrices

José M. Aguilar, Estefanía Álvarez, Beatriz Sánchez, M.L. López-Castejón, Felipe Cordobés

Dpto. de Ing. Química. Univ. de Sevilla. Fac. de Química, c/ Prof. García González s/n. 41.012 – Sevilla (Spain).

fcordobe@us.es

Natural biopolymers, including protein and carbohydrate-based polymers, usually offer improved water solubility, biocompatibility, biodegradability and increased functional capability, which make them highly attractive materials in a wide range of applications. In addition, alginate (ALG) is a low cost material, being an interesting biopolymer for medical applications (e.g. drug delivery, wound healing or scaffolds for regenerative medicine). Alginate biomaterials can be formed by ionic bonds between carboxylic groups using  $\text{Ca}^{2+}$ , thereby inducing chain-chain associations. However, mechanical resistance of these hydrogels is reduced as  $\text{Ca}^{2+}$  are exchanged by monovalent cations from the medium. The addition of soy protein isolate (SPI) could overcome the foregoing limitation, since positively charged amino groups of proteins can stabilize negatively charged alginate-based biomaterials.

The main objective of this work is focussed on the development of a porous matrix by thermo-mechanical conformation and lyophilisation of bioplastics based on ALG/SPI blends. For this it is essential to add a hydrophilic plasticizer (e.g. glycerol, GL) and carry out a fair mixing at different ALG/SPI ratios, followed by injection moulding. Finally, extraction of segregated water soluble phase of bioplastics was carried out by immersing them in aqueous medium at different  $\text{Ca}^{2+}$  contents to assess its effect on ALG/SPI matrices.

Thermomechanical analysis of these blends allows optimization of their composition and injection conditions. Moreover, due to the structuring capability of amino acids groups of SPI, different processing conditions (i.e. injection pressure and moulding temperature) are evaluated by DMTA and water absorption tests in order to optimize ALG/SPI/GL bioplastics. Finally, analysis of mechanical and morphological properties of bioplastic matrices allowed us to select the most suitable formulation and processing conditions for the subsequent development of biomaterials.

This research is part of a project financed by MINECO/FEDER, EU (CTQ2015-71164-P)

**Keywords:** Bioplastics, Porous matrices, DMTA, Alginate, Soy protein.

# Rheology and bonding performance of bioadhesives based on MDI-modified cellulose acetate and castor oil

A. Tenorio-Alfonso<sup>1</sup>, M.C. Sánchez<sup>1,2</sup>, J.M. Franco<sup>1,2</sup>

<sup>1</sup> Department of Chemical Engineering, University of Huelva, Campus El Carmen, Campus ceiA3, 21071, Huelva (Spain).

<sup>2</sup> Pro2TecS-Chemical Product and Process Technology Research Centre, University of Huelva, 21071, Huelva (Spain).

e-mail of the presenter: adrian.tenorio@diq.uhu.es

Traditionally, adhesives have been synthesized from petrochemical derivatives. However, as a consequence of the environmental consciousness, and the scarcity and unstable price of the crude, adhesive production has recently been focused on the utilization of sustainable and renewable raw materials, avoiding the release of substances which are hazardous to the environment and detrimental to the human health. Along last decades, polyurethanes have drawn the attention in the industrial production of adhesives due to its outstanding adhesion performance, along with exceptional flexibility, high resistance, etc.[1] On the other hand, cellulose derivatives and vegetable oils have been proposed to synthesize new eco-friendly alternatives to traditional polyurethanes [2, 3]. In this research, cellulose acetate was functionalized with 4,4'-diphenylmethane diisocyanate (MDI) at different NCO:OH ratios, ranging from 2 up to 4.5, and the resulting biopolymers were mixed with castor oil at 1:1 weight ratio. Afterwards, the resulting bio-based polyurethanes were left for curing. These products were rheologically characterized by applying dynamic oscillatory torsional tests at different temperatures. Moreover, their adhesion performance on metal and wood substrates was analysed by means of standardized mechanical tests studying tension loading (ASTM D906, D1002) and peel strength (ASTM D903). Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) along with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were also performed on these bio-adhesives. All systems exhibited a simple thermo-rheological behaviour within the whole temperature range studied, being able to apply the t-T superposition principle, where shift factors strongly depended on the functionalization degree. Thermal and spectroscopic analysis corroborated the complete disappearance of free isocyanate during the first few days of curing.

**Keywords:** bio-adhesive, castor oil, cellulose acetate, 4,4'-diphenylmethane diisocyanate,

## References

- [1] X. Kong, S.S. Narine. Sequential interpenetrating polymer networks produced from vegetable oil based polyurethane and poly (methyl methacrylate), *Biomacromolecules*, 9: 2221-2229 (2008).
- [2] R. Gallego, J. Arteaga, C. Valencia, J. Franco. Chemical modification of methyl cellulose with HMDI to modulate the thickening properties in castor oil, *Cellulose*, 20: 495-507 (2013).
- [3] M. Malik, R. Kaur. Mechanical and Thermal Properties of Castor Oil-Based Polyurethane Adhesive: Effect of TiO<sub>2</sub> Filler, *Advances in Polymer Technology*, (2016).

## Effect of cellulose ether chemical substitution on structure of o/w emulsions during *in vitro* digestion

M. Espert<sup>1</sup>, J. Borreani<sup>2</sup>, I. Hernando<sup>2</sup>, A. Quiles<sup>2</sup>, A. Salvador<sup>1</sup>, T. Sanz<sup>1</sup>

<sup>1</sup> Instituto de Agroquímica y Tecnología de Alimentos (CSIC), Avda. Agustín Escardino 7, 46980, Paterna, Valencia, (Spain)

<sup>2</sup> Grupo de Microestructura y Química de Alimentos, Departamento de Tecnología de Alimentos, Universitat Politècnica de Valencia, Camino de Vera s/n, 46022, Valencia, (Spain).

e-mail of the presenter: mquichu@tal.upv.es.

This work focuses on the investigation into the structural changes during the *in vitro* digestion of o/w emulsions prepared with different types of cellulose ethers. The cellulose ethers will act as emulsifiers and/or thickeners of the aqueous continuous phase, this ability being dependent on the specific cellulose chemical substitution. Emulsions containing 47% sunflower oil and water were prepared with two types of hydroxypropyl methylcellulose (HPMC) and two types of methyl cellulose (MC), with different hydroxypropyl and methoxyl content. The changes in the emulsion structure were evaluated after mouth, stomach and small intestine *in vitro* digestion by confocal laser microscopy (CLSM) and by small amplitude oscillatory shear (viscoelastic properties). A relationship was found between cellulose ether chemical substitution, initial structure and structural changes during digestion. The emulsions prepared with the cellulose ethers with highest methoxyl content (type MC (>30%M)) presented the highest viscoelasticity (before and after digestion); this was mainly associated with their greater hydrophobicity, which reduces the gelling temperature, so that the system jellified during incubation at 37°C. The total fat released from the emulsion structure after digestion is an indicator of the degree of structural resistance and its emulsifier/thickener capacity. The more resistant the structure is after digestion, the higher the physical barrier that will be exerted during digestion process. The structural resistance/physical barrier was more marked for type MC (>30%M) (a higher methoxyl content) and lower for type HPMC (M/HP:2.9) (a lower methoxyl content). In future research it would be interesting to study the relationship between cellulose ether chemical substitution, structural changes during digestion, fat bioaccessibility and fat digestion.

**Keywords:** Cellulose ethers, emulsion, rheology, structure, CLSM

## Thermo-rheological properties of polypropylene modified bitumens for paving and roofing applications

A.A. Cuadri, F.J. Navarro, F.J. Martínez-Boza, P. Partal

*Departamento de Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro2TecS), Campus de 'El Carmen', Universidad de Huelva, 21071, Huelva (Spain)*

e-mail of the presenter: frando@uhu.es

Bitumen, a by-product of fractional distillation of crude oil, can be described as a colloidal dispersion where the components of highest molecular weight, the asphaltenes, are dispersed into a medium constituted by the remaining components, the maltenes (resins, aromatics and saturates), composition commonly referred to as SARAs fractions [1]. As for its major application, virgin polymers are very useful for road pavements, and waterproofing and roofing membranes in order to improve the main distresses associated with bitumen [2]. In response to the need of reusing polymer wastes, as well as reducing the cost of the polymer modified bitumens, the influence that polymer concentration exerts on the thermo-rheological properties and microstructure of recycled polypropylene modified bitumens were considered. With this aim, blends of a 160/220 penetration grade bitumen with different recycled polymer concentrations, ranging from 2 to 50 wt.%, were prepared. The evolution of the microstructure, mechanical, thermal and rheological behavior of the different binders has been conducted by optical microscopy, tensile tests, differential scanning calorimetry (DSC) measurements, oscillatory and dynamic mechanical thermal analysis (DMTA), respectively. From the experimental results obtained, it can be deduced that recycled polypropylene concentrations up to 5 wt. % lead to enhanced rheological properties of the modified bitumen useful for paving applications. Thus, the glassy region is shifted to lower temperatures and higher viscoelasticity moduli are obtained, improving the bitumen behavior at low and high in-service temperatures, respectively. On the other hand, the development of a continuous polymer-rich phase through the bituminous binders observed for larger recycled polymer concentrations yields modified binders suitable for roofing membranes.

**Keywords:** modified bitumen, recycled polypropylene, bitumen polymer modified, roofing, paving.

### References

- [1] D. Lesueur. The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification, *Adv. Colloid Interface Sci.*, **145**:42-82 (2009).
- [2] A.A. Cuadri, P. Partal, F.J. Navarro, M. García-Morales, C. Gallegos. Influence of processing temperature on the modification route and rheological properties of thiourea dioxide-modified bitumen. *Energy Fuels*, **25**:4055-4062 (2011).

## Rheological properties of a model bitumen rejuvenated by DSA (Dodecenyl succinic anhydride)

F.J. Ortega <sup>1</sup>, M. García-Morales <sup>1</sup>, F. J. Navarro <sup>1</sup>, M. Jasso <sup>2</sup>

<sup>1</sup>*Departamento de Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro2TecS), Campus de 'El Carmen', Universidad de Huelva, 21071, Huelva (Spain)*

<sup>2</sup>*Department of Civil Engineering, Schulich School of Engineering, University of Calgary, 2500 University Drive NW, Calgary, Alberta, T2N 1N4 (Canada)*

frando@uhu.es

One of the key aspects of asphalt recycling is to revert the drawbacks of the ageing process of the bituminous binder in order to restore its original properties. However, most of asphalt rejuvenating agents that are used nowadays, merely act as softening agents by lowering the viscosity through dilution of larger and more polar molecules with a less viscous oily products [1]. Here, a new concept for binder rejuvenation is proposed with the goal of modifying the colloidal arrangement of the binder and so its microstructure by chemical bonding of a reactive surfactant (dodecenyl succinic anhydride, DSA).

In order to characterise the thermomechanical behaviour, viscous flow curves and small amplitude oscillatory shear (SAOS) tests were performed on samples with and without modifying agent.

The results reveal that the addition of DSA to a model bitumen gives rise to remarkable viscosity decrease, at 60°C, pointing out its softening or rejuvenating capability, even better than the chosen benchmark (synthetic oil). In addition, in the linear viscoelastic range, all dynamic material functions ( $G'$ ,  $G''$ ) obtained from frequency sweep tests were successfully superposed onto a master-curve at an arbitrary reference temperature [2]. By comparing the superposed curves, it may be deduced that DSA yields a drop in both elastic and viscous moduli especially at intermediate-high temperatures. Consequently, DSA makes the binder less stiff in the entire temperature interval and, then, it could be potentially used in pavement recycling.

These outcomes may be explained by esterification reactions between the anhydride group of DSA and hydroxyl groups with some polar bitumen molecules, leading to a modification of binder polarity and therefore its micellar structure.

**Keywords:** asphalt, bitumen, rejuvenation, DSA

### References

- [1] M. Zouanis R. B. Mallick, L. Poulikakos, R. Frank, Influence of six rejuvenators on the performance properties of Reclaimed Asphalt Pavement (RAP) binder and 100% recycled asphalt mixtures, *Construction and Building Materials* **71** 538–550 (2014).
- [2] G. Polacco, O. J. Vacin, D. Biondi, J. S. L. Zanzotto, Dynamic Master Curves of Polymer Modified Asphalt from Three Different Geometries. *Applied Rheology* **13** 118-124 (2003).

## Orange juice obtained from powdered freeze-dried fruit puree. Powder particle size and juice viscosity relationship

M.A. Silva Espinoza<sup>1</sup>, E. Algarra Alexandre, M. Uscanga Ramos M.M. Camacho Vidal, N. Martínez Navarrete

*Universitat Politècnica de València. Food Technology Department, Food Investigation and Innovation Group. Camino de Vera s/n, 46022, Valencia (Spain)*

masiles@doctor.upv.es

Fruits are essential components of a healthy diet, as they appear to contribute to the prevention of cardiovascular diseases and some cancers. This protection is attributed to its high bioactive compounds content that contributes to its antioxidant capacity. Nevertheless, fruits have a short shelf life related to its high water content. Freeze-drying (FD) is a dehydration method that provides high quality products. Currently, a variety of fruit juices can be found in the market, but any of them obtained from a freeze-dried puree of the fruit. In this case, the advantage of FD is that the whole edible part of the fruit can be profited so that far fewer by-products, compared to other processes with which to obtain a juice, are generated. After FD the puree, a cake is obtained which must be crushed previously to be rehydrated to obtain the desired viscosity of the juice. In this paper, the relationship between the particle size of the freeze-dried and crushed orange puree and the rheological behavior of the juice obtained after its rehydration was studied. To get the different particle sizes, crushed sample was passed through mesh opening sieves of 0.5, 0.3, 0.2 and 0.15 mm. Each of the obtained powder was rehydrated to the initial water content of the sample and the rheological behavior was characterized throughout the flow curve obtained when applying a 0 to 120 s<sup>-1</sup> shear rate sweep. The rheological behavior of two commercial orange juices was also characterized. The pseudoplastic behavior of all the samples was well fitted to the Ostwald-de-Waele model. A higher consistence index (K) of the rehydrated juices was observed when increasing the particle size. The commercial samples showed K values in the order of those achieved by the rehydrated samples obtained with the powder with the lower particle sizes. These results indicate the need to adequately adjust the particle size of the crushed cake obtained after FD when the obtained powder is going to be used for the preparation of a juice.

**Keywords:** freeze-dried orange, rheological behavior, orange juice, powder particle size

## Viscosity of the juice obtained after the rehydration of a freeze-dried orange puree as affected by the initial water content

M. Uscanga, M.A. Silva, M.M. Camacho and N. Martínez-Navarrete

*Grupo de Investigación e Innovación Alimentaria, Departamento de Tecnología de Alimentos, Universidad Politécnica de Valencia, Camino de Vera s/n, 46022 Valencia, España*

e-mail of the presenter: [masiles@doctor.upv.es](mailto:masiles@doctor.upv.es)

The benefit of fruit consumption in health has been related to the presence of various bioactive compounds. However, their seasonality and short shelf life limit their availability. In fact, fruit consumption has declined steadily in recent years, since the dietary habits of society have changed. The powdered fruit can be an alternative to promote its consumption among the population. Some advantages of this format are the greater stability of the product and the greater convenience of its handling. The fruit powder obtained by freeze-drying (FD) may be rehydrated to obtain a high quality juice. However, some characteristics of the sample prior to FD and during the process may affect the quality of the obtained juice. In this sense, the objective of the present work was to study the influence of the water content of an orange puree prior to be freeze-dried on the viscosity of the juice obtained after the rehydration of the obtained powder. Orange puree added with 5 g arabic gum and 1 g bamboo fibre per 100 g of orange pulp was used for the study. The feed inlet moisture was varied between 80 and 90 g water/100 g mix. Samples (1cm thickness) were frozen to -45 °C, at 0.096 °C/min, for 24 h. A Telstar Lyo Quest 55 freeze-drier (0.063 mbar, 24 h) was after used. Each of the obtained cakes were intensely crushed manually in a mortar to obtain a very fine and uniform powder which was rehydrated (room temperature at 800 rpm for 10 min) to the initial water content of the sample (83 g water/ 100 g mix). The flow curve of each rehydrated sample was obtained (0 to 120 s<sup>-1</sup>). An increase in the viscosity of the rehydrated juice was detected the lower the water content of the sample before FD. If the objective of producing powdered fruit is its subsequent rehydration to obtain a juice, these results indicate the interest of adjust the feed inlet moisture in the case of FD.

**Keywords:** freeze-dried orange, rheological behavior, orange juice, water content, rehydration

## Rheological design of sustainable fluids enhanced with nanoparticles

A. Mejía, M.A. Martín-Alfonso, F.J. Navarro, P. Partal, F.J. Martínez-Boza

*Facultad de Ciencias Experimentales, Universidad de Huelva. Avda Tres de Marzo s/n, Huelva (Spain)*

e-mail of the presenter: frando@uhu.es.

Drilling of deeper wells and Enhance Oil Recovery (EOR) demand a constant searching for adequate fluids to overcome the challenges associated to the extreme temperature and pressure at which these operations take place. In addition, the reduction of the environmental impact associated with these activities is a major concern for the oil industry. For dealing with these challenges the trend is the development of sustainable and environmentally friendly fluids with high efficiency at minimum cost.

Drilling fluids perform several functions such as the removal of the cuttings, the stabilization of the wellbore and the lubrication. Drilling fluid viscous behaviour is a critical issue in the success of drilling operations, particularly for drill cuttings removal. In general, the most important properties in drilling fluids are appropriate viscosity, high-shear thinning behaviour and a finite yield stress for suspending and transferring drill cuttings to the surface.

In this study different drilling fluids have been formulated using vegetable oils and nanoparticles. The rheological behaviour has been characterised using rotational rheometers equipped with pressure cells capable of running tests under pressures up to 2000 bar and 300 °C. The effect that nanoparticle nature and concentration exert on the rheological properties of these fluids, as function of temperature and pressure, has been the major criterion for developing sustainable fluid with enhanced mechanical properties.

**Keywords:** Driling fluid, high pressure, rheology

## Influence of the homogenization pressure on the rheology of biopolymer-stabilized emulsions formulated with thyme oil

L.A. Trujillo-Cayado<sup>1</sup>, J.M. Franco<sup>2</sup>, C. Valencia<sup>2</sup>, M.C. Alfaro<sup>1</sup>, J. Muñoz<sup>1</sup>

<sup>1</sup> Universidad de Sevilla, Grupo de Reología Aplicada. Tecnología de Coloides. Facultad de Química. c/ P. García González, 1, 41012, Sevilla (Spain).

<sup>2</sup> Universidad de Huelva, Grupo Ingeniería de Fluidos Complejos. Facultad de Ciencias Experimentales. Campus El Carmen, 21071, Huelva (Spain).

e-mail of the presenter: ltrujillo@us.es

We report the effects of homogenization pressure (P) and rhamosan/welan gum mass ratio (R/W) on rheological properties, droplet size distribution and physical stability of concentrated thyme oil/water emulsions containing an ecological surfactant. SAOS and steady shear flow properties of emulsions were studied using the surface response methodology. A second order polynomial equation fitted the influence of P and R/W. O/W emulsions were prepared with 30 wt% thyme oil, an essential oil which is an eco-friendly alternative to synthetic VOC compounds. These emulsions contained an ethoxylated fatty acid alkanol amide derived from rapeseed oil, as emulsifier. The gum concentration, 0.4 wt%, in the aqueous solutions of rhamosan, welan and blends of both gums were selected to ensure the formation of soft-gel matrices. Emulsions were prepared with a rotor-stator device followed by a Microfluidizer M110P.

The rheological properties studied were significantly influenced by both R/W and P. Flow curves at steady shear fitted the Cross equation and demonstrated the lack of synergism between rhamosan and welan gums, whose ratio governed the shear thinning properties of emulsions. P was the most sensitive variable for the viscosity, power law index and the frequency dependence of  $G'$  and  $G''$ . The results obtained were consistent with the occurrence of a complex network formed by a continuous phase based on the thermodynamic incompatibility of both anionic polysaccharides and the nonionic surfactant and a dispersed phase consisting of a huge number of submicron thyme oil droplets. We conclude that O/W emulsions exhibiting both small mean oil diameters ( $D_{3,2} < 1 \mu\text{m}$ ) and long-term stability against creaming can be obtained regardless of the P and R/W values used. The longest physical stability was achieved by the emulsion prepared using welan gum as stabilizer at 100 bar and 1-pass.

**Keywords:** biopolymer, emulsion, green surfactant, microfluidization, rheology

## Effect of eco-friendly surfactant concentration on physical stability and rheological properties of green emulsions

L.A. Trujillo-Cayado, M.C. García, J. Santos, J.A. Carmona, M.C. Alfaro

*Universidad de Sevilla, Grupo de Reología Aplicada. Tecnología de Coloides. Facultad de Química. c/ P. García González, 1, 41012, Sevilla (Spain).*

e-mail of the presenter: ltrujillo@us.es

In recent years, the interest in submicron emulsions has increased due to their high stability and potential applications to encapsulate and release active ingredients in many industrial fields such as food industry, pharmaceuticals or agrochemicals. Furthermore, the social demand for eco-friendly solutions to replace hazardous solvents in many dispersion formulations has steadily risen. In this study, we examined the influence of surfactant concentration on the formation and physical stability of submicron O/W emulsions using a high-pressure dual-channel homogenizer (microfluidizer). The formulation involved the use of a blend of two green solvents (*N,N*-dimethyldecanamide and  $\alpha$ -pinene) as dispersed phase and a nonionic polyoxyethylene glycerol ester derived from coconut oil as emulsifier (Levenol® C-201), which enjoys an European eco-label [1]. Therefore, these emulsions may find applications as matrices for agrochemicals. Physical stability and rheological properties of emulsions studied showed an important dependence on the eco-friendly surfactant concentration. The lowest surfactant concentration (1 wt%) was not enough to avoid recoalescence during emulsification and resulted in the onset of a creaming process after a short aging time. On the other hand, the higher surfactant concentrations (4-5 wt%) gave rise to depletion flocculation, which in turn triggered emulsion destabilization by coalescence. The optimum physical stability was exhibited by emulsions containing intermediate surfactant concentrations (2-3 wt%) since coalescence was hardly significant and the onset of a weak creaming destabilization process was substantially delayed.

**Keywords:** Emulsions, Green surfactants, Laser diffraction, Rheology

### References

[1] L.A. Trujillo-Cayado, P. Ramírez, M.C. Alfaro, M. Ruíz, J. Muñoz, Adsorption at the biocompatible  $\alpha$ -pinene–water interface and emulsifying properties of two eco-friendly surfactants. *Colloids and Surfaces B: Biointerfaces*, **122**, 623-629 (2014).

## Molecular Gels & Surfactants.NMR & Rheological Studies

Juan J. Ojeda-Flores<sup>1</sup>, Juan F. Miravet <sup>1</sup>

<sup>1</sup>Departament de Química Inorgànica I Orgànica , Universitat Jaume I, 12071 Castelló, (Spain) .

e-mail of the presenter: [jojeda@uji.es](mailto:jojeda@uji.es)

The interest in gels formed by the aggregation of low molecular weight molecules has grown exponentially in the last decade<sup>1</sup>. These molecules aggregate to produce networks that percolate the solvent and transform it into a viscoelastic material, namely into a gel<sup>2</sup>.

In this work we approach the study of a system based on the interplay of two soft matter building blocks, a surfactant (sodium dodecyl sulfate, SDS) and a molecular hydrogelator with the dual capability of forming hydrogels by itself or mixed micelles with SDS<sup>3</sup>.

In this work the strength of the hydrogels is studied considering different variables such as SDS and hydrogelator concentration. Additionally NMR diffusion studies are found to be very useful to assess the amount of hydrogelator incorporated into the SDS micelles. The results indicate that minute changes in gelator concentration may result in dramatic changes in the strength of the gels.

**Keywords:** Rheology, DOSY, hydrogelator, thixotropy, micelles.

### References

- [1] J.W. Steed, *Chem. Commun.*, **47**: 1379 – 1383 (2011).
- [2] R.G. Weiss, P.Terech, *Molecular Gels: Materials with Self-Assembled N.*, Springer, (2005).
- [3] V.J. Nebot, J.F. Miravet, *Langmuir*, **29**: 9544 – 9550 (2013).

## Optimization of seabuckthorn fruit powder yogurt formulation using rheological analysis

Anca-Mihaela Gătlan, Adriana Dabija, Mircea Adrian Oroian, Gheorghe Gutt, Elena Todosi Sănduleac

Stefan cel Mare University of Suceava, Universitatii Street, 13, Suceava (Romania).

e-mail of the presenter: anca.gatlan@fia.usv.ro

Yogurt is the most consumed dairy product around the world due to its health and nutritional properties, being noted among functional foods. Its consumption brings certain health benefits primarily due to its high content in protein, folic acid, vitamins A, B and minerals. Seabuckthorn is a unique plant, currently being cultivated in several European and Asian countries. It is included in the category of the most nutritious and vitamin-rich fruits found in the plant kingdom, on the basis of its high substance in several natural antioxidants like vitamin C, E, carotenoids, anthocyanins and phenols. The yogurt enrichment with seabuckthorn powder will enhance its nutritional quality and will also give therapeutic value to the yogurt-end product. The aim of this study was to establish the optimum proportion of seabuckthorn powder which, added in the yogurt formulation, would ensure its desirable sensory, physical and rheological properties. A Haake Mars Modular Advanced Rheometer System was used to study the rheological behavior of the yogurt samples with different amounts of seabuckthorn powder (Y-x%SBP). The hysteresis determination for Y-x%SBP was performed by submitting the samples to shear rates ranged between 0.02 and 100 s<sup>-1</sup> (ascending and descending), monitoring the variation of tension and viscosity. Hysteresis was determined as the area between the curves and adjusted to the models of Ostwald-de-Waele, Casson, Bingham and Herschel-Bulkley. The thixotropic characteristics were evaluated through viscosity analysis versus time at a constant shear rate of 100 s<sup>-1</sup>. The viscoelastic properties were studied obtaining the mechanical spectra of the Y-%SBP within the linear viscoelastic zone (G', G'' evolution in 0.01-10 Hz frequency range). The analysis carried out in this work provided an improved yogurt formulation for the manufacture of seabuckthorn powder yogurts on industrial scale.

**Keywords:** seabuckthorn, yogurt, optimum formulation, nutritional quality, health benefits

### References

- [1] M. Selvamuthukumar, F. Khanum, Optimization of seabuckthorn fruit yogurt formulation using response surface methodology, *J. Food Science and Technology*, **52(2)**: 831–839 (2015).
- [2] H.H. Gahrue, M.H. Escandari, G. Mesbahia, M. A. Hanifpour, Scientific and technical aspects of yogurt fortification, *Food Science and Human Wellness*, **4**: 1–8 (2015).
- [3] T. Mathias, I. Carvalho Junior, C. Carvalho, E. Sérvulo, Rheological characterization of coffee-flavored yogurt with different types of thickener, *Alimentos e Nutrição Araraquara*, **22(4)**: 521-529 (2011).
- [4] A. Gunenc, C. Houry, C. Legault, H. Mirrashed, J. Rijke, F. Hosseinian, Seabuckthorn as a novel prebiotic source improves probiotic viability in yogurt, *LWT - Food Science and Technology*, **66**: 490-495 (2016).

## Effect of high pressure processing on the rheological properties of 5% glucomannan gels at several pHs

C. A. Tovar<sup>1</sup>, J. Borderías<sup>2</sup>, B. Herranz<sup>2</sup>

<sup>1</sup>Faculty of Science of Ourense. As Lagoas s/n, 32004 Ourense (Spain)

<sup>2</sup> Institute of Food Science, Technology and Nutrition (ICTAN-CSIC), José Antonio Nováis 10, 28040 Madrid (Spain)

tovar@uvigo.es

The objective of this research is to study the effect of high hydrostatic pressure (HHP=400 MPa) on the viscoelastic and thermo-rheological properties of 5% glucomannan (GM) gels at three pHs: pH=5.2 (native GM); pH=9.1 (GM weakly deacetylated) and pH=11 (GM completely deacetylated). The samples analysed were: control C0 (pH=5.2 and 0 MPa), A0 (pH=9.1 and 0 MPa), B0 (pH=11 and 0 MPa), C400 (pH=5.2 and 400 MPa), A400 (pH=9.1 and 400 MPa), B400 (pH=11 and 400 MPa).

400 MPa produced significant differences in stress ( $\sigma_{max}$ ) and strain ( $\gamma_{max}$ ) amplitudes at pHs= 5.2 and 11. Specifically, at pH=5.2, in C400  $\sigma_{max}$  and  $\gamma_{max}$  were higher than those of C0, while at pH=11  $\sigma_{max}$  and  $\gamma_{max}$  in B400 were lower than those in B0 at frequency 1Hz, being the complex modulus ( $G^*$ ) independent of HHP at both pHs with significantly greater values at pH=11. These data seems to indicate that when GM is in native state HHP=400 MPa improved the structural stability and bond's flexibility in the gel network, maintaining the same degree of intermolecular packing and consequently the network density. Conversely, when GM was completely deacetylated, 400 MPa significantly reduced both  $\sigma_{max}$  and  $\gamma_{max}$ , increasing somewhat the level of intermolecular order which is evidenced in the higher values of ideal-network fraction in B400 vs B0, from mechanical spectra at all frequency range. The main role of the alkalisation process (pH=11) was also reflected in thermal gelation profiles, specifically the greater and constant  $G'$  moduli up to 65 °C and in the  $G''$ -peak at 75 °C for B0 gel, suggests a thermal transition which could be associated to "glass transition" ( $T_g$ ), based on the analogy with the thermal response of partially crystalline polymers [1]. In this case 400 MPa reinforced the crystalline regions, increasing slightly  $G'$  moduli in the plateau zone and shifting  $T_g$  at higher values.

**Keywords:** native deacetylated glucomannan high pressure

### Reference

[1] HM. Moreno, B. Herranz, AJ. Borderías, CA. Tovar, Effect of high pressure treatment on the structural, mechanical and rheological properties of glucomannan gels, *Food Hydrocolloids* 60, 437–444 (2016).

## Release of flavonols in simulated *in vitro* gastrointestinal digestion and its relationship with viscosity in onion and apple products and commercial quercetin supplement

M.D. Alvarez, B. Herranz, I. Fernández-Jalao, C. Sánchez-Moreno, B. De Ancos

*Institute of Food Science, Technology and Nutrition (ICTAN-CSIC), José Antonio Novais 10, Madrid 28040, (Spain).*

mayoyes@ictan.csic.es

Onion and apple are recognized as the major dietary sources of the flavonol quercetin. The benefits on human health attributed to quercetin and quercetin derivatives consumption depends on their bioavailability. The first step for bioavailability is the release of the bioactive compounds from the food matrix known as bioaccessibility. Simulated *in vitro* digestion represents a good system to understand the interaction food matrix-bioactive compound and its performance during human gastrointestinal digestion [1]. The aim of this work was to study the release of flavonols in onion and apple products and in a commercial quercetin supplement throughout *in vitro* gastrointestinal digestion (GID) using a Dynamic Gastrointestinal Digester and its relationship with the viscosity changes in the different digestion phases. For that, flavonols release and viscosity changes at all GID phases (non-digested-ND, oral phase-OP, gastric digest-GD and intestinal digest-ID) of the three samples were studied. The changes in backscattered light monitored in time with a Turbiscan were also measured. The digests in the stomach (acidic conditions) presented more physical stability than in the small intestine (alkaline conditions). A progressive decrease in total flavonols was observed in onion and quercetin supplement from ND to ID phases meanwhile a significant increase in total flavonols released were observed in GD and ID phases of apple. Therefore, apple product presented the higher bioaccessibility (59.72%) followed by onion (16.55%) and quercetin supplement (4.12%). At the same time, a decrease in  $K$  (consistent coefficient) and  $\eta_{a,10}$  (apparent viscosity at shear rate of  $10 \text{ s}^{-1}$ ) values was observed for onion and apple from ND to ID. However, in commercial quercetin,  $K$  and  $\eta_{a,10}$  values were similar among different GID phases and much lower than those in onion and apple. The evolution of the viscosity and backscattered light throughout *in vitro* GID can be related with the release of flavonols.

**Keywords:** *in vitro* digestion, viscosity, flavonols, bioaccessibility, physical stability

### References

[1] T. Sanz, H. Luyten, Effect of thickening agent in the *in vitro* mouth, stomach and intestine release of tyrosol from enriched custards, *Food Hydrocolloids*, **20**:703–711 (2006).

## Rheological and biochemical study of Afuega'l Pitu cheese (PDO)

L.Piñeiro<sup>2</sup>, I.Franco<sup>1</sup>, C.A.Tovar<sup>2</sup>

<sup>1</sup> Área de Tecnología de Alimentos, Facultad de Ciencias, Universidad de Vigo, Ourense (Spain).

<sup>2</sup> Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Vigo, Ourense (Spain).

tovar@uvigo.es

Afuega'l Pitu is a Protected Denomination of Origin (PDO) cheese made in Asturias (northern Spain) from pasteurized cow milk by predominantly acid coagulation. The aim of this study was to analyze the viscoelastic and biochemical parameters of *Atroncau blancu* cheese variety, ripened for 30 days. Eight cheeses (P1–P8) of commercial producers were studied. It was found that samples P1, P2, P3, P4 and P6 exhibited similar values of stress ( $\sigma_{max} = 570 \pm 57$  Pa) and strain amplitude ( $\gamma_{max} = 0.289 \pm 0.030\%$ ). However, P5 showed the highest  $\sigma_{max}$  ( $1003 \pm 100$  Pa) and a low value of  $\gamma_{max}$  ( $0.257 \pm 0.023\%$ ), while P7 and P8 reached the lowest  $\sigma_{max}$  values ( $324 \pm 32$  and  $167 \pm 17$  Pa, respectively) with high and similar  $\gamma_{max}$  values than those of P1–P6. Mechanical spectra were analyzed using the power law fit parameters of storage ( $G_0'$ ) and loss ( $G_0''$ ) moduli at 1 rad/s and 20, 50 and 75 °C. Specifically at 20 °C it was observed the highest values of  $G_0'$  and  $G_0''$  for P5, indicating that the P5 network is formed by the most rigid and compact casein matrix, in agreement with its brittle structure (low  $\gamma_{max}$ ). Conversely, P7 and P8 samples showed lower  $G_0'$  and  $G_0''$  parameters than the others, indicating a softer structure in line with the more deformable network (high  $\gamma_{max}$ ). These results could be explained based on the moisture:protein ratio (MPR), which is the lowest for P5, promoting a greater casein packing, while for P7 and P8 MPR was the highest, producing weaker casein gels. At 50 °C all samples exhibited constant loss factors ( $\tan\delta$ ) from 0.6 to 6 rad/s and then increased with frequency up to 63 rad/s. Nevertheless, at 75 °C  $\tan\delta$  decreased at greater time scale (low frequencies) indicating a shear-induced gel formation [1]. This fact reflects that casein denaturation could promote new intermolecular rearrangements which are ordered under shear oscillation at greater time scale, resulting in more solid-like casein matrix. A factor analysis determined that  $\gamma_{max}$ ,  $G_0'$ ,  $G_0''$  and MPR parameters were the ones which best determined differences among samples.

**Keywords:** acid coagulation, viscoelastic properties, Afuega'l Pitu cheese

### References

[1] R.G. Larson. The Structure and Rheology of Complex Fluids, Oxford University Press, Inc., Chapter, 5 (1999).

## Dough mechanical properties: protein composition and salt concentration

Angela Gomez Gomez<sup>1</sup>, Afroditi Chatzifragkou<sup>1</sup>, Paola Tosi<sup>2</sup>, Julia Rodriguez Garcia<sup>1</sup>

<sup>1</sup> *Department of Food and Nutritional Science, School of Chemistry, Food and Pharmacy, University of Reading, Whiteknights, P.O. Box 226, Reading RG6 6AP (United Kingdom.)*

<sup>2</sup> *Department of Crop Production, School of Agriculture, Policy and Development, University of Reading, Whiteknights, P.O. Box 226, Reading RG6 6AP (United Kingdom).*

j.rodriguezgarcia@reading.ac.uk

High levels of salt intake are associated with hypertension, and another related diseases. Processed foods have a major impact on the total amount of salt consumed by the population. Reformulation of products must be technically feasible and safe, and their taste must remain acceptable to consumers. This approach continues to be extremely challenging for food scientist and technologist. This project primarily addresses the research challenge of understanding the molecular interactions between sodium chloride and wheat proteins, and how they define dough and bread quality. This research will underpin future optimisation of the bread formulation through flour selection and sodium reduction. For this purpose, two types of wheat flour were used; the wheat proteins were analysed by SDS-PAGE (2); and the effect of different sodium chloride concentrations in the extensibility properties of gluten were examined with the Kieffer rig. To calculate the stress and the relative deformation rate of the gluten and dough samples, the extensibility results were related to fundamental rheological parameters by the use of formulas derived from the geometry formed by the Kieffer rig and the dough piece (1). The gluten samples from both flours did not shown significant differences in their mechanical properties. Therefore, gluten composition is not one of the main factors affecting dough extensibility. However, when a commercial bread making procedure was applied significant differences were observed between doughs (3), depending on the flour and the salt concentration used. Dough elaborated with Champion flour and the highest concentration of salt (0.9 %) showed a higher resistance to extension. Regarding to the extensibility, both flour doughs with no salt, had the lowest values of extensibility. So, it is hypothesis that the salt concentration has a bigger effect on dough rheological properties than gluten composition.

Keywords: salt, gluten, dough, extensibility, rheological properties

### References

- [1] B Dunnewid, E.L. Sliwinski, K. Grolle and T. Van Vliet, *The Kieffer dough and gluten extensibility rig - An experimental evaluation*. Journal of Texture Studies, 34: 537-560 (2003).
- [2] N. K. Singh, K. W. Shepherd, G. B. Cornish.. *A simplified SDS-PAGE procedure for separating LMW subunits of glutenin*. Journal of Cereal Science, 14: 203-208 (1991).
- [3] B. J. Dobraszczyk and M. P. Morgenstern. *Rheology and the breadmaking process*. Journal of Cereal Science, 38: 229-2452003.

# Rheological behaviour of fruit and milk-based smoothies

J. Rubio-Merino<sup>1</sup>, F.J. Rubio-Hernández<sup>2</sup>, A.I. Gómez-Merino<sup>2</sup>

<sup>1</sup> Unidad Docente Multiprofesional de Atención Familiar y Comunitaria Distrito Málaga-Guadalhorce, Málaga (Spain)

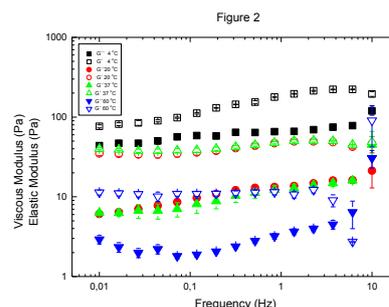
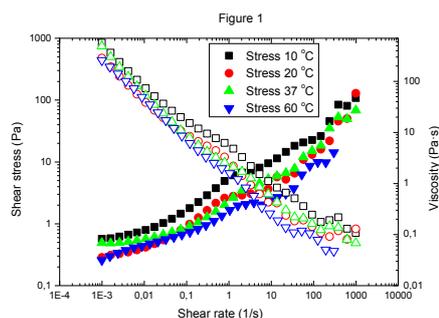
<sup>2</sup> Departamento de Física Aplicada II, Universidad de Málaga, Málaga (Spain)

e-mail of the presenter: fjrubio@uma.es

Two of the most important food attributes for today's fast-moving lifestyle are convenience and healthiness [1-2]. Smoothies, which are blended beverages, are a good example of convenient and healthy food. So, they are gaining increasing market leverage in the beverage sector. Texture and rheological behaviour of foods can determine their acceptability. Therefore, added to nutritious features, smoothies must also account with outstanding mechanical properties. Stability of the products is also a main quality, which can be gained adding a small amount of stabiliser to beverage formulations. But, to avoid opposite effects, stabilizers addition should ameliorate the product texture.

The effects of xanthan gum on the rheological properties of some fruit and milk-based smoothie beverages have been studied. Emphasis is placed on the evaluation of viscous and viscoelastic characteristics.

All samples exhibited shear thinning behaviour with a clear influence of the temperature and proportion and type of the fruit used to obtain the smoothies (Figure 1). The specific dependence of the storage modulus and loss modulus as function of frequency in the linear viscoelastic region was interpreted as gel behaviour in all cases (Figure 2).



**Keywords:** Food Rheology, Smoothies, Beverages.

## References

- [1] Verbeke W., Scholderer J., Lähteenmäki L. Consumer appeal of nutrition and health claims in three existing product concepts, *Appetite*, **52**:684-692 (2009).
- [2] Williams E., Stewart-Knox B., Rowland I. A qualitative analysis of consumer perceptions of mood, food and mood-enhancing functional foods, *Journal of Nutraceuticals, Functional & Medical Foods*, **4**:61-83 (2004).

# The effect of cooking procedures on the rheological properties of olive oils

A. Bettencourt<sup>1</sup>, C. Marques C<sup>1</sup>, L. Pinheiro<sup>1</sup>

<sup>1</sup>Research Institute for Medicines (iMed.Ulisboa), Faculty of Pharmacy, Universidade de Lisboa, Av. Prof Gama Pinto, Lisboa (Portugal)  
asimao@ff.ulisboa.pt

*Introduction:* Extra virgin olive oil (EVOO) is a part of mediterranean diet and it is a key bio-active food for its health beneficial effects [1]. It is often used in different cooking techniques such as frying. However, the high temperatures and the repeated heating cycles associated with frying can lead to chemical changes (e.g. oxidation) which may impair EVOO nutritional properties. While frying is the most studied cooking method, studies dealing with the EVOO subject to other conditions (e.g. soup preparation and stewing, using temperatures around 100°C) are less common. Among the different quality properties, viscosity of EVOO can be indicative of microstructural changes and allow understanding in more detail the mechanisms of olive oil degradation after thermal treatment in distinct cooking processes.

*Aim:* Analyse the effect of temperature on the rheological behaviour of 5 Portuguese EVOO (before and after different simulated cooking conditions).

*Methodologies:* Rheological properties were measured using a digital viscometer (Brookfield DV II+). EVOO were heated at 3 different temperatures (60, 100 and 180 °C) for 30 min. Additionally, for the processing at 180 °C, the samples were reheated 3 times to simulate the reuse of the frying oils.

*Results:* All samples exhibited a newtonian behaviour and no thixotropic effects were observed. On the other hand, a decreased in dynamic viscosity as a function of temperature was observed. Flow activation energies showed slightly differences among samples in terms of temperature sensibility. The rheological evaluation showed that subjecting EVOO to different cooking temperatures resulted in significant viscosity changes.

*Conclusion:* The simplest cooking techniques (low temperatures, no reheat) did not changed significantly the viscosity of EVOO while more aggressive techniques (high temperatures), such as frying caused significant changes.

**Keywords:** extra-virgin olive-oil, frying, activation energy, newtonian, thixotropy

## References

[1] A. Abedinzadeh, M. Last Torbati, S. Azadmard-Damirch, Some Qualitative and Rheological Properties of Virgin Olive Oil-Apple Vinegar Salad Dressing Stabilized With Xanthan Gum. *Adv Pharm Bull*, **6(4)**: 597-606 (2016).

## Rheology of aqueous methylcellulose/tragacanth gum dispersions

R. Moreira, F. Chenlo, C. Silva, M.D. Torres

*Department of Chemical Engineering, Universidade de Santiago de Compostela, rúa Lope Gómez de Marzoa, Santiago de Compostela, E-15782 (Spain).*

e-mail of the presenter: mariadolores.torres.perez@usc.es

The interactions understanding between biopolymers in food and non-food formulations is critically relevant in order to control the rheological, mechanical, structural characteristics and storage stability of the derived products, especially important for those biopolymers with complex features, as tragacanth (T) [1, 2]. The main aim of this work is to explore the rheological behaviour of aqueous methylcellulose/tragacanth (MC-T) dispersions at different gum ratios and temperatures below the gel formation temperatures, which is critically relevant in industrial application processes.

Two independent stock aqueous MC solution (20 g L<sup>-1</sup>) and T dispersion (10 g L<sup>-1</sup>) were prepared in order to obtain systems with comparable apparent viscosities. MC-T dispersions were prepared at different polymer ratios 0:100, 0.25:0.75, 0.5:0.5, 0.75:0.25 and 100:0 and were kept at 4°C at least 12 h before rheological tests. Steady-shear and dynamic rheological tests in a wide range of shear rate (0.1-300 s<sup>-1</sup>) and angular frequency (0.1-62.8 rad s<sup>-1</sup>) at different temperatures (5-35°C) were conducted on a controlled stress rheometer, at least on triplicate.

The apparent viscosity exhibited a Newtonian plateau for pure MC solutions dependent on temperature, whereas pure T dispersions exhibited a strong shear thinning behaviour, with a variation on apparent viscosity about three orders of magnitude at the studied shear rate and temperature ranges. Three different rates of decrease of apparent viscosity with shear rate were identified. MC-T dispersions exhibited a predominant MC effect on apparent viscosity at low shear rates, decreasing the strong shear thinning behaviour of T samples. All samples exhibited predominantly viscous behaviour ( $G'' > G'$ ) at the studied angular frequency and temperature ranges. Experimental data sets were successfully modelled using Cross-Williamson and Maxwell models, being the dependence with temperature established by Arrhenius functions. Cox-Merz rule was evaluated for all samples.

**Keywords:** apparent viscosity, Cox-Merz, hydrocolloid, viscoelasticity

### References

- [1] Farzia, M., Yarmanda, M.S., Safaria, M., Emam-Djomeha, Z., Mohammadifar, M.A., Gum tragacanth dispersions: Particle size and rheological properties affected by high-shear homogenization. *Int. J. Biol. Macromol.* 79, 433-439 (2015).
- [2] Chenlo, F., Moreira, R., Pereira, G., Silva, C., Rheological modelling of binary and ternary systems of tragacanth, guar gum and methylcellulose in dilute range of concentration at different temperatures. *LWT - Food Science and Technology*, 42, 519-524 (2009).

## Hermetic storage of paddy rice: the impact of moisture on the rheology of the pastes

Otilia Carvalho, Patrícia Fradinho, Anabela Raymundo, Isabel Sousa

*LEAF-Linking Landscape, Environment, Agriculture and Food, Instituto Superior de Agronomia, Universidade de Lisboa. Tapada da Ajuda, 1349-017 Lisboa (Portugal).*

e-mail of the presenter: [isabelsousa@isa.ulisboa.pt](mailto:isabelsousa@isa.ulisboa.pt)

Rice is a seasonal crop and storage is very important for year round availability. After harvesting, drying is the most critical operation. Delays in drying, incomplete drying or ineffective drying might reduce grain quality and result in considerable economic losses. The flux of the grain can surpass the drying capacity resulting in difficulties to dry the cereal properly. The aim of this study was to evaluate the impact of the hermetic environmental conditions during a storage period of four months, at three different relative humidity, on the paddy rice quality, through the evaluation of the rheology behavior of rice pastes.

Trials were carried using hermetic bags GrainPro® SuperGrainbag® Farm™ (Philippines) to store two rice varieties: japonica and indica, under three different relative humidity:  $67.5 \pm 0.5\%$ ,  $74.5 \pm 1.5\%$  and  $85.5 \pm 1.5\%$ , at a temperature of  $14.2 \pm 0.1^\circ\text{C}$ , both monitored by Hobo® Data loggers, with the probe inside the bags. Checkpoint II Portable O2 and CO2 Gas Analyzer was used at the top and at the bottom of each bag. At the end of the trials, paddy samples were unshelled and milled, and respective flour was used to measure water activity ( $a_w$ ) using HygroPalm HP23, Rotronic (Bassersdorf, Germany) and to prepare pastes for rheological tests. Aqueous rice pastes 1/10 (w/w) were prepared, 5min under magnetic stirring, and SAOS tests were performed according to previously optimized conditions [1] on a MARS III - controlled-stress rheometer (Haake), using a 35 mm serrated parallel plates and 0.5 mm gap.

There was no significant differences ( $p < 0.005$ ) on  $a_w$  values between the two varieties:  $0.486 a_w$  at  $67.5 \pm 0.5\%$  RH and  $0.576 a_w$   $85.5 \pm 1.5\%$  RH, which are secure values to prevent noxious agents. There was significant differences on gas content for the different RH storage values:  $67.5\%$  (20.4% O2 and 1.2% CO2),  $74.5\%$  (18.5% O2 and 3.7% CO2) or  $85.5 \pm 1.5\%$  (5.9% O2 and 18.9% CO2) indicating a slow respiration rate with a slight increase with RH. When looking at the rheology data it can be seen that there was no relevant differences in the viscoelastic parameters for the hermetically closed and the reference at the same moisture (12% in the grain). For increasing moisture in hermetically closed packed paddy rice, an important decrease on the viscoelastic functions of the respective rice pastes was observed which is consistent with the increase on respiration rate. The physiologic respiration is related with enzymatic activity that leads to depolymerization of the starch polymer with a negative impact on the development of the pastes structure.

**Keywords:** rice, hermetic storage, rheology of rice pastes

### References

[1] Torres, M.D., Raymundo A., Fradinho, P., Sousa, I. Thermorheological and textural behaviour of gluten-free gels obtained from chestnut and rice flours. *Food and Bioprocess Technology: An International Journal*. 7. (4): 1171-1182. (2014).

# Influence of sugars on the apparent viscosity enhancement of aqueous tragacanth gum dispersions

R. Moreira, F. Chenlo, C. Silva, M.D. Torres

*Department of Chemical Engineering, Universidade de Santiago de Compostela, rúa Lope Gómez de Marzoa, Santiago de Compostela, E-15782 (Spain).*

e-mail of the presenter: mariadolores.torres.perez@usc.es

Nowadays, the consumers' demand for food products enriched with natural biopolymers such as tragacanth is increasing. The knowledge of their interplay with commonly used ingredients such as sugars using rheological techniques is a relevant factor in the industrial processing [1], which has been included in the characterisation particularly of new polysaccharides and starches. The main aim of this work is to study the effect of sucrose (S) and glucose (G), over a wide range of concentration and temperature, on the apparent viscosity of aqueous tragacanth gum (T) dispersions.

A stock T (2.5 g L<sup>-1</sup>) was prepared following the protocol established in the literature [2]. The sugar/water ratio (*i.e.* S or G) ranged from 0 to 0.40 (w/v). G and S, previously dissolved in distilled water were added to the stock T with stirring at 1400 rpm for 30 min at room temperature. Steady-shear rheological measurements in a wide range of shear rate (1 - 1000 s<sup>-1</sup>) at different temperatures (from 5 to 65°C) were conducted at least on triplicate on a controlled stress rheometer.

The sugars addition had a noticeable enhancement effect on the apparent viscosity of T. By adding S, the viscosity enhancement led to a plateau upon intermediate shear rates (> 1 s<sup>-1</sup>) shifted (up to 10 s<sup>-1</sup>) with S content and temperature increases. Likewise, the G addition promoted an apparent viscosity peak in a narrow shear rates interval (from 1 to 10 s<sup>-1</sup>) depending on G concentration and temperature. Energy of activation for viscous flow at different shear rates indicated that apparent viscosity varied strongly with temperature at low shear rates, and this behaviour was sharper in the presence of sugars and particularly with G. These results point out the specific interplay of each sugar/biopolymer and consequently the rheological behaviour of biopolymers in the presence of other commonly used sugars, syrups, sweeteners, etc. should be studied.

**Keywords:** biopolymer, glucose, rheology, sucrose, temperature

## References

- [1] Yousefi, A.R., Eivazlou, R., Razavi, S.M.A. Steady shear flow behaviour of sage seed gum affected by various salts and sugars: Time-independent properties. *International Journal of Biological Macromolecules*, 91, 1018–1024 (2016).
- [2] Chenlo, F., Moreira, R., Silva, C., Steady-shear flow of semidilute guar gum solutions with sucrose, glucose and sodium chloride at different temperatures. *Journal of Food Engineering*, 107, 234-240 (2011).

# Rheological properties of wheat flour dough enriched with *Fucus vesiculosus* brown seaweed powder

R. Moreira<sup>1</sup>, J. Sineiro<sup>1</sup>, F. Chenlo<sup>1</sup>, S. Arufe<sup>1</sup>, H. Chiron<sup>2</sup>, G. Della Valle<sup>2</sup>

<sup>1</sup>Chemical Engineering Dept., Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain.

<sup>2</sup>INRA, UR 1268 Biopolymères Interactions Assemblages (BIA), 44 316 Nantes, France.

e-mail of the presenter: [ramon.moreira@usc.es](mailto:ramon.moreira@usc.es)

The recent classification of *Fucus vesiculosus* (FV) seaweed as “novel food” by The European Commission of European Union makes very interesting the study of this seaweed as a food ingredient for wheat bread. However, the use of ingredients can modify final bread texture as consequence of alterations on dough rheological properties and processing behaviour. This makes necessary the study of these properties when FV is added to wheat flour to obtain suitable doughs for wheat bread obtaining.

A formulation based on wheat flour, fresh yeast (2% flour basis, f.b.), salt (1.8% f.b.) and ascorbic acid (0.002% f.b.) supplemented with different amounts of FV powder (2, 4, 6 and 8% f.b.) was employed to obtain enriched doughs after mixing in a spiral mixer (Hobart planetary mixer N50CE). Elongational behaviour of dough was determined at large bi-extensional deformations by Lubricated Squeezing Flow (LSF) tests following an established protocol [1]. Thermomechanical properties of doughs were studied by Dynamic Mechanical Thermal Analysis (DMTA) using a controlled stress rheometer (MCR 301, Anton Paar) with parallel plates (50 mm diameter, 2 mm gap). Experiments were performed inside the linear viscoelastic region (1 Hz, 0.1% strain). Temperature was increased from 25 to 115°C at constant heating rate (3°C/min).

FV powder addition significantly increased dough elongational viscosity. Consistency index (K) values varied from 6.6 to 22.1·10<sup>3</sup> Pa·s<sup>n</sup> and the flow index (n) values varied in a narrower interval (0.24-0.29) indicating a clear shear-thinning behaviour of doughs. The increase of consistency could be explained by the physical action of FV particles that could play a filler-like effect in the dough matrix [2]. Large values of elongational viscosity were coincident with low  $G'_{max}/G'_{min}$  values measured by DMTA that indicate a high structuration of dough gluten network [1]. In our case, such mechanism is still questionable because solid particles, like FV powder, are better known to preclude the formation of gluten network either by competing for available water or because of steric hindrance. Taking into account the rheological changes of enriched doughs compared to typical wheat flour dough the use of FV as ingredient in breadmaking seems to be feasible from a technological point of view.

**Keywords:** seaweed, wheat, bread, LSF, DMTA

## References

- [1] A. Turbin-Orger, A. Shehzad, L. Chaunier, H. Chiron, G. Della Valle. Elongational properties and proofing behaviour of wheat flour dough, *Journal of Food Engineering*, **168**: 129-136 (2016).
- [2] M. Bonnard-Ducasse, G. Della Valle, J. Lefebvre, L. Saulnier. Effect of wheat dietary fibres on bread dough development and rheological properties, *Journal of Cereal Science*, **52**: 200-206 (2010).

## Acknowledgements

The authors acknowledge the financial support of the Ministerio de Economía y Competitividad of Spain and FEDER (CTQ 2013-43616/P).

# Seaweed-enriched gluten-free chestnut doughs: effect of *Bifurcaria bifurcata* addition on rheological behaviour

Ramón Moreira, Jorge Sineiro, Francisco Chenlo, Santiago Arufe, María Dolores Torres

*Chemical Engineering Dept., Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain.*

e-mail of the presenter: ramon.moreira@usc.es

Given the increasing demand of gluten-free products adequate for people with coeliac disease, the development of original formulations of these kinds of products is necessary. In this sense, brown seaweed *Bifurcaria bifurcata* (BB), commonly found in Europe on the Atlantic coast, is suitable for human consumption [1]. It can be employed in gluten-free formulations based on chestnut flour, a typical autochthonous Galician raw material, to improve nutritional and antioxidants properties. The main aim of this work is to study the effect of BB addition on rheological properties of chestnut flour doughs.

A gluten-free formulation (control) based on chestnut (*Castanea sativa*) flour, 2% of guar gum (flour basis, f.b.) and 1.8% f.b. of sodium chloride was supplemented with different amounts of BB dried powder (3, 6 and 9% f.b.) and mixed in a laboratory kneader to obtain seaweed-enriched chestnut flour doughs with similar consistency ( $1.10 \pm 0.07$  Nm). Rheological and thermomechanical analyses were carried out by means of Creep-Recovery (C&R), Small Amplitude Oscillatory Shear (SAOS) tests (30°C) and Dynamic Thermal Mechanical Analysis (DMTA) (30-180°C) following established protocols [2, 3].

BB addition increased water absorption of doughs to obtain similar consistencies. SAOS tests showed that  $G'$  and  $G''$  values increased in a similar manner with increasing angular frequency.  $G'$  values were larger than  $G''$  indicating that elastic proportion was dominant over the viscous one, a typical trend observed in gluten-free doughs [2]. Addition of BB > 6% significantly increased  $G'$  values. C&R results revealed similar viscoelastic behaviours of doughs. However, doughs with BB > 6% significantly increased zero shear viscosity and DMTA tests indicated significant drop of peak temperature of starch gelatinization. These rheological trends of dough properties with BB addition allow establishing the threshold BB content in order to enrich chestnut doughs without modifications on the rheological properties of control samples.

**Keywords:** creep-recovery, DMTA, starch, viscoelasticity.

## References

- [1] E. Gómez-Ordóñez, A. Jiménez-Escrig, P. Rupérez. Dietary fibre and physicochemical properties of several edible seaweeds from the north western spanish coast. *Food Research International* 43: 2289-2294 (2010).
- [2] R. Moreira, F. Chenlo, S. Arufe, S. N. Rubinos. Physicochemical characterization of white, yellow and purple maize flours and rheological characterization of their doughs. *Journal of Food Science and Technology* 52: 7954-7963 (2015).
- [3] R. Moreira, F. Chenlo, S. Arufe. Starch transitions of different gluten free flour doughs determined by dynamic thermal mechanical analysis and differential scanning calorimetry. *Carbohydrate Polymers* 127: 160-167 (2015).

## Acknowledgements

The authors acknowledge the partial financial support of the Ministerio de Economía y Competitividad of Spain and FEDER (CTQ 2013-43616/P).

## Flow curve of biopolymer of chia (*Salvia hispanica* L.) with monovalent ions

Emmanuel Flores Huicochea<sup>1</sup>, Rodolfo Rendón Villalobos<sup>1</sup>, Luis Ángel Cruz Amador<sup>1</sup>

<sup>1</sup> *Instituto Politécnico Nacional, Centro de Desarrollo de Productos Bióticos, km 6.5 carr. Yautepec-Jojutla, San Isidro, Yautepec, Morelos (México).*

e-mail of the presenter: [efloreshu@outlook.com](mailto:efloreshu@outlook.com) , [efloresh@ipn.mx](mailto:efloresh@ipn.mx)

The chia (*Salvia hispanica* L.) is pre-Columbian food native from central and south of Mexico. It was part of Aztec diet [1]. The chia is a source of omega-3, protein and polysaccharides [2], [3]. Nowadays, exists reports of uses and applications of seed chia like fat replacer[4] or egg replacer[5]. However, there are few studies related to biopolymer of chia, due is difficult separate it from the seed. We reported the flow curve, viscosity vs strain rate, of chia (*Salvia hispanica* L.) biopolymer on the concentration interval from 0.037 to 0.97 %, at two temperatures (25 and 40 °C) and ions Na<sup>+</sup> (0, 10, 25 mM) are reported. The profile of flow curves is similar to reported to others biopolymers. The strain rate rise produced a reduction on viscosity, the ions added reduces the maximal viscosity. Nevertheless, the temperature rise, 25 to 40 °C without ions added, over the concentration interval studied increase the maximal viscosity until 300 Pa · s at 40 °C, but with ions added there is drop on viscosity. The effect of temperature was increase the maximal viscosity and the increase on ions decrease the viscosity. The temperature and ions has effect over molecular volume, the first increase and the second decrease, that behaviour could be explained due chia biopolymer is a polyelectrolytic. Further studies related with the effect of temperature and ions over intrinsic viscosity could be useful to obtain a deep understanding.

Keywords: chia, flow curve, viscosity

### References

- [1] D. Carrasco and S. Sessions, *Daily Life of the Aztecs, 2nd Edition*. ABC-CLIO, 2011.
- [2] R. Ayerza and W. Coates, *Plantas medicinales*. Buenos Aires, Argentina: Del nuevo extremo, 2006.
- [3] V. Y. Ixtaina, S. M. Nolasco, and M. C. Tomás, "Physical properties of chia (*Salvia hispanica* L.) seeds," *Ind. Crops Prod.*, vol. 28, no. 3, pp. 286–293, Nov. 2008.
- [4] P. H. H. Terry, M. Hancock, and K. McCreless, "The Effects Chia Seeds as a Fat Replacer on the Physical and Sensory Characteristics of Muffins," *J. Acad. Nutr. Diet.*, vol. 113, no. 9, Supplement, p. A60, 2013.
- [5] R. Borneo, A. Aguirre, A. E. Leon, and A. E. León, "Chia (*Salvia hispanica* L) Gel Can Be Used as Egg or Oil Replacer in Cake Formulations," *J. Am. Diet. Assoc.*, vol. 110, no. 6, pp. 946–949, 2010.

# Viscosity Profile of Selected Monofloral Portuguese honeys

Pinheiro L<sup>1</sup>, Gonçalves J<sup>1</sup>, Faustino C<sup>1</sup>

<sup>1</sup>Research Institute for Medicines (iMed.U LISBOA), Faculty of Pharmacy, Universidade de Lisboa, Av. Prof. Gama Pinto, Lisboa (Portugal)

e-mail of the presenter: lpinheiro@ff.ul.pt

Honey, a well-known natural product resulting from a creative makeover process performed by honeybees (*Apis mellifera*), is a supersaturated solution of sugars with low water content and low concentrations of bioactive compounds. The presence of sugars, organic acids, proteins and other colloidal material makes the honey a material of variable composition and distinct rheological behavior.

Viscosity and other rheological parameters of honey are vital parameters for applications associated to the processing, pumping, heating, mixing, filtering, transport, storage, quality control and sensory properties. Additionally, the viscosity of honey influences honey's antimicrobial efficiency, since its high values provides a physical barrier to external pathogens [1].

Steady shear measurements were carried out on commercial Portuguese monofloral honeys from different floral origin (orange blossom, eucalyptus, lavender and heather), in order to obtain flow and viscosity curves over a convenient shear rates range, in ascending and descending ramps. The parameters of the Ostwald-De-Waele model described the flow behaviour of honey samples under investigation.

In the literature, honeys have showed a broad rheological behaviour, ranging from Newtonian to non-Newtonian, depending on botanical source, water content, degree of crystallization, presence of colloidal material, such as proteins and polysaccharides [2]. Rheological behaviour of studied honey samples was influenced by floral origin and physicochemical composition. Orange blossom and lavender honeys displayed Newtonian profiles while eucalyptus and heather honeys presented non-Newtonian behaviour with shear-thinning properties. Heather honey also exhibited thixotropy, suggesting the presence of colloidal substances, namely high protein content.

**Keywords:** honey, viscosity, rheology, shear-thinning, thixotropy

## References

- [1] C. Faustino, L. Pinheiro, Antimicrobial properties and therapeutic benefits of honey in the quest for more efficient antimicrobial agents. In: A. Méndez-Vilas, ed. *The Battle Against Microbial Pathogens: Basic Science, Technological Advances and Educational Programs*. Badajoz, Spain. Formatex; 2015, p. 98-108.
- [2] I. Dobre, L.A. Georgescu, P. Alexe, O. Escuredo, M.C. Seijo, Rheological behaviour of different honey types from Romania. *Food Res. Int.*, 49:126–132 (2012).

## Effect of by-products from rice industry in rheological properties of gluten-free baking doughs

Patrícia Fradinho, Joana Loureiro, Anabela Raymundo, Isabel Sousa

LEAF-Linking Landscape, Environment, Agriculture and Food, Instituto Superior de Agronomia, Universidade de Lisboa. Tapada da Ajuda, 1349-017 Lisboa (Portugal).

e-mail of the presenter: pfradinho@isa.ulisboa.pt

It is well known that rice milling produces several by-products, namely broken rice and rice bran, which accounts for more than 20% of the processed rice. This work gathers two purposes: i) valorisation of by-products from the rice industry (broken rice and rice bran), ii) study the effect of rice bran incorporation on texture and rheology properties of gluten free baking products, namely cookies, bread, pizza and pasta.

Rice bran has a major drawback due to its high lipid content which makes it favourable to peroxidase action, promoting oxidation and rancidity. To prevent rice bran's oxidative process and make it suitable for food applications, rice bran was stabilized according to previous work [1].

The optimised bran incorporations were: 2% *agulha* (indica) bran (180 to 350  $\mu\text{m}$ ) for cookies; 2% parboiled bran (180 to 350  $\mu\text{m}$ ) for bread; and 2% *carolino* (japonica) bran (180 to 350  $\mu\text{m}$ ) for pasta. For pizza, a higher size of bran particles, 350 to 500  $\mu\text{m}$ , proved to work better and the addition was of 10% of parboiled rice bran. A control dough without rice bran was prepared for each type of product.

The texture analysis of the doughs and respective baking products was performed using a texturometer TA-XTplus (Stable Micro Systems) in penetration mode. Dough's texture profile analysis was assessed using a 10 mm probe that entered the sample at 0.5 mm s<sup>-1</sup>. Firmness of the products was determined immediately after preparation and along storage time of 8 days for cookies and of 2 days for bread, giving information about the aging kinetics of each product.

Rheological behaviour of the doughs was accessed by small-amplitude oscillatory shear (SAOS) measurements in a MARS III controlled-stress rheometer (Haake), coupled to a UTC-Peltier system for temperature control. A serrated parallel plate sensor system with 20 or 35 mm diameter and 0.5 or 1 mm gap was used, according to each dough characteristics.

Rice bran is positively associated with texture parameters, since increases firmness and decreases adhesiveness and cohesiveness in all products. However, the incorporation of high bran contents lead to unacceptably high values of bread firmness.

With the exception of pasta, rice bran is responsible for increasing the structure stability of the doughs of the developed products.

**Keywords:** rice bran, bakery products, dough, SAOS, texture

### References

[1] P. Fradinho, A. Raymundo, I. Sousa, Estabilização enzimática do óleo de farelo de arroz. Livro de Actas do 12º Encontro de Química dos Alimentos - SPQ, Lisboa, ISBN-978-989-98541-6-1: Pp 26–29 (2014).

**Acknowledgments:** This work was supported by COMPETE program: QREN – “Arroz +” project 38749/13, in co-promotion with two rice milling companies.

## Rheological evaluation of gelled structures of rice flour for the production of different food products

Anabela Raymundo, Ana Morais, Patrícia Fradinho, Isabel Sousa

*LEAF-Linking Landscape, Environment, Agriculture and Food, Instituto Superior de Agronomia, Universidade de Lisboa. Tapada da Ajuda, 1349-017 Lisboa (Portugal).*

e-mail of the presenter: anabraymundo@isa.ulisboa.pt

Food gels are viscoelastic materials and several food products can be designed based on this structure, with different applications, such as toppings for pastry, puddings and baby foods.

The gelling agents in food industry are usually polysaccharides and proteins and in the present work, the use of rice flour as a gelling agent was studied, in order to obtain products with different market positions.

The relevance of this study is based on the urgent need to increase the efficiency of production systems, as it is the case of the rice industry. The rice production generates 40% (w/w) of by-products, and 12% corresponds to broken grain, that can be milled to obtain flour, which has a high potential as a gelling agent and can be used for the production of added-value foods, particularly for the gluten-free food sector.

Rheology and texture characterisation of commercial toppings, puddings and baby foods was performed and the respective results were used as a data base to be targeted by the product development.

To obtain the gel products, suspensions of rice flour with different concentrations were prepared, at room temperature, in distilled water, under stirring (600 rpm) for 30 min. For the rheological assays, gelation was performed *in situ*, placing these suspensions on the rheometer to be cooled at 2°C/min down to 5°C, after the heating cycle from 20 to 90 °C for 30 min. The gels for texture evaluation were prepared in a similar manner, but the cooling was done first to room temperature and then in the fridge with no control of the cooling rate.

From the SAOS measurements – frequency sweep tests, at 5°C (after de heat/cooling cycle), within the viscoelastic linear region, it was possible to observe the impact of rice flour concentration, sugar, sweeteners and different hydrocolloids (xanthan gum, gelatine and carrageen) on the gel structure obtained.

A critical value of 5% (w/w) for the concentration of rice flour (japonica Portuguese variety – *carolino*) was reached to obtain food gels with commercial purposes. In addition, more than 8% of rice flour concentration showed a negative impact on the texture sensory perception of these gels. The use of the hydrocolloids to produce complex binary systems with rice flour was the key to design gel structures with the three different fields of applications proposed: 0.25% of xanthan gum turned possible to obtain a typical topping gel structure; 1% of gelatine a pudding like structure and 0.25% of k-carrageenan a baby food like structure were produced.

The gel texture analysis provided important information to correlate the results with the sensory evaluation.

**Keywords:** rice flour, gel, SAOS, texture, structure

**Acknowledgments:** This work was supported by: i) COMPETE program: QREN Arroz + project: 38749/13; Portuguese Foundation for Science and Technology (FCT) through the research unit UID/AGR/04129/2013 (LEAF).

# Psyllium Husk' Rheological Properties for Application in Gluten-Free Pasta

Patrícia Fradinho, Isabel Sousa, Anabela Raymundo

LEAF-Linking Landscape, Environment, Agriculture and Food, Instituto Superior de Agronomia, Universidade de Lisboa. Tapada da Ajuda, 1349-017 Lisboa (Portugal).

e-mail of the presenter: anabraymundo@isa.ulisboa.pt

Psyllium husk comes from the seeds of *Plantago* and is an excellent source of dietary fibres. Since 2012 it has an health claim from FDA posting that Psyllium soluble fibre is associated with the coronary heart disease risk reduction [1].

The authors have already successfully incorporated Psyllium in staple foods, such as cookies [2] and pasta [3]. However, a fundamental approach is needed in order to understand the thermal properties of Psyllium for further application in gluten-free foods. This preliminary study has the purpose of assessing the optimal processing conditions of Psyllium solutions prior to dough incorporation, in order to develop fresh pasta.

Particle size is a key subject, therefore Psyllium was milled and only the particle size fraction lower than 180  $\mu\text{m}$  was used. Due to Psyllium high swelling power at high temperatures [2], which could interfere with its application in pasta making process, low psyllium concentrations were used in this work. Aqueous dispersions with 1 and 2% (w/w) of Psyllium husk were mixed for 5 min and thermally processed at 60°C and at 90°C. Then, the mixtures were placed in the rheometer for gelation *in situ* with a cooling rate of 4°C/min. Rheology behaviour of Psyllium gels was accessed by small-amplitude oscillatory shear (SAOS) measurements, at 20°C, in a MARS III controlled-stress rheometer (Haake), coupled to a UTC-Peltier system for temperature control. A cone-plate sensor system with 35 mm diameter and 2° angle was used.

From the mechanical spectra it was observed that both the concentrations and thermal processing conditions play an important role in psyllium gelation. Psyllium solutions prepared at 90°C show a weak-gel like behaviour. However, these gels are more structured than the ones prepared at 60°C. Regarding Psyllium concentration it is observed that 2% gels exhibit higher viscoelastic moduli than 1% gels, meaning that a stronger structure was formed. For pasta making, both Psyllium concentrations seems to be adequate, however a processing temperature of 90°C is more suited to confer the elasticity/extensibility needed.

**Keywords:** Psyllium, SAOS, gelation, mechanical spectrum

## References

- [1] FDA. CFR – code of federal regulations title 21 [on-line]. U.S. Food and Drug Administration web site. Available: <http://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=101.81> (2012).
- [2] A. Raymundo, P. Fradinho, M.C. Nunes. Effect of Psyllium fibre content on the textural and rheological characteristics of biscuit and biscuit dough. *Bioactive Carbohydrates and Dietary Fibre*, **3**: 96-105 (2014).
- [3] P. Fradinho, C. Nunes, A. Raymundo, Desenvolvimento de um alimento funcional: massa enriquecida com fibra de Psyllium. *Atas do 11º Encontro de Química dos Alimentos-CD ROM*. Ed. J.S. Amaral, I. Mafra, L. Barros, J. Barreira, I.C.F.R. Ferreira, M. B. Oliveira, Instituto Politécnico de Bragança. ISBN: 978-972-745-141-8. (2012).

**Acknowledgements:** Patricia Fradinho acknowledges her PhD Grant from Instituto Superior de Agronomia, Universidade de Lisboa.

## Flow behaviour and viscoelasticity of nanoemulsions with different thickening agents

C. Arancibia<sup>1</sup>, S. Fiszman<sup>2</sup> and A. Tárrega<sup>2</sup>

<sup>1</sup> Universidad de Santiago de Chile, Obispo Umaña 050, 9170201 Santiago (Chile).

<sup>2</sup> Instituto de Agroquímica y Tecnología de Alimentos (IATA-CSIC), Avda. Agustín Escardino 7, 46980 Paterna (España).

e-mail of the presenter: carla.arancibia@usach.cl

Nanoemulsions consist of small oil droplets (diameter < 100 nm) dispersed in an aqueous phase; they can modify some food physical properties and improve the bioavailability of functional components added in their structure [1]. The incorporation of thickening agents into emulsions represents one of the most common strategies used to stabilize and to modify the texture of emulsion-based food. The objective of study was to evaluate the effect of different type of hydrocolloids on the rheological properties of nanoemulsions based on avocado oil. Nanoemulsion (10% avocado oil, 7.5% Tween 80 and purified water) was prepared by sonication and they had a particle size around 120 nm (Zetasizer NanoS90, Malvern Instruments, UK). Four samples were prepared by adding different hydrocolloids to the emulsion: one sample with only starch (5%) and three samples containing starch and a second hydrocolloid (carboxymethylcellulose-0.1%, carrageenan-0.2%, and xanthan gum-0.2%). Rheological measurements were carried out in a controlled stress rheometer RS1 (Thermo Haake, Germany), using parallel plates geometry (60 mm diameter; 1-mm gap), and a sample temperature of  $10\pm 1^\circ\text{C}$ . The flow behaviour of each sample was measured and shear stress values were recorded up and down between shear rates of 0 to 200  $\text{s}^{-1}$  over a 60-s period. Mechanical spectra were obtained from measurements in the frequency range 0.01-10 Hz. Experimental data of ascending flow curve of samples were fitted to Ostwal-de Waale model ( $R^2 > 0.99$ ). All the samples showed a typical shear thinning behaviour and observable hysteresis loops. The incorporation of a second hydrocolloid increased slightly consistency and decreased flow index values. The viscoelastic properties of the samples showed a weak-gel-like structure. The addition of a second hydrocolloid modified mainly loss modulus and  $\tan \delta$  values. Differences in the rheological properties of nanoemulsions due to thickener type will be discussed.

**Keywords:** Nanoemulsions, thickening agents, flow properties, viscoelasticity

### References

[1] D. J. McClements, Nanoemulsion-based oral delivery systems for lipophilic bioactive components: nutraceuticals and pharmaceuticals, *Therapeutic Delivery*, **4**: 841-857 (2013).

## Developing innovative cheese products with *Chlorella*

A.P. Batista<sup>1</sup>, S. Ramos<sup>2</sup>, B. Archer de Carvalho<sup>1</sup>, I. Sousa<sup>1</sup>, A. Raymundo<sup>1</sup>

1. LEAF-Linking Landscape, Environment, Agriculture and Food. Instituto Superior de Agronomia. Universidade de Lisboa. Tapada da Ajuda. 1349-017 Lisboa. Portugal. 2. Queijos Santiago. Montemuro. 2669-909 Malveira. Portugal.

e-mail of the presenter: [paulabatista@isa.ulisboa.pt](mailto:paulabatista@isa.ulisboa.pt)

Food Industry is constantly in need of innovation even in more traditional sectors. The use of microalgae in cheese products can bring some nutritional advantages as well as technological improvements. *Chlorella* has previously shown a positive significant effect in the rheological behaviour of o/w emulsions [1] and gelled biopolymer systems [2] so it may also have an impact in complex cheese matrixes rheology.

In the present work, freeze dried *Chlorella* biomass, from marine origin, was added to raw milk at 1 to 5 g/L for fresh cheese production trials at pilot scale in a dairy industry R&D Unit. The milk-to-cheese production yield was calculated and all cheeses were analysed in terms of linear viscoelastic rheology (mechanical spectra), texture (TPA in compression mode and cutting test), colour ( $L^*a^*b^*$ ) and gross chemical composition.

The addition of *Chlorella* resulted in an 11% increase in the cheese yield, rising from 330 g/L (control) to 368 g/L (5 g/L *Chlorella*). An increase of the green colour ( $a^*$ ) was also verified, as well as a decrease in lightness ( $L^*$ ), proportional to the increase of microalgae concentration. In terms of texture, both TPA and cutting tests revealed an increase in firmness (and cohesiveness for TPA) with microalgae concentration up to 3 g/L. Cheeses with higher *Chlorella* incorporation (4 and 5 g/L) showed lower texture parameter values than the control. This could probably be related to the higher water retention capacity of the algae, "softening" the cheese matrix texture. The linear viscoelastic properties of the fresh cheeses were analysed by frequency sweeps, and the resulting mechanical spectrum revealed well-structured gels ( $\tan \delta \sim 0.2$  for all frequency range). As observed for texture parameters,  $G'$  values increased with alga incorporation up to 3 g/L, and further decreased for 4 and 5 g/L of *Chlorella* addition.

**Keywords:** *Chlorella*, cheese, texture, SAOS

### References

- [1] Raymundo A, Gouveia L, Batista AP, Empis J, Sousa I, Fat mimetic capacity of *Chlorella vulgaris* biomass in oil-in-water food emulsions stabilized by pea protein, *Food Research International*, **38**: 961-965 (2005).
- [2] Batista AP, Gouveia L, Nunes MC, Franco JM, Raymundo A, Microalgae biomass as a novel functional ingredient in mixed gel systems, In *Gums and Stabilisers for the Food Industry 14*, Eds. PA Williams & GO Phillips. RSC Publishing. pp. 487-494 (2008).

**Acknowledgements:** The authors thank Eng° João Santiago and Queijos Santiago for enabling this research project at industrial environment and Buggypower Portugal for providing *Chlorella* biomass. This work was supported by national funds from Fundação para a Ciência e a Tecnologia (Portugal) through the research unit UID/AGR/04129/2013 (LEAF).

## *In vitro* stomach incubation in a rheometer

Espert M.<sup>1</sup>, Salvador A<sup>1</sup>., Hernandez M.J.<sup>2</sup> & Sanz T.<sup>1</sup>

<sup>1</sup> Institute of Agrochemistry and Food Technology (IATA-CSIC). C/ Catedrático Agustín Escardino Benlloch, 7. 46980 Paterna, Valencia (Spain).

<sup>2</sup> Faculty of Pharmacy, University of Valencia. Avda. Vicente Andrés Estellés s/n, 46100 Burjassot, Valencia (Spain).

e-mail: tesanz@iata.csic.es

Information about the structural changes which occur during food digestion is very valuable for the design of food with novel functionality or for a better understanding of the behavior of conventional food. In this work the structural changes occurring during *in vitro* digestion were measured in a rheometer.

The systems studied were four types of hydrocolloids (two different types of methylcellulose (MC) (A4M and MX), one type of hydroxypropylmethylcellulose (HPMC) (F4M) and xanthan gum (XG)) and four types of emulsions composed of sunflower oil (47%), water and one of the four hydrocolloids in a concentration of 2%.

*In vitro* stomach incubation was carried out in a controlled stress rheometer (AR-G2, TA Instruments, Crawley, England) equipped with the starch cell device. Viscosity data at a constant shear rate and temperature (37°C) were recorded versus time. Gastric fluid containing pepsin, NaCl, CaCl, KCl, Na<sub>2</sub>CO<sub>3</sub> was added to the sample placed in the cylindrical cup of the cell and the pH was adjusted to 2.0 with concentrated HCl. Viscosity was monitorized during 60 minutes. The results of this investigation will be applied in the rational design of non digestible emulsions and satiating foods.

**Keywords:** emulsion, cellulose ethers, xanthan gum, *in vitro* gastric digestion, rheology.

## Rheological Evaluation of Bread Dough Grown From Fermented Whey

Christine Macedo, Cristiana Nunes, Ana Lima, Ricardo Ferreira, Isabel Sousa, Anabela Raymundo

*LEAF-Linking Landscape, Environment, Agriculture and Food, Instituto Superior de Agronomia, Universidade de Lisboa. Tapada da Ajuda, 1349-017 Lisboa (Portugal).*

e-mail of the presenter: [christine.macedo@yahoo.com.br](mailto:christine.macedo@yahoo.com.br)

Cheese is a premium product from milk that is widely consumed throughout the world. One of the main constraints associated with cheese production is the generation of high volumes of by-products, namely cheese whey, which has high pollutant potential due to its composition (water, lactose, proteins and fats). For the manufacture of 1 kg of cheese, about 10 L of milk are required, leading to the production of 8 to 9 L of whey. Due to its excellent nutritional composition, the reuse of whey as a food ingredient must be considered. The whey fermentation can be a preliminary process of stabilisation and an important tool to enhance its bioactivity and to remove allergenic proteins and also lactose.

In previous studies, it was verified that fermentation of whey increases its bioactivity (antioxidant, antihypertensive, antitumor, lipid-lowering, antiviral, and antibacterial) potential.

The use of fermented whey as a food ingredient can be a contribution to improve the functional profile of certain foods, adding value to them. At the same time, this approach may contribute to the incorporation of an important by-product in the value chain, which is aligned with the circular economy concept.

The main goal of this work was to evaluate the maximum content of fermented whey to be incorporated in traditional bread production. The impact of fermented whey incorporation on dough structure was evaluated. The characterization of the fermented serum, in terms of centesimal composition (proteins, lipids, ashes, carbohydrates and dry matter) was performed. In addition, its bioactivity (with antibacterial activities against several pathogenic bacteria, as well as anti-inflammatory and anticancer bioactivities demonstrated through several biochemical and *in vitro* assays) was also evaluated. Different levels of serum incorporation have been tested in a bread formulation already developed in previous work. Bread physic-chemical characterisation was performed: acidity in lactic acid, pH, ashes, fat, water activity, colour and texture (TPA) and its evolution over time was followed. The effect of whey addition on the crumb and bread crust appearance was also monitored. Dough texture after fermentation, mechanical spectra (SAOS) and overrun variation were also accessed.

It was verified that the serum presents high bioactivity after fermentation and affects the rheological and texture properties of the bread. Nevertheless, it is possible to optimise a formulation with similar sensory properties of the traditional bread, but with an incremented bioactivity, having great potential for possible further development and commercialization.

**Keywords:** bread, whey, bioactivity, fermentation, structure.

**Acknowledgments:** This work was supported by Queijo Saloio S.A. Dairy Industry and a PhD grant from University of Pará - Brazil

## A comparative study of flaxseed chia-quinoa dough: thixotropic and viscoelastic behaviour

J. Rubio-Merino<sup>1</sup>, E. Amate-Ruiz<sup>2</sup>, A.I. Gómez-Merino<sup>2</sup>, F.J. Rubio-Hernández<sup>2</sup>, J.L. Arjona-Escudero<sup>3</sup>, I.M. Santos-Ráez<sup>3</sup>

<sup>1</sup> Unidad Docente Multiprofesional de Atención Familiar y Comunitaria Distrito Málaga-Guadalhorce, Málaga, (Spain).

<sup>2</sup> Dep. Física Aplicada II, Universidad de Málaga, Dr Ortiz Ramos s/n, Málaga (Spain).

<sup>3</sup> Dep. Ingeniería Mecánica Térmica y de Fluidos, Universidad de Málaga, Dr Ortiz Ramos s/n, Málaga (Spain).  
e-mail of the presenter: aimerino@uma.es.

Gluten is a source of vegetal protein. In terms of its nutritional value, gluten is considered to be poorer than proteins from animal sources and can cause allergic reactions and intolerances [1]. Quinoa, as other cereals, has attracted much interest because of its high nutritional value and for the absence of gluten. In spite of this, the absence of gluten in these flours, results in major problems for many pasta and bakery products. Attempts to use proteins from alternative flours as a partial substitute in wheat products have generally been unsuccessful, because of the contrasting differences between proteins: water-solubility, differences in primary structure and their size distributions, accounted for viscoelastic properties that are unique to wheat gluten proteins. The major protein fraction of quinoa seeds is formed by globulin, which does not possess the requisites to confer elasticity to the dough [2]. However, the hydrocolloids present in chia and flaxseed could improve the elastic properties of the quinoa chia or quinoa-flaxseed mass.

The effect of chia and flaxseed (10 % weight) addition to quinoa dough was studied. Special attention to thixotropic and viscoelastic properties of the dough was paid. The thixotropic loop of the three masses (Figure 1) show a very similar behaviour of both seeds although the thixotropic area for the stress loop is higher in chia than in flaxseed. However, the viscoelastic properties of the quinoa-flaxseed dough are more similar to the wheat dough. In addition, the sensory properties of the quinoa-flaxseed mass are within better levels of acceptability than the quinoa chia dough, suggesting a good commercial viability of the former products.

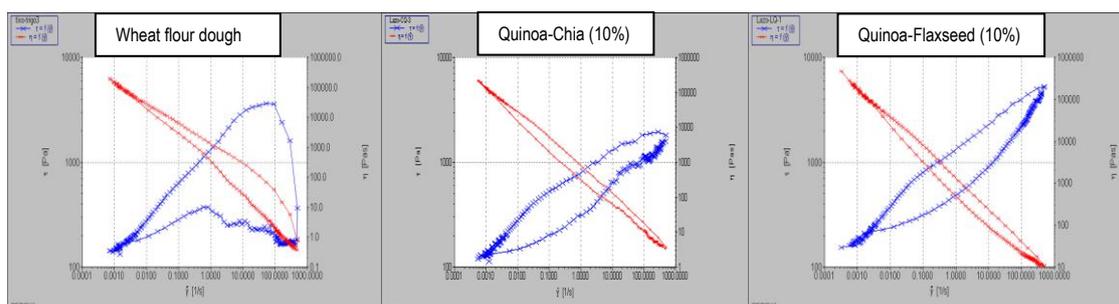


Figure 1. Thixotropic loop of the three composite masses, chia and flaxseed are in 10 % weight.

**Keywords:** Flaxseeds, Chia Seeds, Quinoa, Thixotropy, Viscoelasticity.

### References

- [1] E. Gallagher, T.R. Gormeley, E.K. Arendt, Recent advances in the formulation of gluten-free cereal-based products. *Trends in Food Science Technology* **15**: 143–152 (2004).
- [2] A.S. Thatam, L. Hayes, P.R. Shewry, D.W. Urry, Wheat seed proteins exhibit a complex mechanism of protein elasticity. *Biochimica et Biophysica Acta* **1548**: 187–193 (2001).

## Rheological and textural behaviour of fresh and frozen mashed native yellow potatoes (*Solanum goniocalyx*)

Quispe M.L.<sup>1</sup>, Velezmoro S.C.<sup>1</sup>, Vargas D.F.<sup>1</sup>, Betalleluz-Pallardel I.<sup>1</sup>

<sup>1</sup>Universidad Nacional Agraria La Molina, Av. La Molina s/n, Lima (Perú).

ibp@lamolina.edu.pe

In the Andes of South America, farmers use to grow varieties of potatoes that are not seen outside this region. These native Andean potatoes show an important diversity in taste, texture, shapes, colors and have high quality culinary, as well. Some of the most popular varieties have a intense yellow-colored flesh due to their high level of carotenoids. In this study, the aim was to assess the effects of freezing and thawing on textural and rheological properties of potato mash from two native potatoes: "Peruanita" and "Ambo". Three treatments were studied: cooked with skin (SP), cooked without skin (PSA) and cooked without skin and immersion treatment with 3% citric acid for 5 minutes (PCA), all of them packed in thermoformed PET containers (250g), frozen at -20°C and, finally, air-thawed at 4°C. Texture profile analysis (TPA) and oscillatory rheometry were performed for determination of textural parameters (hardness, adhesiveness, springiness, cohesiveness and gumminess) and viscoelastic characteristics such  $G'$  storage modulu,  $G''$  loss modulus and complex viscosity  $\eta^*$ , as well. In fresh (F) and freeze/thaw (F/T) samples, behavior was predominantly more elastic ( $G' > G''$ ), so it can be told that they were not true gels but showed a structure somewhere between a concentrated biopolymer and a true gel. F showed higher values of  $G'$  and  $G''$  as compared to F/T counterparts. Linear regressions of  $\ln \omega$  vs  $\ln G'$  and  $\ln G''$ , and positive slopes on the trends tell about the shear-thinning nature of all of the mashed potatoes; it is known that true gels have zero slopes, but weak gels and highly concentrated solutions have positive slopes [1]. On the other hand,  $\ln K'$  and  $\ln K''$  values were lower in F/T. TPA parameters were lower in the F/T samples. These results indicate that freeze/thaw processing weakened the structure of natural mashed potatoes producing a far more diluted dispersion. "Peruanita"/SP and "Ambo"/PSA showed minor changes after freezing, which makes them suitable for this kind of processing.

**Keywords:** potatoes, freezing, rheology, texture.

[1] M.D. Alvarez, C. Fernández, W.Canet. Rheological behaviour of fresh and frozen potato puree in steady and dynamic shear at different temperatures, *Eur Food Res Technol*, 218: 544-553 (2004).

# Effect of pH and temperature in hydrocolloids and hydrocolloids based emulsions

Espert M.<sup>1</sup>, Sanz T.<sup>1</sup>, Hernandez M.J.<sup>2</sup> & Salvador A<sup>1</sup>.

*1 Institute of Agrochemistry and Food Technology (IATA-CSIC). C/ Catedrático Agustín Escardino Benlloch, 7. 46980 Paterna, Valencia (Spain).*

*2 Faculty of Pharmacy, University of Valencia. Avda. Vicente Andrés Estellés s/n, 46100 Burjassot, Valencia (Spain).*

e-mail: asalvador@iata.csic.es

The effect of pH and temperature on the rheological properties of single hydrated hydrocolloids and O/W hydrocolloid stabilized emulsions was studied. The hydrated polysaccharide network constitutes the continuous phase of the emulsion and is therefore the first barrier to come into contact with the possible alterations. Thus the changes in the single hydrocolloid structure are expected to be closely related to the structural changes of the emulsions.

The hydrocolloids studied were: two types of methylcellulose (MC) (A4M and MX), a hydroxypropylmethylcellulose (HPMC) (F4M) and xanthan gum (XG), always at a concentration of 2%. The emulsions were composed of sunflower oil, water and the hydrocolloid.

Cellulose ethers are nonionic and are widely used for their efficient thickening, surface activity and the ability to form thermal gels that melt upon cooling. The temperature at which the gelation begins and the texture of the gel formed are dependent on the type and substitution level of the hydrocolloid. MC or HPMC aqueous solutions have gel temperature ranging from 50 to 85°C and gel strengths varies depending on degree of methyl/hydroxypropyl substitution. As the methyl concentration increases, the gel formed on heating becomes firmer. The addition of hydroxypropyl groups to methylcellulose tends to reduce the rigidity of the gel and increase its critical thermal gelation temperature. Hydroxypropyl substituents are more hydrophilic than methyl groups. The introduction of the hydrophobic groups provides the polymer with surface activity and specific hydration-dehydration characteristics.

Xanthan gum is an anionic polysaccharide, obtained by bacterial fermentation, with the ability to form high viscosity solution stables over a wide range of temperatures and pH. This hydrocolloid is widely used in food products to improve the rheological and textural characteristics, increase the oxidative stability or to avoid destabilization processes in emulsions.

Rheological properties of the hydrocolloid hydrated solution and the O/W emulsions were analyzed by a controlled stress rheometer (AR-G2, TA Instruments (Crawley, England)) using a 40mm diameter plate-plate sensor geometry with serrated surface. Temperature sweeps were carried out at a frequency of 1 Hz, 1°C/min, in the linear viscoelastic region, from 20°C to 70°C and from 20°C to 37°C, followed by an oscillatory time sweep at 37°C during the time required to stabilize the sample. Once the sample structure is stable at 37°C, small amplitude oscillatory frequency tests (from 10 to 0.01Hz) and flow tests were carried out in different experiments. The samples were measured at the initial pH and at pH 2.0 after adjusting with HCl (6N).

The final aim is to increase knowledge about the behavior of hydrocolloids and hydrocolloids stabilized emulsions at the temperature and the acid pH of the stomach. The acquired knowledge will be used in the design of emulsions for weight control.

**Keywords:** cellulose ethers, xanthan gum, emulsion, gastric structuring, rheology.

## Rheological properties of kuzu starch-galactomannan pastes

Bertrand Jóźwiak, Magdalena Orczykowska, Marek Dziubiński

*Lodz University of Technology, Łódź, Poland*

bertrand.jozwiak@dokt.p.lodz.pl

Kuzu (kudzu) is a plant of *Pueraria* genus from Southeast Asia. Its root is a medical raw material which has been used in traditional medicine since ancient times. Kuzu is a rich source of minerals, does not contain gluten or lactose, is effective in a fight against addictions, prevents cancer, helps in weight loss and body detoxification, as well as reduces blood pressure and the risk of heart attack. Starch contained in kuzu root provides an alternative to commonly used thickening/binding agents such as gelatin or potato starch. In the literature, there is lack of comprehensive information about rheological properties of kuzu starch-hydrocolloid mixtures, despite the considerable possibilities of their practical application.

The aim of this study was a comprehensive description of rheological properties of starch-galactomannan pastes, depending on mannose-to-galactose ratio in galactomannan molecule (the so-called substitution degree). The samples of 3% w/v aqueous suspensions of Japanese white kuzu starch with 0.3% w/v hydrocolloid additives (fenugreek gum, guar gum, tara gum, locust bean gum) were pasted at 95°C for 75 min, stored at 5°C for 24 h, and then subjected to oscillatory and creep tests at 25°C. The obtained experimental data were described by means of the modified fractional Kelvin-Voigt model with two built-in springpot-type elements. The model was derived on the basis of differential calculus of fractional order and thereby enabled the characterization of dissipative processes inside the material in the entire range of viscoelastic plateau. This approach allowed to determine 17 rheological parameters providing a lot of additional information about structure and viscoelastic properties of kuzu starch-galactomannan pastes in comparison to the classical analysis of oscillatory and creep tests. It is particularly important in materials engineering, in product design/evaluation for food and pharmaceutical industries.

## Rheological characterization of yogurt with different types of fibres

Adriana Dabija<sup>1</sup>, Mircea Adrian Oroian<sup>1</sup>, Anca-Mihaela Sidor<sup>1</sup>, Georgiana Gabriela Codină<sup>1</sup>

<sup>1</sup> Stefan cel Mare University of Suceava, Universitatii Street, 13, Suceava, Romania

e-mail: [adriana.dabija@fia.usv.ro](mailto:adriana.dabija@fia.usv.ro)

Yogurt is the most important fermented dairy product with beneficial effects on the human body. It is a functional food whose quality can be improved by fibres addition, such as: pea fibres, wheat fibres, oat fibres, apple fibres. Various types of fibres were added in the yogurt formulation due to their ability to improve the structure and textural properties of the finished product. The yogurt and fibres mixture reduced yogurt syneresis and improved textural properties, increasing gel firmness. In order to study the structural modification of yogurt by fibres addition, a rotational rheometer Thermo Haake Mars was used. The rheological properties (viscosity and tension) depending on shear rate (rinsing curve from 0.02 to 100 s<sup>-1</sup> and descending curve from 100 to 0.02 s<sup>-1</sup>) were determined. Also, there were performed thixotropy tests, by measuring the viscosity at a constant shear rate of 100 s<sup>-1</sup> as a function of time of 10 minutes. Hysteresis was determined as the area between the curves and adjusted to the models of Ostwald-de-Waele, Casson, Bingham and Herschel-Bulkley. All samples showed pseudoplastic and thixotropic response. When compared to yogurt control samples (with no fibres), the yogurt samples with different fibres addition presented satisfactory rheological properties. All the fibres obtained as a by-product of industrial food processing were compatible with the yogurt-manufacturing process, so the enriched yogurt would be considered an alternative to incorporate fibres in the human diet.

**Keywords:** functional food, textural properties, viscosity, thixotropy

### References

- [1] T. Mathias, I. Carvalho Junior, C. Carvalho, E. Sérvulo, Rheological characterization of coffee-flavored yogurt with different types of thickener, *Alimentos e Nutrição Araraquara*, 22:4, 521-529, 2011
- [2] H.H. Gahruie, M.H. Escandari, G. Mesbahia, M. A. Hanifpour, Scientific and technical aspects of yogurt fortification, *Food Science and Human Wellness* 4,1-8, 2015
- [3] J. Miocinovic, Z. Miloradovic, M. Josipovic, A. Nedeljkovic, M. Radovanovic, P. Pudja, Rheological and textural properties of goat and cow milk set type yoghurts, *International Dairy Journal*, 58, 43-45, 2016
- [4] M. O. Ramírez-Sucre, J.F. Vélez-Ruiz, Physicochemical, rheological and stability characterization of a caramel flavored yogurt, *LWT - Food Science and Technology*, 51, 233-241, 2013

## Effect of xanthan gum on the rheological properties of toddler gluten-free biscuit dough and final biscuit quality

S. Benkadri<sup>a</sup>, T. Sanz<sup>b</sup>, A. Salvador<sup>b</sup>, M. N. Zidoune<sup>a</sup>

<sup>a</sup> *Institut de la Nutrition, de l'Alimentation et des Technologies Agro-alimentaires (I.N.A.T.A-A.), route Ain Elbey, 25000 Constantine, Algérie*

<sup>b</sup> *Instituto de Agroquímica y Tecnología de Alimentos (ATA-CSIC), Avda. Agustín Escardino, 7, 46980 Paterna, Valencia, Spain*

e-mail : soulef\_ben@yahoo.fr

The replacement of gluten presents a major technological challenge, as it is an essential structure-building protein in flour, which is responsible for the viscoelastic characteristics of dough, and contributes to the appearance and structure of many cereal-based baked products. Composite flour of rice-chick pea (R-CP) was used to develop a complementary food as a biscuit form for celiac children. The main aim of this present work was to assess the effect of hydrocolloids such as xanthan gum addition at different levels (0 %, 0,5 %, 1 %, 1,5 %) on the rheological properties of biscuit dough and final quality of the baked biscuit compared with control wheat flour (WF). Results obtained showed that the incorporation of xanthan to R-CP flour significantly ( $p < 0.05$ ) affected various textural and linear viscoelastic properties of dough, as well as the texture and dimensions of baked biscuit. Increasing xanthan level increases dough hardness and viscosity. However a decrease in dough springiness was noted after addition of xanthan to reach a value close to that of wheat control (WF) dough. The same trend was observed for the spread of biscuits. Adhesiveness of the R-CP dough without xanthan was also reduced, but remains higher than that of the control (WF) dough. Addition of xanthan gum resulted in significant improvement in thickness and specific volume of biscuits. An increase in the moisture content and the  $w_a$  of baked biscuits with increasing level of xanthan, showing water holding capacity of gums, was traduced in reduction of biscuit hardness.

**Keywords:** celiac children, biscuit, xanthan, rheology, texture

## Effects of acidification and exogenous protein on rheological properties of gluten-free starch-based doughs

M. Villanueva<sup>a</sup>, S. Pérez-Quirce<sup>a</sup>, F. Ronda<sup>a</sup>

<sup>a</sup> *Department of Agriculture and Forestry Engineering, Food Technology. College of Agricultural and Forestry Engineering, University of Valladolid. Avd. Madrid s/n 34004, Palencia, Spain*  
e-mail : [fronda@iaf.uva.es](mailto:fronda@iaf.uva.es)

Gluten has a very important role in products for their singular viscoelastic properties. Thus, the removal of gluten from gluten free (GF) products has a significant impact on their structure, texture and sensory attributes. Generally, GF baked products have poor physicochemical and sensory quality, lack fibre, vitamins and nutrients, which results in a worsening effect on the already nutritionally unbalanced diet of celiac sufferers. Incorporation of exogenous proteins is considered a good supplement to increase both nutritional and functional values in GF products. In addition, acetic and lactic acids produced by the exogenous microflora or added to breadmaking matrices confer suitable properties to final breads. The impact of acid incorporation (acetic+lactic, 0.5%) into doughs formulated with two different starches (corn and potato) enriched with soy protein isolated (SPI) added at 5% dose, has been investigated on dough viscoelastic properties. The results obtained indicate that starch source, protein incorporation and dough acidification markedly affected to dough viscoelasticity. Corn starch application resulted in doughs of less consistency, elastic and viscous moduli as well as steady viscosity and higher compliances compared to potato starch doughs, which showed higher elastic modulus. Supplementation of doughs with SPI led to a threefold more consistent matrices (higher viscoelastic moduli and steady viscosities, and lower instantaneous and retarded elastic compliances) with respect to the non-enriched doughs. The acidification of protein-enriched GF doughs decreased markedly these effects, lowering the viscoelastic moduli and steady viscosity and increasing all compliances and  $\tan \delta$ , regardless the starch used. However, the acidification effect was hardly observed in non-protein added doughs.

**Keywords:** Gluten free dough, viscoelasticity, starch, soy protein isolate, acidification.

# Effect of partial substitution of rice flour with buckwheat flour on gluten-free bread quality and rheology of dough

J.Harasym <sup>a,b</sup>, M.Villanueva <sup>a</sup>, F.Ronda <sup>a</sup>

<sup>a</sup> Department of Agriculture and Forestry Engineering, Food Technology. College of Agricultural and Forestry Engineering, University of Valladolid. Avd. Madrid s/n 34004, Palencia, Spain

<sup>b</sup> Department of Biotechnology and Food Analysis, Faculty of Engineering and Economics, Wrocław University of Economics, Komandorska 118/120, 53345 Wrocław, Poland

e-mail : fronda@iaf.uva.es

The rice flour is along with the maize one of the most popular flour used for gluten-free breadmaking. However now the poor nutritional quality of gluten-free food ignites the new research for its improvement without losing the sensorial quality. The solution could be exploration of other – gluten-free raw flours as buckwheat. The replacement of rice flour with buckwheat flour resulted in new mixtures with breadmaking possibility. The aim of this present work was to assess the effect of buckwheat flour (BF) addition at different levels (30, 50, 70 %) on the rheological properties of bread dough and final quality of the baked bread compared with control rice flour (RF). Results obtained showed that the incorporation of BF into rice flour haven't changed significantly ( $p < 0.05$ ) the storage  $G'$  and viscous  $G''$  moduli compared to RF doughs, however the value of  $\tan(\delta)_1$  of the dough decreased significantly with addition of BF resulting in domination of elastic behavior in doughs with higher addition of BF. Also for the same samples the resulting  $\tau(\max)$  of dough decreased. Breads with higher addition of BF revealed lower loaf weight loss and lower specific volume. The values of texture like hardness, elasticity, gumminess, masticability and resilience were higher for all breads with BF addition comparing to weak RF bread structure. Expected statistically significant rise in hardness were observed in all BF breads while hardness increments after 7 days were the same for all BF breads and statistical significantly higher than in control RF.

Keywords: celiac disease, gluten-free bread, rice, buckwheat, rheology

## Enrichment of gluten-free rice-based doughs with yeast and fungi (1-3)(1-6)- $\beta$ -glucans extracts

Sandra Perez-Quirce, Antonio Vela, Pedro A. Caballero, Felicidad Ronda

*Department of Agriculture and Forestry Engineering, Food Technology, College of Agricultural and Forestry Engineering, University of Valladolid, Av. Madrid, 44, 34004 Palencia, Spain*

e-mail : fronda@iaf.uva.es

$\beta$ -glucan (BG) is an interesting hydrocolloid with positive effects on human health such as immune-stimulation, anti-inflammatory, antimicrobial, anti-tumoral, cholesterol-lowering, antidiabetic and hypoglycemic activity. BG is also an alternative fibre source. Its application on gluten-free breads enrichment has a special interest to people suffering from celiac disease with significant incidences associated to auto-immune diseases and unbalanced diet. This work has approached to study the effect of fortification with (1-3)(1-6)- $\beta$ -glucan extracts derived from yeasts –soluble (SBG) and insoluble (IBG)- and fungi -*Pleurotus Ostreatus*- (FBG), incorporated in four doses (0%, 0,5%, 1% y 2% rice flour based) to gluten-free rice based doughs. A fundamental rheology approach (oscillatory and creep-recovery tests) was adopted to assess the viscoelasticity of these dough matrices which give information of the dough properties related to ease of handling during bread making and dough development capability during fermentation and baking.

The lowest values of  $G'$  and  $G''$  and the highest compliances were obtained for SBG-enriched samples, while doughs with FBG or IBG showed an opposite trend, increasing their resistance to deformation as the concentration increased. Higher consistent doughs (FBG and IBG enriched doughs) corresponded to those with larger dynamic moduli and poorer frequency dependence, lower elastic deformation at a constant stress, and higher viscosity at steady state. The necessity of a fine dough hydration optimization depending on the BG type and concentration was concluded. Empirical, large deformation rheological (extrusion) tests which were also carried out in the study, proved to be a convenient and simple procedure

**Keywords:** (1-3)(1-6)- $\beta$ -glucan, empirical rheology, fundamental rheology, gluten-free dough

# Rheological study of the aggregation state of alumina nanofluids.

J.L. Arjona-Escudero<sup>1</sup>, I.M. Santos-Ráez<sup>1</sup>, A.I. Gómez-Merino<sup>2</sup>, F.J. Rubio-Hernández<sup>2</sup>

<sup>1</sup> Dep. Ingeniería Mecánica Térmica y de Fluidos, Universidad de Málaga, Dr Ortiz Ramos s/n, Málaga (Spain).

<sup>2</sup> Dep. Física Aplicada II, Universidad de Málaga, Dr Ortiz Ramos s/n, Málaga (Spain).

e-mail of the presenter: aimerino@uma.es.

The presence of alumina solid particles in aqueous phase induces a change in the viscosity of the suspension from Newtonian to non-Newtonian flow. Besides, the presence of solid particles is adequate for the use as a heat exchanger fluid. The effect of nanoparticle size on thermal properties of nanofluids is still today a question, which is far from being answered. In this respect, the results reported in the literature are contradictory [1], probably due to the formation of aggregates when particles are dispersed in the liquid phase. Regarding to the nanoparticle shape influence in thermal conductivity, cylinders and spheres have been considered as the more effective in heat transfer.

Spherical nanoparticles of alumina, which is one of the most investigated nanofluid, dispersed in water were used in this study. TEM images showed a mean average diameter of 50 nm. However, DLS measurements showed monodispersed particles of 260 nm. Very recently [2], the relationship between shear rheology and aggregation state of suspensions has been reviewed. Mechanical and physical properties of the resultant materials depend on shape, size and size distribution, which are considered determining parameters in the formation of particle aggregates. The steady shear flow (figure 1) has shown that these clusters, when they are at rest, are formed by highly branched aggregates that erode when shear rate increases, until a suspension of individual particles is achieved. These results are in good agreement with the intrinsic viscosity obtained by Money and Krieger-Dougherty models. In both cases, these values are far from the 2.5 corresponding to spherical particles. The temperature effects were also taken into account.

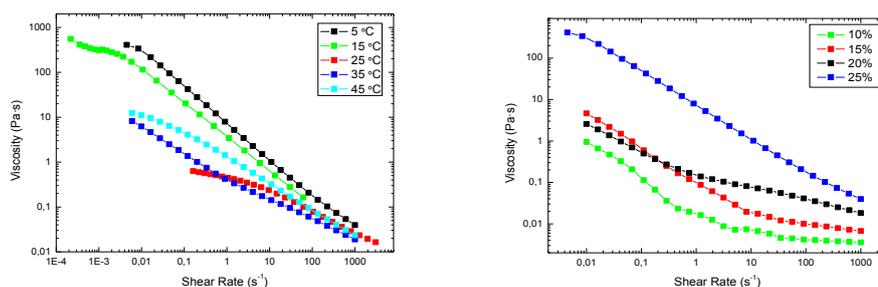


Figure 1. Viscosity curves of alumina, temperature and volume fraction effects.

**Keywords:** Intrinsic viscosity, Shear-thinning, Heat Transfer Nanofluids, Alumina.

## References

- [1] M. Lomascolo, G. Colangelo, M. Milanese, A. de Risi, A. Review of heat transfer in nanofluids: conductive, convective and radiative experimental results. *Renewable and Sustainable Energy Reviews*, **43**: 1182-1198 (2015).
- [2] D.B. Genovese, Shear rheology of hard-sphere, dispersed, and aggregated suspensions, and filler-matrix composites, *Adv. Colloid Interface Sci.*, **171**: 1-16 (2012).

## Gibbs free energy of activation for viscous flow in alumina suspensions

I.M. Santos-Ráez<sup>1</sup>, J.L. Arjona-Escudero<sup>1</sup>, A.I. Gómez-Merino<sup>2</sup>, F.J. Rubio-Hernández<sup>2</sup>

<sup>1</sup> Dep. Ingeniería Mecánica Térmica y de Fluidos, Universidad de Málaga, Dr Ortiz Ramos s/n, Málaga (Spain).

<sup>2</sup> Dep. Física Aplicada II, Universidad de Málaga, Dr Ortiz Ramos s/n, Málaga (Spain).

e-mail of the presenter: fjrubio@uma.es.

The presence of alumina solid particles in aqueous phase induces the appearance of two main effects: the distortion of the flow field, which in turn increases the viscosity of the suspension when compared to the viscosity of the carrier liquid and the change from Newtonian to non-Newtonian flow depending on the size, shape and concentration of particles. In addition, the presence of solid particles produces an increase in the thermal conductivity of the nanofluid, although sedimentation of the solid phase should be avoided. The zeta-potential greatly affects the flow properties of a suspension but this parameter can be evaluated by different electrokinetic techniques: electrophoresis, electroviscous effect, conductivity, streaming potential, etc. On the other hand, there are other rheological and thermodynamic parameters related to zeta-potential, this is the case of the yield stress value and the Gibbs free energy due to the adsorption of the charge determining ions. There are a number of yield stress–DLVO models that have been validated for many aqueous suspensions. All of them predict a linear decrease of the yield stress with the square of  $\zeta$ -potential.

The viscosity curves of alumina suspensions vs shear rate exhibit a shear thinning behaviour with the volume fraction at any pH and temperature values [1] (Figure 1). The temperature dependency of the Newtonian viscosity components was analysed in terms of the well-known Arrhenius equation, while the shear thinning region viscosity dependence with temperature was evaluated by means of the Andrade-Eyring equation [2], at two different volume fractions (Figure 2). In order to elucidate the suspension microstructure during the shear thinning viscous flow an assessment of the Gibbs free energy activation was made, comparing zeta-potentials obtained by electrophoresis and rheological methods. An agreement of electrokinetic, thermodynamic and rheological parameters was found.

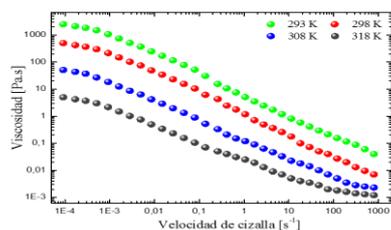


Figure 1. Viscosity curves of alumina, temperature effect,  $\phi = 0,15$ .

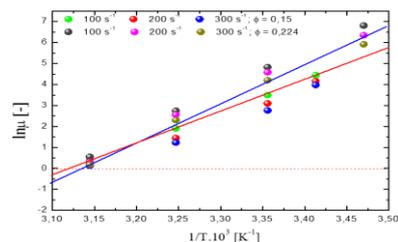


Figure 2. Viscosity vs  $1/T$ .

**Keywords:** Activation Energy, Gibbs Free Energy, Shear-Thinning, Alumina Suspensions.

### References

- [1] N. Kovalchuk, V. Starov, R. Holdich, Effect of aggregation on the viscosity of colloid suspension, *Colloid J.* **72**: 647–652 (2010).  
 [2] F.J. Rubio-Hernández, A.I. Gómez-Merino, R. Delgado-García, N.M. Páez-Flor, An activation energy approach for viscous flow: A complementary tool for the study of microstructural evolutions in sheared suspensions, *Powder Technology*, 308 (2017) 318-323.

## Interfacial rheology and emulsifying properties of bio-based surfactants obtained from coconut oil

P. Ramírez<sup>1\*</sup>, L. A. Trujillo<sup>1</sup>, J.A. Carmona, M.J. Martín, M.C. García.

<sup>1</sup>Universidad de Sevilla, Grupo de Reología Aplicada. Tecnología de Coloides. Facultad de Química. c/ P. García González, 1, 41012, Sevilla (Spain).

e-mail of the presenter: pramirez@us.es

The development of bio-based products is one of the main strategies of the European Commission for sustainable growth. Polyoxyethylene glycerol esters (Levenol C-201, Levenol H&B and Levenol F200) are obtained from materials of biological origin (coconut oil) and accomplish the requirements to be used as ecological emulsifying agents [1]. One of the main goals of the present work was to characterize the surface and interfacial properties (equilibrium, dynamics and dilatational rheology) at the  $\alpha$ -pinene/water interface of an eco-friendly surfactant, Levenol F200, in order to complete the previous studies carried out with Levenol C-201 and Levenol H&B [1]. It was shown that adsorption of Levenol F200 is favored at lower surfactant concentrations than Levenol C-201 and Levenol H&B. At higher surfactant concentration the surface pressure attained was slightly lower than Levenol C-201 but much higher than Levenol H&B. Furthermore, from dynamic surface tension measurements it was observed that Levenol F200 was partly solubilized into  $\alpha$ -pinene. From dilatational rheology measurements, the limiting interfacial elasticity as a function of surface pressure was plotted. The occurrence of a maximum in this plot confirmed the existence of different states of the adsorbed surfactant.

The other target of this investigation was to compare the yield of these three surfactants derived from coconut oil for the development of oil-in-water emulsions formulated with a green solvent ( $\alpha$ -pinene). Rheology, laser diffraction, optical microscopy and multiple light scattering were the main techniques used to assess the emulsification properties of the surfactants. Nevertheless, it has been demonstrated that the use of the non-ionic surfactant with higher number of ethoxylated groups (Levenol C-201) is adequate for two reasons: (a) it provides the sufficient viscosity to prevent creaming and (b) it is the best to avoid destabilization by coalescence.

**Keywords:**  $\alpha$ -pinene, bio-based surfactant, emulsion, interfacial rheology, laser diffraction.

### References

[1] L.A. Trujillo-Cayado, P. Ramírez, M.C. Alfaro, M. Ruíz, J. Muñoz, Adsorption at the biocompatible  $\alpha$ -pinene–water interface and emulsifying properties of two eco-friendly surfactants. *Colloids and Surfaces B: Biointerfaces*, **122**, 623-629 (2014).

## Emulsions structure and viscosity changes during process of hydrophilic/oleophilic granular structures imbibition

O. Shtyka, L. Przybysz, M. Błaszczuk, J. Sęk

*Lodz University of Technology, Lodz, Poland*

e-mail of the presenter: [olga.shtyka@gmail.com](mailto:olga.shtyka@gmail.com)

The spontaneous imbibition is phenomenon of a wetting permeant transport in the porous media due to the capillary pressure, which is compensated by the viscous drag force and gravity acceleration. The multiphase liquids as emulsions, penetrate in a granular medium in the different manner than single-phase liquids. The currently investigated issues are changes of the emulsions arise structure and therefore, such rheological property as viscosity versus penetration path during the imbibition process. The influential factors and mechanisms of their effect as the permeant composition and its initial viscosity, the porous medium structure and wettability, were presently studied and analyzed.

The process of granular media imbibition with emulsions was investigated experimentally using the classical wicking test. To identify the changes in emulsions structures nephelometrical method (Turbiscan<sup>TM</sup> LAB) and microscopic images analysis (Leica DMI3000B with camera Lumenera Infinity 1) were applied. The variations of a permeant viscosity with the height of penetration were measured by means of a rheometer Bohlin CVO-120. The permeants were represented by oil-in-water emulsions which differed by the dispersed phase concentration  $\varphi$  in a range of 10–50 vol%. A non-ionic surfactant was added to stabilize emulsions in fraction of 1–5 vol%.

The results of such research give the possibility to define tendencies of the dispersed phase distribution and viscosity changes in the penetrated emulsions during imbibition occurring in the granular media. The mathematical models were developed to describe the mentioned processes in terms of such dependence:  $\eta=f(h)$  and  $\varphi=f(h)$ . This allows to predict a tendency of emulsions transport in the granular structures driven by the capillary force by means of the Washburn equation modification considering changes of the penetrating dispersion structure and viscosity. The proposed approach is of importance from the practical point due to frequent application of dispersions and imbibition as a fundamental phenomenon in numerous industries processes and its occurrence in nature.

# Effects of hydrophobic additives on the rheology of hydraulic grouts

Luis G. Baltazar<sup>1</sup>, Fernando M.A. Henriques<sup>1</sup>, Diogo Miguel<sup>1</sup>, Maria Teresa Cidade<sup>2</sup>

<sup>1</sup> Dpto Engenharia Civil, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica (Portugal)

<sup>2</sup> Dpto. Ciência dos Materiais and Cenimat/I3N, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica (Portugal)

e-mail of the presenter: mtc@fct.unl.pt

Many historic buildings all over Europe are made of stone masonry walls. Unfortunately, stone masonry walls have demonstrated particular weakness, specially the multiple-leaf masonry walls. Some of the major causes for deterioration of multiple-leaf masonry are attributable to inadequate connections between leafs, voids, and the poor quality of mortar, so the load bearing capacity of such walls, especially horizontal loading, is very low. Rehabilitation and strengthening of this kind of masonry has undergone a remarkable development on the basis of new techniques and materials. Among those available, grout injection technique (or grouting) is applied to multiple-leaf masonry mainly to enhance the mechanical properties of the weak inner core, as well as to re-instate the connection between external leafs [1]. Over the last years, some researches [2,3,4] have studied the use of several admixtures and additives in hydraulic grouts with the purpose of improve their fresh performance. The use of hydrophobic additives, such as silicone, in injection grouts is one of the main trends in development of grouts with improved injectability by reducing their wettability. The aim of this study is to better understand the effect of hydrophobic additives (type and content) on the rheological performance of injection grouts. The effects of three different materials with hydrophobic properties, such as polydimethylsiloxan, linseed oil and a commercial available mass-hydrophobic agent, on the rheological properties of hydraulic lime-based grouts were analysed. The test results showed that the grouts with hydrophobic additives exhibited the characteristics that better follow the Herschel-Bulkley model. The results also showed that all the hydrophobic additives lead to the reduction of grout fluidity and the linseed oil was the most harmful. For instance when the content of linseed oil was 1.5 wt%, the yield stress values were increased by 80% compared to the reference grout.

**Keywords:** injection grouts, rheological properties, hydrophobic additive, stone masonry

## References

- [1] M. Corradi, A. Borri, A. Vignoli, Strengthening techniques tested on masonry structures struck by the Umbrian–Marche earthquake of 1997–1998. *Construction and Building Materials* **16(4)**: page 229–239 (2002).
- [2] I. Griffin, Pozzolanas as additives for grouts: An investigation of their working properties and performance characteristics *Studies in Conservation* **49(1)**: page 23–34 (2004).
- [3] A. Kalagri, A. Miltiadou-Fezans, E. Vintzileou, Design and evaluation of hydraulic lime grouts for the strengthening of stone masonry historic structures. *Materials and Structures* **43**: page 1135–1146 (2010).
- [4] L.G. Baltazar, F.M.A. Henriques, M.T. Cidade, Contribution to the design of hydraulic lime-based grouts for masonry consolidation. *Journal of Civil Engineering and Management* **21(6)**: page 698-709 (2015).

## Flow dynamics of air bubbles rising in yield stress fluids

M. F. Naccache, W. Lopez, P. R. De Souza Mendes, A. Alvarez, A. Abdu

*Pontifícia Universidade Católica do Rio de Janeiro, R. Marques de São Vicente 225, Rio de Janeiro, RJ, Brazil*

naccache@puc-rio.br

Flow of gas bubbles in complex fluids is present in processes of several industrial sectors, from oil and gas to food and drink industries. To study and optimize these processes we need to understand the flow dynamics. This work presents an experimental and numerical analysis of the influence of yield stress, elasticity and thixotropy on bubble shape and displacement due to buoyancy. Experiments are performed in an acrylic tank with square cross section. Air bubbles are injected using a syringe pump connected to a tube that is inserted at the bottom of the tank. A high-speed camera is used to obtain the sequence of pictures that gives the bubble shape and terminal velocity. Fluids with elasto-viscoplastic and thixotropic behaviors are used in the experiments. The flow curve, viscous and elastic modulus are obtained for both fluids. Results are obtained for a range of low to moderate Reynolds number, which is defined using a viscosity evaluated at a shear rate given by the ratio of the terminal velocity to the effective bubble radius, which is the radius of a spherical bubble with the same volume. The effect of yield stress is evaluated through its dimensionless parameter, the Bingham number. Elasticity effects are accounted via the Deborah number. Although it is not possible to isolate the influence of the different contributions, we can identify some tendencies. We estimate a critical value of Bingham number, above which there is no flow. The bubble terminal velocity increases faster up to a certain diameter, when inertia become more important, widening the bubbles and reducing the velocity variation. On the other side, elasticity changes the bubble to a tail and cusped shape. It is interesting to note that the change of shape does not affect much the drag coefficient, which seems to vary only with the Reynolds number. Indeed, we propose a direct correlation between the drag coefficient and the Reynolds number. Moreover, it is also observed that shear history and thixotropy have important effects on bubble displacement. The numerical solution is obtained for a viscoplastic fluid modeled by the Herschel-Bulkley equation, using the finite volume technique. Velocity and pressure fields around the bubble are obtained, helping the understanding of flow dynamics. Since elasticity and thixotropy are not considered, we can isolate and evaluate inertia/buoyancy and yield stress effects. Finally, a qualitative comparison with the experimental results is performed.

**Keywords:** yield stress, thixotropy, flow of bubbles, elasto-viscoplastic fluids

# The impact of thickeners and surfactants on the rheology of hair cleansing products

A Nunes<sup>1</sup>, J Marto<sup>2</sup>, J Sotomayor<sup>3</sup>, HM Ribeiro<sup>2</sup>

<sup>1</sup> Chemistry Department, Faculty of Science and Technology, Universidade Nova de Lisboa, Caparica, Portugal

<sup>2</sup> Research Institute for Medicine and Pharmaceutical Science (iMed.U LISBOA), Faculty of Pharmacy, Universidade de Lisboa, Lisboa, Portugal

<sup>3</sup> REQUIMTE, Chemistry Department, Faculty of Science and Technology, Universidade Nova de Lisboa, Caparica, Portugal

e-mail of the presenter: hribeiro@campus.ul.pt

The cosmetic industry has been, over time, undergoing a technological advance in shampoo formulations. The shampoo formulation comprises, among others, water, surfactants, thickening agents and other components. The main constituent of hair cleansing product is the surfactant due to its detergent properties. With the growth in demand for environmentally-friendly products steadily on the rise, it's natural that only naturally-derived surfactants are a category sparking interest among formulators.

To meet this objective, 16 formulations composed of naturally-derived surfactants, including alkyl polyglucosides (sugar based) formed, in this case, by decyl glucoside, and acylamino acids (amino acids based) formed by potassium cocoyl glycinate and sodium cocoyl glycinate. Different thickeners, cocamide DEA, sugar based composed of PEG-18 glyceryl oleate, PEG-free formed by sorbitan sesquicaprylate and, finally, HPMC were used to assess the rheological characterization, the foaming and pH. A formulation with sodium laureth sulfate (SLES) was used as control.

The pH was measured with a potentiometer while the foaming and foam stability were determined using a vortex for 15 seconds and measuring the foam height for 100 minutes. Non-destructive oscillatory experiments were performed with a controlled stress Kinesus Rheometer (Malvern) using cone and plate geometry (truncated cone angle 4° and radius 40mm).

Concerning the pH values, it can be stated that the values vary between 8.91 and 5.73 appropriate for shampoos. The formulation with higher pH it's the one that has the SLES as surfactant and the traditional thickener while, the formulation with SLES as surfactant and a sugar based thickener has the lowest pH. Concerning the stability of the formed foam, it has been found that when HPMC is used, it promotes stable foam formation, unlike the traditional and PEG-free thickeners. The formulation with higher foam stability it's the one that has the amino acid based as a surfactant and HPMC as a thickener while, the formulation with the SLES as a surfactant and the traditional thickener was found form less foam.

HPMC is the thickener that presented the higher values of shampoos' viscosity regardless the surfactant used. In all formulations, the  $G' > G''$ , meaning, these formulations have the viscous module superior to the elastic module presenting a weak network that allows the good flow allowing a good spreadability of the products on the hair.

In conclusion, both thickeners and surfactants have great impact in hair cleansing products properties depending on their chemical origin of the raw material.

**Keywords:** Shampoo, Thickener, Surfactant, Eco-friendly products, Rheology.

## Sustainable exfoliators: The influence of *Quercus Suber* bark particle size on rheological properties and on *in vivo* efficacy

J Marto<sup>1</sup>, P Prazeres<sup>2</sup>, P Pinto<sup>1,3</sup>, HM Ribeiro<sup>1</sup>

<sup>1</sup> Research Institute for Medicine and Pharmaceutical Science (iMed.Ulisboa), Faculty of Pharmacy, Universidade de Lisboa, Lisboa, Portugal.

<sup>2</sup>Paralab, Tv. Calvário da Giesta, Valbom, Portugal

<sup>3</sup>PhD Trials®, Rua das Murtas, nº1B, 1º, Lisboa, Portugal

e-mail of the presenter: jmmarto@ff.ulisboa.pt

*Quercus Suber* Bark particles (QSBP) from *Quercus suber L.* is a natural, renewable and biodegradable biomaterial with multifunctional proprieties. They are used primarily for exfoliation. QSBP are ideal for sensitive skin as they remove dead cells without irritation compared to other natural exfoliators, namely seeds and walnut shells, which can have sharp edges.

In this study the rheological behaviour and particle size were evaluated on two different exfoliators containing only natural ingredients and powdered QSB, differing only on particle size of QSBP (C500 – 2.5% of QSBP with 500 µm; C100 – 2.5% of QSBP with 100 µm; P – without particles). The exfoliators were characterized in terms of *in vivo* efficacy tests, using 5 human volunteers and powdered QSB by SEM.

Rotational viscosity was determined using a C40 mm cone geometry, with an angle of 4°. Flow curves were generated by ramping the shear rate from 0 to 100 s<sup>-1</sup> in 120 seconds (ascent curve) and then from 100 to 0 s<sup>-1</sup> in 120 seconds (descent curve) and recording the shear stress throughout. Dynamic viscosity measurements were carried out between 1 and 1000 Pa on a logarithmic increment. Oscillation frequency sweep tests were performed at frequencies ranging between 0.01 and 1 Hz.

All exfoliators show shear thinning behaviour. The C500 had a higher viscosity compared to the C100. It was observed that  $G'$  increases with increasing particle size. This indicates that the structure of the exfoliators become more robust with higher particle size. The system maintained the gel-like properties ( $G' > G''$ ), which assured stability during the stress tests and exhibited long-term storage stability. The *in vivo* efficacy of exfoliators was demonstrated on skin texture with an improvement of skin roughness for both formulations.

The structural properties increased markedly for high particle size of QSBP, what contributes to increase the formulation shelf-life and *in vivo* efficacy. Thus, the use of QSBP as a multifunctional solid ingredient contributed to achieve sustainable and innovative exfoliators with *in vivo* efficacy.

**Keywords:** *Quercus suber* bark particles; Rheology; Sustainable; Exfoliators; *in vivo* efficacy

## A Preformulation Study of Hydrogels through a Double Crosslinking Strategy

M. Pleguezuelos-Villa<sup>1</sup>, A. Nácher<sup>1</sup>, S. Mir-Palomo<sup>1</sup>, M. J. Hernández<sup>2</sup>, O. Vila Buso<sup>3</sup>, V. Alonso Usero<sup>4</sup>, A. Torrens<sup>5</sup>, O. Díez-Sales<sup>1</sup>

<sup>1</sup> *The Interuniversity Research Institute of Molecular Recognition and Technological Development (IDM). Politechnic Univ. Valencia. Department of Pharmacy and Pharmaceutical Technology. Univ. Valencia (Spain)*

<sup>2</sup> *Department of Earth Physics and Thermodynamics. Univ. Valencia (Spain)*

<sup>3</sup> *Department of Physical Chemistry. Univ. Valencia (Spain)*

<sup>4</sup> *Department of Dermatology, Hospital 9 Octubre. Valencia (Spain)*

<sup>5</sup> *Sesderma S.L. Valencia (Spain)*

e-mail of the presenter: [maplevi@alumni.uv.es](mailto:maplevi@alumni.uv.es)

Hydrogels (HG) are polymeric three-dimensional macromolecular networks formed by basic elements physical or chemically interconnected and swollen by a solvent. Polymeric HG have multiple applications, including their use in developing materials for tissue regeneration due to their excellent biocompatibility and their frequent use as drug delivery systems because of their ability to hold liquids and bioactive compounds. In this work, two polymeric HG have been prepared with highly biocompatible components such as gelatin (GE), chitosan (CH) and hyaluronic acid (HA), stabilized with  $\beta$ -glycerophosphate (BGP) and different concentrations of genipin, achieving different degrees of crosslinking. HG rheological properties were determined by means of flow and oscillatory tests. The use of these HG as drug carrier systems has also been tested. These studies demonstrate that double crosslinked GE-AH and CH-HA hydrogels are potentially useful for drug delivery.

**Keywords:** drug delivery, chitosan, gelatin, hyaluronic acid, genipine.

### References

- [1] Jalani, G. Rosenzweig, DH. Makhoul, G. Abdalla, S. Cecere, R. Vetrone, F. Tough, in-situ thermogelling, injectable hydrogels for biomedical applications, *Macromol Biosci*, volume: 15(4):473-80, 2015.
- [2] Reyes-Ortega, F. Cifuentes, A. Rodríguez, G. Aguilar, MR. González-Gómez, Á. Solis. Bioactive bilayered dressing for compromised epidermal tissue regeneration with sequential activity of complementary agents, *Acta Biomater*, volume: 23:103-15, 2015.

## Rheological parameters on microstructure of topical formulations assessment

M. Pleguezuelos-Villa<sup>1</sup>, A. Nácher<sup>1</sup>, O. Díez-Sales<sup>1</sup>, M. Merino-Sanjuán<sup>1</sup>, D. Peris-González<sup>3</sup>,  
M. J. Hernández<sup>2</sup>, V. Merino<sup>1</sup>

<sup>1</sup> The Interuniversity Research Institute of Molecular Recognition and Technological Development (IDM). Politechnic Univ. Valencia. Department of Pharmacy and Pharmaceutical Technology. Univ. Valencia (Spain)

<sup>2</sup> Department of Earth Physics and Thermodynamics. Univ. Valencia (Spain)

<sup>3</sup> Clinical Affairs and Development Kern Pharma. Madrid (Spain)

e-mail of the presenter: maplevi@alumni.uv.es

Generic drug products for topical administration tend to mimic reference products. If possible they tend to accomplish qualitative sameness (Q1, same components as the reference product) and quantitative sameness (Q2, same concentration as the reference). Nevertheless, although being Q1 and Q2 equivalent, differences in the manufacturing process between them could alter the delivery of the compound into the skin from a topical drug. This can be attributed to changes in microstructure due to elaboration procedures.

It is possible to claim biowaiver and avoid in vivo bioequivalence study if proof of similarity in Q3 is obtained. According to specialized publications Q3 refers to same components in same concentration with the same arrangement of matter (microstructure) as the reference. Q3 microstructure sameness includes identical rheology, type of emulsion and physical state of drug in semisolid system. Until now, the tests required (and the level of similarity required) to demonstrate identical rheology have not been defined.

The aim of this work was to study possible differences in the rheological properties of two semi-solid formulations of diclofenac diethyl amine (used as topical antiinflammatory) attributed to the manufacturing method.

Flow curves and viscoelastic tests (oscillatory tests) in linear viscoelastic region were performed in a controlled stress rheometer (RS1, ThermoHaake) at 25°C using formulation A (Voltadol Forte®) as reference and formulation B (Kern Pharma Diclofenaco 2% Emulgel) as test.

The rheological results showed a shear thinning behaviour for both formulations with similar zero viscosity and shear rate dependence. The dynamic spectra in all cases corresponded to the characteristic behaviour of structured gels ( $G' > G''$ ), where elastic behaviour predominated over viscous behavior.

These results showed that the selected parameters are useful to study internal microstructure of biphasic systems and can be used to evaluate Q3 similarity.

**Keywords:** microstructure sameness, zero viscosity, shear rate dependence, elastic behaviour, viscous behaviour.

### References

[1] Lauterbach, A. Müller-Goymann, CC. Comparison of rheological properties, follicular penetration, drug release, and permeation behavior of a novel topical drug delivery system and a conventional cream, *Eur J Pharm Biopharm*, volume: 88(3):614-24, 2014.

[2] Reyes-Ortega, F. Cifuentes, A. Rodríguez, G. Aguilar, MR. González-Gómez, Á. Solís. Bioactive bilayered dressing for compromised epidermal tissue regeneration with sequential activity of complementary agents, *Acta Biomater*, volume: 23:103-15, 2015.

## A comparative rheological study of several dentifrices trademarks

J.A. Picó<sup>1</sup>, J. Peris<sup>1</sup>, A.Sánchez<sup>1</sup>, M.J. Hernández<sup>2</sup> A. Nacher<sup>3</sup>, O. Diez-Sales<sup>3</sup>,

<sup>1</sup>Research and Development Department, KOROTT, SL. Polígono Santiago Payá, 03801 Alcoy (Spain)

<sup>2</sup>Department of Thermodynamics, Faculty of Physics, University of Valencia, 46100 Burjassot, Valencia (Spain)

<sup>3</sup>Dep. Pharmaceutics and Pharmaceutical Technology, Fac. Pharmacy, Univ. Valencia, 46100 Burjassot (Spain)

e-mail of the presenter: japico@korott.com

Dentifrices are considered to be semi-solid products which are designed to clean the teeth and provide a fresh and pleasant breath. These products are a mix of abrasives (e.g. hydrated silica), humectants, water, surfactants, agents for preventing tooth decay (e.g. fluoride), thickeners (e.g. cellulose gum, xanthan gum and carrageenans) and flavour, among others. In order to be an acceptable product it should be easily extrudable from the package ("squeezing out"), keep enough tightness ("stand up") over the toothbrush, generate a pleasant foam and have a good flavor for the consumer. The scientific literature about their composition, manufacturing, quality control and rheological properties is very limited.

A total of 13 dentifrices manufactured by 5 benchmarks distributed in mass markets in Spain (Binaca<sup>®</sup>, Colgate<sup>®</sup>, Kempfor<sup>®</sup>, Korott<sup>®</sup>, Sensodyne<sup>®</sup> and Signal). Flow curves in steady state and SAOS experiments were carried out with a controlled stress rheometer DHR-1 (TA Instruments), using serrated parallel plates. All measurements were performed at 20°C, controlling temperature by a Peltier plate.

All the dentifrices studied showed a highly shear thinning and viscoelastic behaviour, with a typical weak gel-like structure. Significant differences were observed in zero shear viscosity, what correspond to visual consistency over the toothbrush ("stand up"). As a consequence of the different shear thinning behavior, these differences are reduced for brushing shear rates.

Differences observed in viscoelastic behaviour could be a consequence of the different hydrocolloids and silica used, together with the humectants concentration present in their formulation.

**Keywords:** dentifrices, rheology, viscosity, viscoelasticity

### References

- [1] Pader, M. *Oral Hygiene Products and Practice*, 1<sup>a</sup> edn, Marcel Dekker, Inc, New York (1988).
- [2] Pader, M. "Dentifrice Rheology" in *Rheological Properties of Cosmetics and Toiletries*, ed. Dennis Laba, 1<sup>a</sup> edn, Marcel Dekker, Inc, New York, pp. 247-252 (1993).
- [3] Prencipe, M., Masters, J.G., Thomas, K.P. & Norfleet, J. 2016, 01-02-2016-last update, *Squeezing out a better toothpaste* [Homepage of British American Tobacco], [Online]. Available: <https://industrydocuments.library.ucsf.edu/tobacco/docs/#id=sgfb0205> [1995, Febrero 2013].

## Influence of hydrated silica on rheological properties of base formulations for toothpastes

J.A. Picó<sup>1</sup>, J. Peris<sup>1</sup>, A. Sánchez<sup>1</sup>, M.J. Hernández<sup>2</sup>, A. Nacher<sup>3</sup>, O. Díez-Sales<sup>3</sup>

<sup>1</sup>Research and Development Department, KOROTT, SL. Polígono Santiago Payá, 03801 Alcoy (Spain)

<sup>2</sup>Department of Thermodynamics, Faculty of Physics, University of Valencia, 46100 Burjassot, Valencia (Spain)

<sup>3</sup>Dep. Pharmaceutics and Pharmaceutical Technology, Fac. Pharmacy, Univ. Valencia, 46100 Burjassot (Spain)

e-mail of the presenter: japico@korott.com

Toothpastes are complex systems formed by a mix of water, humectants, thickeners, surfactants, abrasives, agents for preventing tooth decay, and flavour among others. The abrasive agents more widely used in these oral care products are hydrated silica. Hydrated silica is a generic name applied to all synthetic silicon dioxides produced via a liquid process. They are two types: silica gels and precipitated silica<sup>1</sup>. Due to mild abrasive and controlled structure, precipitated silica are used as mild abrasives and polishing agents in toothpaste formulations. The properties of precipitated silica are related to the structure, particle size and surface silanol group density. Depending of manufacturing process silica with thickening and/or abrasive properties can be obtained<sup>2</sup>.

The main goal of this work was to analyze the influence of both thickening and abrasive silica on rheological properties of base formulations for dentifrices (sorbitol-water-PEG12-CMC). Flow curves and dynamic spectra at 20°C were recorded using a DHR-1 control stress rheometer (TA Instruments).

The incorporation of thickening silica gives rise a highly shear thinning behavior systems with a higher zero shear viscosity and a weak gel structure ( $G' > G''$ ). It is likely that silanol groups (Si-OH) form hydrogen bonds with water and other humectants (sorbitol and PEG-12). On the other hand, the presence of abrasive silica does not appreciably affect flow behavior and produced not structured systems ( $G'' > G'$ ).

Therefore, knowledge of the rheological properties of the studied silica is very important as it would improve the development of new toothpastes formulations.

**Keywords:** humectants, hydrocolloids, hydrated silica, toothpaste, rheology

### References

- [1] Pader, M. "Dentifrice Rheology" in *Rheological Properties of Cosmetics and Toiletries*, ed. Dennis Laba, 1<sup>st</sup> edn, Marcel Dekker, Inc, New York, pp. 247-252 (1993).
- [2] Wason, S.K. *Cosmetic properties and structure of fine-particle synthetic precipitated silicas*, *Journal of the Society of Cosmetics Chemists* volume: 29 no. 8, page 497-521 (1978).

## Rheological properties and particle size distribution of face creams

Bayarri S<sup>1</sup>, Gómez J.L., Alonso M<sup>1</sup>

<sup>1</sup> RNB S.L, Polígono Industrial La Pobla-LEliana,  
C/Ausias March, Parc. Nº 14  
46185 La Pobla de Vallbona, Valencia (Spain)

sbayarri@rnbcosmeticos.com

This work studies the relationship between the rheological properties and particle size distribution of facial creams. Rheological measurements (flow curves and mechanical spectra) were carried out in a controlled stress rheometer RS1 using cone (C60/2°) and plate geometry, and a sample temperature of 25±1°C. In addition, particle size distribution was obtained by a Malvern Mastersizer laser diffraction analyzer. Control rate and control stress were used to study flow behaviour. Dynamic spectra were obtained from measurements within the frequency range 0.01-10 Hz at 25°C. The oscillatory rheological parameters used to compare the viscoelastic properties of the samples were storage modulus ( $G'$ ), loss modulus ( $G''$ ), and loss angle ( $\tan \delta$ ) at 1 Hz, while mean viscosity values (20-80s<sup>-1</sup>) from CR and  $\eta_0$  (Carreau model) from CS were used as flow parameters. Differences of facial creams are discussed on the basis of the rheological and particle size measurements.

**Keywords:** particle size, rheological behaviour, facial creams, emulsions

## Photoprotective rheology: guarantee of effectiveness and safety of photoprotection

M Reis Jr, J Reis, J Santos, A Almeida, Vera Isaac

*Faculdade de Ciências Farmacêuticas, UNESP – Univ Estadual Paulista, DFM – Laboratório de Cosmetologia – LaCos, São Paulo, Brazil.*

e-mail of the presenter: veraisaac@fctfar.unesp.br

Photoprotection is one way to prevent skin cancer. For the cosmetic product to be effective, the film formed on the skin must have a homogeneous application, facilitated by the spreadability of the product and also be uniform. The composition of the formulation may assist in the production easy-to-spread products which maintain the product on the surface of the skin without promoting permeation and / or penetration, since photoprotection will only occur when the photoprotect is maintained on the surface of the skin. The composition of the formulation may assist in the production easy-to-spread products which maintain the product on the surface of the skin without promoting permeation and / or penetration, since photoprotection will only occur when the photoprotect is maintained on the surface of the skin. The rheology may help in choosing the best photoprotector by indication of products with a lower hysteresis area, which may indicate less disorganization of the system during application, making possible the product from remaining properly on the surface of the skin. Thus, the determination of hysteresis is of fundamental importance in the development of photoprotectors. The emulsions proposed in this study are of the O / A type, with adequate sensorial to a photoprotector in which a sunscreen obtained by molecular hybridization was incorporated. The formulations were maintained under greenhouse thermal stress at 45 degrees and under indirect lighting to simulate possible system instability under conditions of use. The tests were performed in triplicate and four times: on day 2, day 30, day 60 and day 90, in Brookfield, RV-DV III. The determined parameters were 0 to 100 s<sup>-1</sup> shear rate for the rise curve and 100 to 0 for the descent curve. Next, the area of hysteresis was calculated to relate to the disorganization of the system and to infer about the release of the photoprotective active. The results indicate that the rheological model is Hershel Bulkley and the area of hysteresis is influenced by the storage temperature under stress, however, the small area of hysteresis obtained in all the analyzed formulations allows to infer that there is no release of the active, which allows conclude that the proposed photoprotective cosmetic product is effective by staying on the surface of the skin and safe for protecting the skin from ultraviolet radiation.

**Keywords:** Sunscreens, Rheology, Safety and efficacy of cosmetics.

### References

Chiari, B.G., *et al.* Cosmetics' Quality Control. In: Latest Research into Quality Control. INTECH, cap. 16, 337-364, 2012.

## Crucial viscoelastic features for polymer 3D printing

M. I. Calafel<sup>1</sup>, R. H. Aguirresarobe<sup>1</sup>, A. Santamaria<sup>1</sup>, N. Sadaba<sup>2</sup>, M. Boix<sup>3</sup>, B. Pascual<sup>3</sup>, I. Conde<sup>3</sup>

<sup>1</sup>*Institute of Polymer Materials (POLYMAT) and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country (UPV/EHU), Paseo Manuel de Lardizabal 3, 20018 Donostia-San Sebastián (Spain).*

<sup>2</sup>*Institute of Polymer Materials (POLYMAT), Mining-Metallurgy Engineering and Materials Science Department, Faculty of Engineering, University of the Basque Country (UPV/EHU), Alameda de Urquijo s/n, 4013 Bilbao (Spain).*

<sup>3</sup>*ERCROS S.A., Departamento de Innovación y Tecnología de la División de Plásticos, Diagonal 595. 08014-Barcelona (Spain).*

antxon.santamaria@ehu.eus

The so called “Additive manufacturing” is a new manufacturing process which consists in translating virtual solid model data into physical models in a quick and easy process (1). The most known example is 3D printing. This technology is considered a revolutionary route for processing and is currently being used in automotive and aerospace industries, as well as in medicine.

Many practical applications of 3D are carried out using polymers, but the number of scientific papers dealing with the physical basis of printing polymers is scarce (2). However, knowing the welding process involved in the additive manufacturing during 3D printing is a crucial issue, to implant the pillars of a sound knowledge in this field. Welding polymer layers implies a diffusion process of the polymer chains from one sheet to the other, which is governed by the viscoelastic behaviour in the terminal or flow zone. The time span of the terminal zone depends on temperature, in a way which is conditioned by the micro-structure and molecular mass distribution of the polymer. The time interval for the diffusion of the chains, which is equivalent to the time span of the terminal zone, is reduced as temperature is decreased. Therefore, in 3D printing of amorphous polymers welding becomes practically impossible at temperatures close to the glass transition  $T_g$ .

In this contribution we analyse the dynamic viscoelasticity of novel copolymers of polyvinyl chloride and different polyacrylates, to determine the frequency and temperature limits of the terminal zone. This permits to ascertain the priority of the materials to be used in 3D printing, considering the established printing velocity and temperature. An advanced printing machine is used to manufacture objects and, so, account for the relationship between the viscoelastic data and the quality of the elaborated articles.

**Keywords:** 3D printing, welding, polymer diffusion, viscoelasticity

### References

[1] I. Gibson, D. Rosen, B. Stucker, “*Additive Manufacturing Technologies*”, Springer Science, New York (2015).

[2] K. Migler et al. XVIIth International Congress on Rheology, 2016, Kyoto, Japan (2016).

## Flowing from rheology to tribology. Resolving the rub in food friction

R. E. D. Rudge<sup>1,2</sup>, M. Workamp<sup>2</sup>, P. de Visser<sup>2</sup>, E. Scholten<sup>1</sup>, J. A. Dijkman<sup>2</sup>

<sup>1</sup> *Physics and Physical Chemistry of Foods, Wageningen University & Research, Wageningen, The Netherlands*

<sup>2</sup> *Physical Chemistry and Soft Matter, Wageningen University & Research, Wageningen, The Netherlands*

e-mail of the presenter: Raisa.Rudge@wur.nl

There is an increasing need to understand the behaviour of foods in terms of their mouthfeel, in which both rheological and tribological aspects play a role. Rheology is able to capture the first parts of oral food processing, where there is a large fluid pressure separating the surfaces of the tongue and the palate. This would correspond to the hydrodynamic regime of the friction or Stribeck curve [1, 2, 3]. As the fluid film becomes thinner, sample behaviour moves towards the mixed regime of the Stribeck curve and can no longer be described by rheology. This regime therefore requires tribological interpretation. The tribology lens gives more insight into sensory attributes such as creaminess, fattiness or smoothness of the food system [2, 3]. However, the different friction meters or tribometers currently being used have their limitations. The frictional behaviour of soft solids depends on both the physicochemical characteristics of the gel and on the conditions used during measurement, making it more complex than the frictional behaviour of solids [4]. We aim to add microscopic insight to the tribology field by a combination of novel rheo-tribology tools and optical tweezer experiments. To demonstrate the effectiveness of our approach, we perform friction measurements on different soft solids and reveal the role of adhesion, electrostatics and lubrication. These new advances in rheology and tribology both give more insight into gel friction and may lead to the development of new (food) materials with previously unattainable characteristics.

**Keywords:** Rheology, Tribology, Soft solids, Friction.

### References

- [1] B.N.J. Persson, M. Scaraggi, Lubricated sliding dynamics: Flow factors and Stribeck curve, *Eur. Phys. J.E*, 34: 113-134 (2011).
- [2] S. Prakash, D. Dan Yi Tan, J. Chen, Title, *Food Research International*, 54: 1627-1635 (2013).
- [3] J. R. Stokes, M. W. Boehm, S.K. Baier, oral processing, texture and mouthfeel: from rheology to tribology and beyond, *Current Opinion in Colloid and Interface Science*, 18: 349-359 (2013).
- [4] J.P. Gong, Friction and lubrication of hydrogels- its richness and complexity, *Soft matter*, 2: 544-522 – (2006).

# Low temperature rheological performance of modified bituminous binders

A. Yuliestyan, A.A. Cuadri, M. García-Morales, P. Partal

*Departamento de Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro2TecS), Campus de El Carmen, Universidad de Huelva, 21071, Huelva (Spain)*

e-mail of the presenter: [partal@uhu.es](mailto:partal@uhu.es)

In the past decades, increasing load traffic prone to be the root of issues related to asphalt paving rheological performance, besides the extreme temperature during winter and summer that exacerbates the situation. To cope with those issues, performance of binder, a constituent in asphalt paving, can be modified by polymer. Binder rheological performance at low temperature regime is commonly assessed with either bending beam rheometer (BBR) or dynamic shear rheometry (DSR) using a parallel-plate geometry. However, the second option may face an issue associated to device compliance when working with sample around its glassy region and extremely small strain applied [1].

As an alternative, this work proposes a rheological characterization by attaching a solid rectangular fixture (SRF) in the DSR (allowing material rheological properties gathered in torsional mode) for the assessment at low temperature of neat bitumens and binders modified by EVA, SBS and wax. Frequency sweeps, from 1 to 100 rad/s for four different set of temperature between -30 and 0 °C, were performed on bituminous binders by applying an oscillatory torsion within its linear viscoelasticity, previously measured using stress sweep tests for each temperature tested. A master curves at the reference temperature of -10°C were constructed using time-temperature superposition principle (TTSP) for determining its mechanical glass transition temperature ( $T_{G, DMTA}$ ). In addition, a modulated differential scanning calorimetry (MDSC) technique was also utilized for the confirmation. Finally, to assess the non-linear material performance between -30 to 0 °C, strain breakage tests were performed by gradually increasing a dynamic shear load to reach a condition above which material could not sustain load to cause damage.

The results suggest that the rheological performance of bituminous binder at low temperature could be revealed by utilizing SRF attached to DSR with torsional mode, providing an alternative to commonly used methods.

**Keywords:** polymer modified bitumen, asphalt pavement, rheology, low temperature

## References

[1] D.W. Christensen, D.A. Anderson, Interpretation of dynamic mechanical test for paving grade asphalt cements, *J. Assoc. Asph. Paving Technol.*, 61: page 67 – 116 (1992).

## On the shear-induced structural degradation of lithium and calcium lubricating greases

C. Roman, C. Valencia and J. M. Franco

*Departamento de Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro2TecS), Campus de "El Carmen", Universidad de Huelva, 21071, Huelva (SPAIN)*

E-mail of the presenter: claudia.roman@diq.uhu.es

Lubricating greases are of utmost importance for both industrial applications and everyday lubrication because they are designed to maximize efficiency and prolong the useful service life of all moving equipment [1]. In general, lubricants require wide experience and knowledge to obtain a relevant behavior for a specific application. In that sense, high-shear testing protocols for a set of commercial specimens were used in order to acquire new knowledge and understanding how high-shear working treatments influence grease microstructure using the atomic force microscopy (AFM) technique. With the help of a controlled-strain ARES (UK) rheometer and a controlled-stress Physica MCR-501 (Anton Paar, Austria) rheometer coupled with a tribological cell it was possible to simulate the friction and internal wear processes.

The AFM results brought to light a diversity of morphological characteristics depending on the nature and concentration of the thickener and viscosity of the base oil. Based on both rheological and tribological tests, the AFM results reveal important microstructural changes as a consequence of the internal wear processes, which mainly depend on the grease composition. These changes are directly associated with the degree of non-reversible microstructure destruction, which increases with temperature and depends on the shear treatments applied.

**Keywords:** rheology, tribology, microstructure, AFM, lubricating grease

### References

[1] G. Gow, Lubricating grease. In Chemistry and Technology of Lubricants, 3rd edn.; Mortier, R. M., Fox, M. F., Orszulik, S., Eds.; *Springer Science+Business Media B.V.*, 411-432 (2010).

## Remedying slip effects in the shear flow of gellan sheared gels

M.C. García, S. Sánchez, J. Santos, M.C. Alfaro, J. Muñoz

*Universidad de Sevilla, Grupo de Reología Aplicada. Tecnología de Coloides. Facultad de Química. c/ P. García González, 1, 41012, Sevilla (Spain).*

e-mail of the presenter: [jmunoz@us.es](mailto:jmunoz@us.es)

Gellan gum is a microbial anionic biopolymer that is mainly used as gelling agent or to prepare sheared gels, also called fluid gels.

Sheared gels can be tuned to exhibit a relatively low consistency but high elasticity, which support their applications as suspension stabilisers and satiety agent. The structure behind the rheology of sheared gels basically consists of aqueous dispersions based on a network of either meso or microgels, depending on gum concentration, type and concentration of gel-promoting cation and processing variables. Therefore, they are prone to undergo wall depletion phenomena under shear. This contribution highlights the dramatic errors which would be made if slip effects were not avoided. In addition, we also illustrate how to successfully overcome this problem for  $\text{Ca}^{2+}$ -induced fluid gels prepared with low-acyl gellan gum.

We will exhibit the most sensitive plots to detect the occurrence of wall slip when stepwise flow curves are run with cone & plate, standard plate & plate and serrated plate & plate measuring geometries. We will demonstrate the efficiency of the serrated plate & plate geometry to avoid wall slip. Furthermore, we will show how far the linear viscoelastic range (LVR) determined by small amplitude oscillatory shear and the apparent yield stress estimated from the Herschel-Bulkley equation are underestimated unless wall slip is prevented. In order to get a deeper insight into the onset of shear flow of fluid gels, linear and non-linear creep tests were carried out and the results were compared to those calculated from flow curves. We demonstrate that creep compliance is the rheological test of choice to accurately determine a practical yield stress for very shear thinning materials, since they are quite sensitive to track the transition from, in practice, the quiescent state to shear flow.

**Keywords:** Slip effects, Fluids gels, Yield stress, Creep test, Gellan gum

## Shear and axial measurements on magnetorheological fluids

Carlos A. Gracia Fernández<sup>1</sup>, Modesto T López-López<sup>2</sup>

<sup>1</sup> *TA Instruments-Waters Crommatografía, Ronda Can Fatjó, Cerdanyola del Vallés (Spain).*

<sup>2</sup> *Departamento de física Aplicada, Universidad de Granada, Campus de Fuentenueva, Granada (Spain)*

cgracia@tainstruments.com

Magnetorheological (MR) Fluids are suspensions of micron-sized particles of magnetizable materials. These suspensions are characterized by the tunability of their rheological properties by means of magnetic field application, a phenomenon known as the MR effect.

The commercial trademark of MR Fluid used in the present work is MRHCCS4-A from Liquid Research Limited (UK). In addition, we used a non-commercial MR fluid characterized by having particle content close to the maximum-packing fraction.

The magneto-rheological properties of were measured at several magnetic field intensities in shear and compression allowing a comprehensive characterization of their mechanical properties. The results show that when the magnetic field was varied, from 0 mT and 1000 mT the change in the storage compression modulus is more than 10 times bigger than the change in storage shear modulus for the commercial fluid MRHCCS4-A reaching the saturation. The change in the storage compression modulus and the shear compression modulus is pretty similar for the highly concentration suspension (carbonyl iron powder in oil).

**Keywords:** MRFluids, Shear Modulus, Bulk Compression Modulus.

## Blood analogue fluid flows in complex geometries

Rui P. O. Campos<sup>1</sup>, Rui A. Lima<sup>1</sup> and Laura Campo-Deaño<sup>2</sup>

<sup>1</sup> Departamento de Engenharia Mecânica, Escola de Engenharia da Universidade do Minho, Campus de Azurém, 4800-058 Guimarães (Portugal).

<sup>2</sup> Departamento de Engenharia Mecânica, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, s/n, 4200-465 Porto (Portugal).

campo@fe.up.pt

It is well known that the complex flow behaviour of blood is closely related with some cardiovascular diseases, for that reason a complete understanding of the hemodynamics and fluid-structure interaction of blood flow flowing through the main vessels of the human body is of great interest. Nevertheless, the manipulation of real blood is sometimes difficult due to the ethical and hazardous issues that it involves and in this context the development of blood analogue solutions is crucial. Several fluid analogues to whole human blood have been developed and more recently some particulate blood analogue solutions were also obtained to study not only the whole rheological behaviour but also the physiological behaviour as it is important to simulate the Cell Free Layer (CFL) that exists in microcirculation [1,2]. In this work, some blood analogues (particulate and non-particulate) were used to study their flow behaviour in more complex geometries as bifurcations and confluences. The rheological characterization of the analogues was carried out by means of a rotational rheometer and Micro-PIV (Particle Image Velocimetry) and flow visualization techniques were used to obtain the velocity profiles and to observe the CFL, respectively. The deformation index of the particles of particulate blood analogue was analysed as well and compared with data of incubated real human erythrocytes.

**Keywords:** Rheology, blood analogues, microfluidics, flow characterization, Cell Free Layer (CFL)

### References

[1] L. Campo-Deano, R.P.A. Dullens, D.G.A.L. Aarts, F.T. Pinho and M.S.N. Oliveira, Viscoelasticity of blood and viscoelastic blood analogues for use in polydimethylsiloxane in vitro models of the circulatory system, *Biomicrofluidics*, **7**: 034102 (2013).

[2] J. Calejo, D. Pinho, F. J. Galindo-Rosales, R. Lima and L. Campo-Deaño, Particulate Blood Analogues Reproducing the Erythrocytes Cell-Free Layer in a Microfluidic Device Containing a Hyperbolic Contraction, *Micromachines*, **7**(1): 4 (2016).

## Viscosity index improvers for multi-grade oil of copolymers polyethylene-propylene and hydrogenated poly (isoprene-co-styrene)

Ioana Stanciu

University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry, 4-12 Elisabeta Blvd, 030018, Bucharest (Romania)

istanciu75@yahoo.com

To establish the ability of Infineum SV 260 and Paratone 8900 copolymers solutions in SAE 10W mineral oil as solvent to perform at low and high temperatures in a vehicle's engine, that is their capacity to improve the oil viscosity index, the viscosity- temperature characteristics of their 3, 3.5, 4, 4.5 and 5 % solutions were determined. The kinematic viscosities of the mineral oil SAE 10W and concentrated copolymer Infineum SV 260 and Paratone 8900 solutions were determined using a set of Schott Ubbelohde-type viscometers selected according to the values of their constants and viscosities of solutions, so that the margins of the uncertainty, inherent in the Hagebach-Couette correction, does not exceed the error allowed for the measurements. It was obtained that the both copolymer increase very much the viscosity index, as much as their concentration is higher. Infineum SV 260 produces a lower increase of viscosity indices comparative with Paratone 8900: 3.13 times for a concentration of 3%, 4.21 times for 3.5%, 4.42 times for 4%, 4.57 times for 4.5% and 4.71 times for 5% compared with 4.38, 4.7, 4.86, 5.18 and 5.33 times, respectively [1].

The values of the viscosity-temperature coefficients, calculated from the kinematic viscosities of solutions at 40 and 100°C, show also that Paratone 8900 is a better viscosity index improver than Infineum SV 260 irrespective of concentration.

**Keywords:** copolymer, viscosity

### References

- [1] C.M. Fernandes, P.M Amaro, R.C. Martins, J.H. Seabra, *Tribology International*, **66**: 194-202 (2013).

## Can MWCNTs localize in the least favorable phase in a binary immiscible polymer blend?

Claudia Roman<sup>1</sup>, Moisés García-Morales<sup>1</sup> and Tony McNally<sup>2</sup>

<sup>1</sup> *Departamento de Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro2TecS), Campus de "El Carmen", Universidad de Huelva, 21071, Huelva (SPAIN)*

<sup>2</sup> *International Institute for Nanocomposites Manufacturing (IINM), Warwick Manufacturing Group (WMG), The University of Warwick, CV4 7AL, Coventry (UNITED KINGDOM)*

e-mail of the presenter: moises.garcia@diq.uhu.es

Immiscible polymer blends may provide improved performance as compared to their separate constituents. Moreover, the nanocomposites of polymer blends and multi-walled carbon nanotubes (MWCNTs) are of special interest in a number of advanced applications. In that sense, their potential performance is conditioned by the phase where the MWCNTs localize. In this paper we present a study on blends with varying PMMA:LDPE ratios, as a function of the MWCNT concentration. The so-called "wetting coefficient", based merely on thermodynamic considerations, suggests the MWCNTs preferential localization in the PMMA phase. However, experimental work carried out on selected blends led to a different conclusion. The filled and unfilled 20:80 blends, in which LDPE constitutes the major phase, exhibited quite different results, in terms of elasticity at low frequency. However, the linear viscoelastic moduli of the filled 80:20 blend did not differ qualitatively from its unfilled counterpart, which reveals that the CNTs were not localized in the PMMA major phase. These results demonstrate that other parameters can govern the selective localization of CNTs in immiscible polymer blends. In our case, the non-functionalized MWCNTs concentrated in the LDPE phase, which is the polymer first to melt, and did not have the chance to further migrate to the thermodynamically most favorable PMMA phase over the short extrusion period used. With regard to the electrical properties, the so-called "double percolation" [1] determines if the nanocomposite becomes an electrical semi-conductive material. In that sense, the above filled 80:20 and 20:80 blends presented electrical resistivity values on the order of  $10^5$  and  $10^{12}$   $\Omega \cdot \text{cm}$ , respectively. As proved by SEM observations, the LDPE phase was (at least partially) continuous in both samples. However, only in the 80:20 blend was the "effective" CNT concentration in LDPE high enough such that electrical percolation was attained.

**Keywords:** PMMA, LDPE, MWCNT, nanocomposite, rheology

### References

[1] M. Sumita, K. Sakata, S. Asai, K. Miyasaka, H. Nakagawa, Dispersion of fillers and the electrical conductivity of polymer blends filled with carbon black, *Polymer Bulletin*, **25**: 265 – 271 (1991).

# Improving the properties of biodegradable Poly(butylene adipate-co-terephthalate) for packaging: From processing to application

Leire Sangroniz, Ainara Sangroniz, Marian Iriarte, Agustin Etxeberria, Antxon Santamaria

POLYMAT and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel de Lardizabal 3, 20018 Donostia-San Sebastián, Spain  
leire.sangroniz@ehu.es

Nowadays commodity polymers are widely used in packaging applications; however, the major drawback of these polymers is that once they are used they are disposed in landfills or in incinerators. In order to overcome this problem, biodegradable polymers have been widely studied in the last years. In general biodegradable polymers exhibit poor mechanical and barrier properties, thus different techniques have been used to improve their properties, so they can be suitable for the required application [1].

In this work, biodegradable Poly(butylene adipate-co-terephthalate) polymer, which exhibits weak barrier character, is investigated. To improve these properties a non-biodegradable polymer commercially known as Blox, which is a poly(amino-ether) resin, is blended with PBAT obtaining immiscible blends. The characterization of the barrier properties to different penetrants shows that the addition of Blox leads to a huge improvement. Since this blend has potential applications in the packaging sector, the study of its properties related to processing conditions becomes a necessary task.

In industry, films are obtained usually by blown film extrusion, so the rheological properties of the blends in shear and in elongation flow have to be studied. For that, small amplitude oscillatory shear (SAOS) measurements in the molten state have been performed, studying the effect of adding Blox on the viscoelasticity, which is relevant for processing. On the other hand, from an academic point of view, it is interesting studying the effect of the composition of the blend on the linear viscoelastic properties and the estimation of the interfacial tension of the blends. Regarding to the elongational flow, the blend has to exhibit adequate melt strength to be suitable for processing by blown film extrusion. In addition, the mechanical properties of the blends have been studied by DMTA measurements in order to assess its suitability for the final application [1, 2].

**Keywords:** immiscible blend, biodegradable, SAOS, elongational flow, barrier character

## References

- [1] H. Eslami, M.R. Kamal, Effect of chain extender on the rheological and mechanical properties of biodegradable poly(lactic acid)/Poly[(butylene succinate)-co-adipate] blends, *Journal of Applied Polymer Science*, **129**: 2418-2428 (2013).
- [2] R. Al-Itry, K. Lamnawar, A. Maazouz, Biopolymer Blends Based on Poly(lactic acid): Shear and Elongation Rheology/Structure/Blowing Process Relationships, *Polymers*, **7**: 939-962 (2015).

## Relationship between interfacial and emulsifying characteristics of a quinoa protein concentrate

López-Castejón, M.L., Carrera, C., Ruiz, M., Fuente, J., Bengoechea, C.

*Universidad de Sevilla, Departamento de Ingeniería Química, c/ Prof. García González 1, 41012 Sevilla (Spain).*

e-mail of the presenter: cbengoechea@us.es

Protein concentrates are used as a functional ingredient primarily to increase nutritional quality and to provide desirable sensory characteristics such as structure, texture, flavour, and colour to formulated food products. The protein concentrates and isolates used by the food industry today are mostly derived from soybean, whey and wheat. However, because of dietary restrictions and preferences (related allergenicity, vegetarianism, Halal requirements, etc.), food manufacturers and consumers are looking for alternative protein sources. Quinoa is a pseudo-cereal that is of increasing interest worldwide as an alternative staple food and considered by the FAO as a perfect food (FAO, 1985). It can be considered highly suitable for the preparation of protein concentrate because of their high protein content and wide acceptability.

Emulsification and foaming are two important functional characteristics of proteins that affect the behaviour of various industrial products, including foods, cosmetics and packing material (Httiarachy and Kalapathy, 1998). Emulsion capacity and stability are critical parameters that affect the choice of protein for use in an industrial process (Wagner and Guenuen, 1999). Both parameters are closely related to the ability of proteins to reduce tension in the water–oil interface helping prevent coalescence, as we have previously observed with other proteins.

The protein concentrate of quinoa was obtained by protein solubility at alkaline pH value, followed by precipitation at an acid pH value. The aim of this work was to study the effect of concentration and pH on the adsorption of quinoa protein concentrate at the oil/water interface and on the rheological properties of the interfacial films. Then, an evaluation of emulsifying (emulsifying capacity and stability) properties of quinoa protein concentrate in relation to their interfacial behavior (adsorption kinetic and rheological properties) was carried out. This research is part of a project financed by MINECO/FEDER, EU (CTQ2015-71164-P).

**Keywords:** quinoa, emulsion, interfacial properties

### References

- [1] Food and Agriculture Organization (FAO), 1985. Food and Agriculture Organization of the United States/World Health Organization/United Nations University, Energy and Protein Requirements Report of a joint FAO/WHO/UNU meeting. World Health Organization, Geneva.
- [2] N.S. Httiarachy, U. Kalapathy Functional properties of soy proteins J.R. Whitaker, F. Shahidi, A. Lopez-Munguia, R.Y. Yada, G. Fuller (Eds.), Functional Properties of Proteins and Lipids, Washington, DC, USA, page 80–95 (1998)
- [3] J.Wagner, J.Guenuen, Surface functional properties of native, acid treated and reduced soy glycinin. 2. Emulsifying properties. J. Agric. Food Chem. 47, page 2181–2187 (1999)

## Effect of the addition of cellulosic fibers on the physico-chemical properties of soy protein bioplastics

Gamero, S., Jiménez, M., Fuente, J., Bengoechea, C.

*Universidad de Sevilla, Departamento de ingeniería química, C/Profesor García González, 1 (SPAIN).*

e-mail of the presenter: cbengoechea@us.es

Plastics derived from petrochemicals have been extensively used in many applications for a very long time, which eventually have resulted in a serious environmental issue mainly due to the non-biodegradability of those materials. Thus, the progressive replacement of those traditional plastics by new plastics based on ingredients with a higher degradability is of special interest in the industry. Some of these environmentally friendly materials are based on biopolymers (e.g. proteins, polysaccharides). The present work focuses on bioplastics based on a soy protein isolate (SPI) plasticized by glycerol (GL), keeping a SPI/GL ratio equal to 1 in all cases. These materials have been processed by means of a lab scale injection moulding machine (MiniJet2, Haake) using a procedure described elsewhere [1]. The influence of the addition of different contents (0.1-10 wt.%) of cellulosic fibers (CF), either bleached (CFb) or unbleached (CFu), into the matrix have been evaluated on terms of their flexural viscoelastic properties (storage and loss moduli,  $E'$ ,  $E''$ , respectively), tensile properties (Young modulus,  $E$ ; stress and strain at fracture,  $\sigma_f$  and  $\varepsilon_f$ ) and water uptake. When lignin is present in the fiber (5.2% in CFu), fiber contents as high as 5% produce significant differences for  $E'$  and  $E''$  in the whole frequency interval studied (0.05-20 Hz). On the other hand, higher fiber contents (e.g. 10%) are needed to observe a significant difference in those viscoelastic properties when CF has been bleached (0.4% lignin content in CFb). As for the mechanical properties, they were specially affected at fiber contents higher than 1%, observing slightly higher  $E$  and lower  $\varepsilon_f$  values for CFu samples. Although water uptake of the SPI/GL bioplastics diminished when CF content was higher than 1%, it has a maximum at 0.1% when CFb was used. Consequently, a small amount of CF may be used in the formulation of these bioplastics to enhance their water affinity.

**Keywords:** bioplastic, soy protein, cellulose, lignin, rheology

### References

[1] L. Fernández-Espada, C. Bengoechea, F. Cordobés, A. Guerrero, *Journal of Applied Polymer Science*, **133(24)**: 43524 (2016).

### Acknowledgements

This research is part of a project financed by MINECO/FEDER, EU (CTQ2015-71164-P).

# Soy-based nanocomposites materials: A comparison between injection moulding and extrusion

M.Felix<sup>1</sup>, I. Martínez<sup>2</sup>, J.M. Aguilar<sup>1</sup>, A. Guerrero<sup>1</sup>

<sup>1</sup>University of Seville, Facultad de Química, C/ Profesor García González 1, Seville (Spain).

<sup>2</sup>Dpto. Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro2TecS), Universidad de Huelva-Campus Excelencia CeIA3, Campus El Carmen, 21071, Huelva (Spain)

e-mail of the presenter: mfelix@us.es

The development of superabsorbent biopolymers requires a deep knowledge of the physical, chemical and functional properties of the proteins to be used, as well as of the processing techniques for the polymeric matrixes (eg. extrusion, injection moulding or compression). The formulation and processing of these materials must be evaluated in terms of their physicochemical properties [1]. To obtain superabsorbent materials a highly hydrophilic protein, such as soy protein isolate (SPI) is required. This protein system has been used to create suitable bioplastics in combination with a proper plasticiser, exhibiting a high water uptake capacity [2]. In addition, Natural Montmorillonite (MMT-Na<sup>+</sup>) has been used in order to enhance the mechanical and barrier properties of bioplastics. It is widely available in nature as micron-size tactoids. However, the dispersion of such particles within a polymer structure is complex and the efficient dispersion of nanoclays in biopolymer matrices is a key factor in these materials (where an exfoliated MMT-Na<sup>+</sup> is desirable). In this context, MMT-Na<sup>+</sup>/Protein dispersion in an extruder is one of the most promising techniques due to high shear mixing inside the extrude, which may allow obtaining a desirable exfoliated structure. On the other hand, injection moulding is one of the most versatile and used polymer processing techniques [3], being particularly useful for polymeric materials that deviate from a typical thermoplastic behaviour (Eg. protein-based bioplastics). The overall objective of this work is to determine the influence of two processing techniques for traditional plastics, extrusion or injection moulding, on the SPI/MMT nanocomposite materials performance. For this purpose, mechanical properties of nanocomposites were evaluated by dynamic mechanical analysis (DMTA) and tensile tests. Additionally, the structure was characterized by transmission electron microscopy (TEM) and the water uptake capacity was determined.

**Keywords:** Extrusion, Injection moulding, MMT-Na<sup>+</sup>, Nanocomposites, Soy protein

## References

- [1] Alexandre, M., Dubois, P. Polymer-Layered Silicate Nanocomposites: Preparation, Properties and Uses of a New Class of Materials. *Mater. Sci. Eng. R-Reports*, **28** (1–2), 1–63 (2000).
- [2] Fernández-Espada, L., Bengoechea, C., Cordobés, F., Guerrero, A. Thermomechanical Properties and Water Uptake Capacity of Soy Protein-Based Bioplastics Processed by Injection Molding. *J. Appl. Polym. Sci.* **133** (24), 124-132 (2016).
- [2] Mungara, P., Zhang, J., Zhang, S., Jane, J.-L. Soy Protein Utilization in Compression-Molded, Extruded, and Injection-Molded Degradable Plastics; *CRC Press LLC*, pp 621–638 (2002).

## Linear viscoelasticity of aqueous dispersions containing blends of tragacanth and locust bean gum polysaccharides

Martin Alfonso, J.E.<sup>1,2</sup>, Valencia, C.<sup>1,2</sup>, Franco, J.M.

<sup>1</sup> *Department of Chemical Engineering and Material Science, University of Huelva, 21071 Huelva, Spain.*

<sup>2</sup> *Pro2TecS – Chemical Process and Product Technology Research Center. 21071 Huelva. Spain.*

e-mail: jose.martin@diq.uhu.es

Currently, polysaccharides play a leading role as large source of biomass-based materials useful for various applications. They can be processed in different ways but their ability to form gels under specific conditions is particularly interesting: polysaccharide hydrogels have been proposed for food, cosmetic, biomedical, or pharmaceutical applications [1]. Locust bean gum (LBG) is a nonionic polysaccharide biopolymer derived from the seed of the carob tree and exists in solution with water as a random coil. This polysaccharide has a wide potential in drug formulation due to their extensive application as food additives and their recognized lack of toxicity. Therefore, tragacanth gum (GT) is a complex, highly branched and anionic polysaccharide consisting of small proportions of protein. The blending of two or more polysaccharides can provide hydrogels with either reinforced rheological properties, better than those obtained with the neat biopolymers, or useful combination of properties. However, up to now a study the rheological properties of LBG/TG gel has not yet been explored. The aim of this work was to characterize the rheological response for locust bean gum solutions, tragacanth gum solutions and their synergistic mixed gel to obtain a depth understanding of the interactions occurring between both gums, to somewhat predict specific future applications of these gels.

**Keywords:** Locust bean gum, tragacanth gum, binary hydrogels, rheology.

### References

[1] Rinaudo, Main properties and current applications of some polysaccharides as biomaterials. *Polymer International*, 57: 397–430 (2008).

## Thermo-rheological behaviour and microstructure of egg white-based biocomposites

I. Díaz, I. Martínez, P. Partal

*Dpto. Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro2TecS),  
Universidad de Huelva-Campus Excelencia Ceia3, Campus El Carmen, 21071, Huelva, España*

isabel.dianez@diq.uhu.es

The serious problem of environmental pollution caused by plastic waste forces to the search of eco-friendly sustainable alternatives to traditional petroleum-based plastics, which are still widely used in all kind of industries. However, the use of bioplastics has awakened interest in fields like packaging and food industries, agriculture or even medicine. In these areas, key points such as the renewability, biodegradability and biocompatibility of many of these materials can promote the use of bioplastics instead of traditional plastics.

Moreover, bioplastics can show improved mechanical, thermal and barrier properties when reinforced and/or modified with the adequate types of nanoparticles, being this improvement largely dependent on the final microstructure of the biocomposite [1].

Thus, in this study different kind of nanoparticles has been incorporated to an egg white protein-based matrix, with the aim of evaluating the influence of both the nature and morphology of the additives on the microstructure and, consequently, the physicochemical, mechanical and thermo-rheological properties of the biocomposites obtained.

Nanoparticles used were halloysite nanotubes (HNT); phyllosilicate clay platelets such as natural (MMT-Na) and organo-modified (OMMT) montmorillonite; and cellulose nanofibres (CNF). In all cases, samples were obtained by thermomechanical processing and characterised by thermoplastic processing monitoring, dynamic thermomechanical analysis (DMTA), tensile tests, transmission electron microscopy (TEM) and water uptake capacity.

By analysing the results obtained, it can be observed how chemical nature (hydrophilic or hydrophobic) and aspect ratio of the different types of nanoparticles clearly influence the final properties studied for these biocomposites.

**Keywords:** egg white, biocomposite, nanoclay, cellulose, thermomechanical

### References

[1] N. Peelman, P. Ragaert, B. De Meulenaer, D. Adons, R. Peeters, L. Cardon, F. Van Impe, F. Devlieghere, Application of bioplastics for food packaging, *Trends in Food Science & Technology*, **32**: pages 128 – 141 (2013).

## Rheological properties of aqueous solutions of diutan gum

M.C. García, J.A. Carmona, M.J. Martín, J. Santos, M.C. Alfaro

*Universidad de Sevilla, Grupo de Reología Aplicada. Tecnología de Coloides. Facultad de Química. c/ P. García González, 1, 41012, Sevilla (Spain).*

e-mail of the presenter: joseacarmona@us.es

Diutan gum (DG) is an anionic polysaccharide obtained by aerobic fermentation from *Sphingomonas* sp. ATCC 53159. Its structure is composed of a repeated configuration of rhamnose, glucose, glucuronic acid and glucose units [1]. The main applications of DG are in personal care formulations, industrial, oilfield and civil engineering due to its capability to modify the rheology of different aqueous solutions. This study assesses the influence of DG concentration, from 0.1 wt % to 0.5 wt %, on the rheological properties of 0.5% wt NaCl aqueous solutions. A controlled-stress AR-2000 rheometer (TA Instruments) was utilized in order to calculate a) the linear viscoelastic properties by small amplitude oscillatory shear, b) the zero-shear viscosity by creep compliance tests and c) the inception of non-linear flow properties by tests at fixed shear stress. Additionally, a Haake-MARS controlled-stress rheometer (Thermo) was used to study flow properties by carrying out step-wise flow curves.

The mechanical spectra showed values of the elastic component,  $G'$ , above the viscous component,  $G''$ , although a crossover could be achieved at low frequency, which allowed the terminal relaxation time to be determined.  $G'$  and  $G''$  moduli increased with DG concentration, whereas the characteristic crossover frequency steadily decreased. Shear thinning behaviour was found upon running step-wise flow curves in the DG concentration range studied, with a tendency to reach the zero shear Newtonian viscosity ( $\eta_0$ ) at very low shear rates. On top of that, the concentration dependence of  $\eta_0$  was determined by means of linear creep tests. These values were compared to those calculated by extrapolation of flow curves at low shear rates.

**Keywords:** Diutan gum, creep tests, viscoelasticity, zero-shear viscosity, shear flow.

### References

- [1] T. A. Chowdhury, B. Lindberg, U. Lindquist, J. Baird, Structural studies of an extracellular polysaccharide, S-657, elaborated by *Xanthomonas* ATCC 53159. *Carbohydr Res* 164 (1987)117–122.

## Shear rheology of welan gum solutions

J.A. Carmona, L.A. Trujillo-Cayado, M.C. García, N. Calero, P. Ramírez

<sup>1</sup>Universidad de Sevilla, Grupo de Reología Aplicada. Tecnología de Coloides. Facultad de Química. c/ P. García González, 1, 41012, Sevilla (Spain).

E-mail of the presenter: joseacarmona@us.es

We report a rheological characterization of welan gum aqueous solutions at 20°C. Welan gum has found different applications depending on its compliance with the different safety regulations existing around the world. Welan gum has been approved in some countries as food, cosmetic and pharmaceutical additive. This gum has also been used for upstream operations of the petroleum industry and can find potential applications in fracking. However, it is mainly used for improving the mechanical properties of cement formulation due to its thickening, suspending and binding properties [1]. Therefore, studying the rheological properties of this gum is of key importance. Small amplitude oscillatory shear measurements of welan gum suspensions showed weak gel-like behaviour in the concentration range studied (0.2-0.4) % (w/w). Regarding flow curves, welan solutions exhibited shear thinning behaviour with a tendency to reach the low shear rate Newtonian region. The zero shear viscosity calculated from flow curves increased with gum concentration, whereas the power law index,  $n$ , decreased. In addition, parallel superposition tests have been carried out. This type of test allows capturing the variation of the parallel viscoelastic properties ( $G'$  and  $G''$ ) when a steady shear stress and oscillatory shear are applied simultaneously. From these measurements, a decrease in both viscoelastic moduli was observed when increasing shear stress. On top of that, the crossover frequency locating the terminal relaxation time showed a tendency to shift to higher frequencies as the shear stress applied was increased. In conclusion, the evolution of typical linear dynamic viscoelastic functions with shear stress allowed us to monitor the structural breakdown of welan solutions under non-linear shear flow conditions.

**Keywords:** Parallel superposition, Welan gum, Shear flow, Shear thinning, Viscoelasticity.

### References

[1] K. H. Khayat, A. Yahia, (1997). ACI Materials Journal, 94, 365-372 (1997).

## Investigation of sol-gel phase transitions of colloidal chitosan solutions conducted by rheometric and light scattering technics

Patryk Ziolkowski\*, Piotr Owczarz, Marek Dziubiński

*Department of Chemical Engineering, Faculty of Process and Environmental Engineering, Lodz University of Technology (Poland)*

e-mail of the presenter: patryk.ziolkowski@dokt.p.lodz.pl

Over the last years, hydrogels have become more popular due to their potential use in drug delivery systems, food and cosmetics industries. One of the best materials which are used to prepare hydrogels is chitosan - chitin derivative. In the present study, chitosan hydrogels are considered as physical gels. In those systems, the cross-linked structure is formed by the non-covalent bindings.

The aim of this study is to determine, based on rheological measurements, phase transition mechanism in chitosan hydrogels under effect of temperature increase. The chitosan salt solution with addition of sodium  $\beta$ -glycerophosphate ( $\beta$ -NaGP) as a neutralizing agent and solutions without buffer were the test samples. The addition of  $\beta$ -NaGP maintains the sample pH in the physiological range, preventing immediate precipitation or gelation, and enable control the phase transition process by adjusting the temperature. The measurements of rheological properties were conducted in a plate-plate system of a rotational rheometer Anton Paar Physica MCR 502 coupled with SALS (small angle light scattering) system. A plate of 43 mm diameter was used. The gelation process was conducted in non-isothermal conditions. Chitosan solutions were heated with constant heating rate of 1 K/min from 5°C to 60/80°C.

Comparison of chitosan solutions containing  $\beta$ -NaGP and without this addition reveals that solutions with higher pH value show lower gelation temperature (close to physiological temperature of human). Another basic difference in the gelation phenomena between the two types of solutions is revealed in the variations of storage and loss moduli. A more rapid change for solutions without the addition of  $\beta$ -NaGP compared with the solutions containing the buffer can be observed. Additionally analysis of scattering pattern from SALS images was performed.





## organized by:



VNIVERSITAT  
D VALÈNCIA



## sponsors:



## media sponsors:

