



Romanian Society
of Rheology



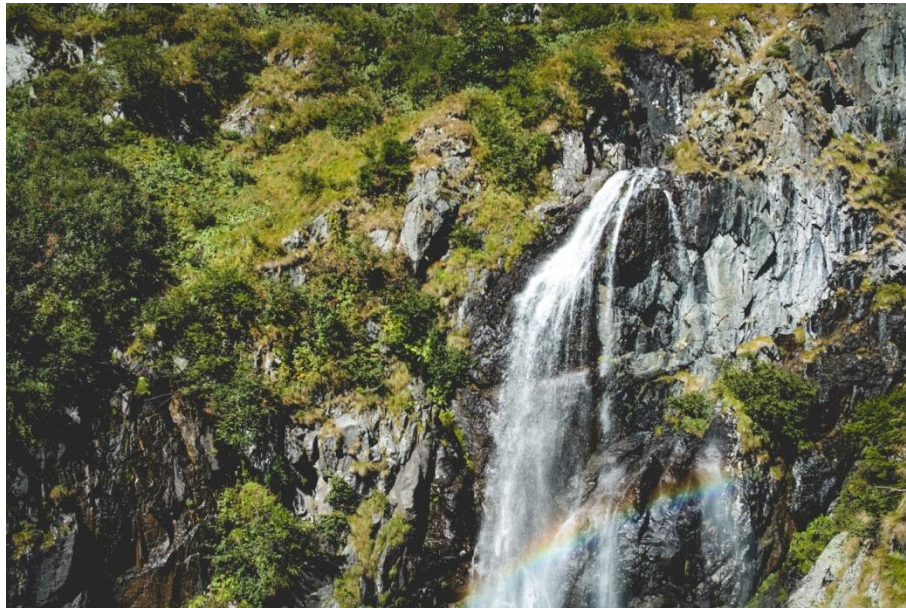
"PETRU PONI" Institute of
Macromolecular Chemistry
Iasi, Romania

INTERNATIONAL CONFERENCE ON RHEOLOGY

*Understanding the Viscoelastic Behavior
of Materials – Progress and Challenges*

(Online scientific event)

CONFERENCE PROGRAM



IASI, ROMANIA, MAY 26th, 2022

Scientific Committee

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ORAL PRESENTATIONS

8⁴⁰ – 17⁰⁰

PC – Plenary Conference (45 min, Q & A included)

C – Conference (30 min, Q & A included)

L – Lectures (15 min, Q & A included)

"Petru Poni" Institute of Macromolecular Chemistry is inviting you to a scheduled Zoom meeting:

Topic: Rheology Conference

Time: May 26th, 2022, 8³⁰ - 18⁰⁰ (local time in Iasi, GMT+3)

Join Zoom Meeting:

<https://us06web.zoom.us/j/82097395470?pwd=SmlEVStYMIoxV204ek5CcTZoUmhIQT09>

Meeting ID: 820 9739 5470

Passcode: 603106

IT Support: **Eng. Iulian PARFENI**
Eng. Catalin BUZDUGAN

POSTER SESSION

17⁰⁰ – 17⁴⁰

P – POSTER

Posters will be displayed at the following address:

<https://reologie.ro/international-conference-on-rheology-may-2022/>

and they can be seen during the entire Conference

LANGUAGE

The conference language is English.

PROGRAM AT A GLANCE

The hours represent local time: EEST, GMT+3

8³⁰ - 8⁴⁰ **Introductory remarks**

Session 1

Chair: Prof. Dr. Corneliu BALAN

8⁴⁰ – 9²⁵ **PC1** Roland KADAR

9²⁵ – 9⁵⁵ **C1** Daniela IONITA

9⁵⁵ – 10¹⁰ **L1** Vlad SOCOLIUC

10¹⁰ – 10²⁵ **L2** Edith PEUVREL-DISDIER

10²⁵ – 10³⁵ **Break**

Session 2

Chair: Conf. Dr. Adina Lucretia MICLAUS

10³⁵ – 11⁰⁵ **C2** Marius CHERECHES

11⁰⁵ – 11²⁰ **L3** Luiza Madalina GRADINARU

11²⁰ – 11³⁵ **L4** Elena-Emilia TUDOROIU

11³⁵ – 11⁵⁰ **L5** Maria-Manuela IFTIME

11⁵⁰ – 12⁰⁰ **Break**

Session 3

Chair: Dr. Diana CIOLACU

12⁰⁰ – 12³⁰ **C3** Daniela IVANOV

12³⁰ – 12⁴⁵ **L6** Simona Luminita NICA

12⁴⁵ – 13⁰⁰ **L7** Cristina-Eliza BRUNCHI

13⁰⁰ – 13¹⁵ **L8** Magdalena AFLORI

13¹⁵ – 14⁰⁰ **Break**

Session 4

Chair: Dr. Mariana CRISTEA

14⁰⁰ – 14⁴⁵ **PC2** Corneliu BALAN

14⁴⁵ – 15⁰⁰ **L9** Ana-Maria BRATU

15⁰⁰ – 15¹⁵ **L10** Claudiu PATRASCU

15¹⁵ – 15³⁰ **L11** Nicoleta-Octavia TANASE

15³⁰ – 15⁴⁵ **Break**

Session 5

Chair: Dr. Maria BERCEA

15⁴⁵ – 16⁰⁰ **L12** Martin MASUELLI

16⁰⁰ – 16¹⁵ **L13** Fernanda TORRES

16¹⁵ – 16³⁰ **L14** Martin MASUELLI

16³⁰ – 16⁴⁵ **L15** Lismet LAZO

16⁴⁵ – 17⁰⁰ **L16** Robert GRADINARU

17⁰⁰ – 17⁴⁰ **Session POSTERS**

**Chairs: Dr. Andreea Irina BARZIC,
Dr. Anca FILIMON, Dr. Maricel DANU**

P1 Anda Mihaela CRACIUN

P2 Raluca Nicoleta DARIE-NITA

P3 Diana CIOLACU

P4 Marieta NICHIFOR

P5 Alexandra CROITORIU

P6 Alexandra CROITORIU

P7 Diana SERBEZEANU

P8 Tachita VLAD-BUBULAC

P9 Dana M. SUFLET

P10 Mihaela Dorina ONOFREI

P11 Adina Maria DOBOS

P12 Mirela TEODORESCU

P13 Ioana-Victoria PLATON

P14 Stefania-Claudia JITARU

P15 Ioana-Alexandra PLUGARU

17⁴⁰ – 18⁰⁰ **Concluding remarks**

PROGRAM

Thursday, May 26th, 2022

8³⁰ – 8⁴⁰

Introductory remarks

Session 1

Chair: Prof. Corneliu BALAN

8⁴⁰ – 9²⁵

Plenary Conference (PC1)

CELLULOSE NANOCRYSTALS IN SIMPLE AND NOT SO SIMPLE FLOWS

Roland KADAR

Chalmers University of Technology, Göteborg, Sweden

Wallenberg Wood Science Center (WWSC), Chalmers, Göteborg, Sweden

9²⁵ – 9⁵⁵

Conference (C1)

**CHALLENGES IN THE EVALUATION OF LOSS FACTOR PROBED BY DMA
VERSUS THE RELATION STRUCTURE-PROPERTY OF POLYMERS**

Daniela IONITA, Mariana CRISTEA, Constantin GAINA, Bogdan C. SIMIONESCU

“Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania

9⁵⁵ – 10¹⁰

Lecture (L1)

**FERROFLUID BASED BIDISPERSE MAGNETORHEOLOGICAL SUSPENSIONS:
THE INFLUENCE OF PARTICLE SIZE**

Daniela SUSAN-RESIGA^{1,2}, Vlad SOCOLIUC¹, Ladislau VEKAS^{1,3}

¹ Romanian Academy – Timisoara Branch, Center for Fundamental and Advanced Technical Research, Laboratory for Magnetic Fluids, Timisoara, Romania

² West University of Timisoara, Faculty of Physics, Timisoara, Romania

³ Politehnica University of Timisoara, Research Center for Complex Fluids Systems Engineering, Timisoara, Romania

10¹⁰ – 10²⁵

Lecture (L2)

**FOAMABILITY OF LINEAR AND BRANCHED POLYPROPYLENES BY PHYSICAL
EXTRUSION FOAMING - INPUT OF THE THERMOMECHANICAL ANALYSIS OF
PRESSURE DROP IN THE DIE**

**Carlos SANDINO¹, Edith PEUVREL-DISDIER¹, Jean-François AGASSANT¹,
Séverine A.E. BOYER¹, Patrice LAURE^{1,2}, Geoffrey HIBERT³, Yves TROLEZ³**

¹ MINES Paris - PSL, CEMEF – Centre de Mise en Forme des Matériaux, UMR CNRS 7635, Sophia Antipolis, France

² Laboratoire J.-A. Dieudonné, CNRS UMR 6621, Université Côte d'Azur, Nice, France

³ TotalEnergies One Tech Belgium, Zone Industrielle Feluy C, Feluy, Belgium

10²⁵ – 10³⁵

Break

Session 2

Chair: Conf. Adina Lucretia MICLAUS

10³⁵ – 11⁰⁵

Conference (C2)

PEG NANOPARTICLE ENHANCED FLUIDS WITH Al₂O₃ AND ZnO. VISCOSITY STUDIES

Marius CHERECHES¹, Constanta IBANESCU², Maricel DANU^{2,3},

Elena Ionela CHERECHES¹, Alina Adriana MINEA¹

¹ "Gheorghe Asachi" Technical University of Iasi, Faculty of Materials Science and Engineering, Iasi, Romania

² "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection "Cristofor Simionescu", Iasi, Romania

³ "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

11⁰⁵ – 11²⁰

Lecture (L3)

TAILORING THE PROPERTIES OF ELECTROSPUN POLYURETHANE-BASED MAGNETIC NANOCOMPOSITES BY USING THE RHEOLOGICAL DATA

Luiza Madalina GRADINARU¹, Maria BERCEA¹, Stelian VLAD¹,

Romeo Cristian CIOBANU^{2,3}

¹ "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

² "Gheorghe Asachi" Technical University of Iasi, Electrical Engineering Faculty, Iasi, Romania

³ All Green SRL, Iasi, Romania

11²⁰ – 11³⁵

Lecture (L4)

ANALYSIS OF *IN VITRO* RELEASE PROFILES AND RHEOLOGICAL PARAMETERS FOR SOME NAPROXEN-BASED TOPICAL SEMI-SOLID SYSTEMS

Elena-Emilia TUDOROIU¹, Mihaela Violeta GHICA¹, Cristina-Elena DINU-PIRVU¹,

Lacramioara POPA¹, Madalina Georgiana ALBU KAYA², Valentina ANUȚA¹,

Razvan Mihai PRISADA¹, Bruno Stefan VELESCU³, Alina-Ruxandra ORTAN⁴

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² Department of Collagen, Division Leather and Footwear Research Institute, National Research and Development Institute for Textile and Leather, Bucharest, Romania

³ Department of Pharmacology and Clinical Pharmacy, Faculty of Pharmacy, Carol Davila University of Medicine and Pharmacy Bucharest, Romania

⁴ Department of Mathematics, Physics and Measurements, Faculty of Land Reclamation and Environmental Engineering, University of Agronomic Sciences and Veterinary Medicine of Bucharest, Romania

11³⁵ – 11⁵⁰

Lecture (L5)

EFFECT OF CROSSLINKING DEGREE ON THE RHEOLOGY OF SALICYL-IMINE-CHITOSAN HYDROGELS

Manuela-Maria IFTIME, Simona MORARIU

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

11⁵⁰ – 12⁰⁰

Break

Session 3

Chair: Dr. Diana CIOLACU

12⁰⁰ – 12³⁰

Conference (C3)

HYALURONAN IN BIOLOGICAL FLUIDS AND ITS RELATED BIOMEDICAL APPLICATIONS

Daniela IVANOV

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

12³⁰ – 12⁴⁵

Lecture (L6)

THE ROLE OF DIAMINE MOIETIES ON THE RHEOLOGICAL BEHAVIOUR OF SOME POLYIMIDES

Simona Luminita NICA, Raluca Marinica ALBU, Luminita Ioana BURUIANA, Andreea Irina BARZIC

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

12⁴⁵ – 13⁰⁰

Lecture (L7)

VISCOELASTIC PROPERTIES OF XANTHAN IN AQUEOUS SOLUTIONS

Cristina-Eliza BRUNCHI

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

13⁰⁰ – 13¹⁵

Lecture (L8)

PARTNERSHIPS FOR KNOWLEDGE TRANSFER IN THE FIELD OF POLYMER MATERIALS USED IN BIOMEDICAL ENGINEERING – POINGBIO

Magdalena AFLORI, Maria SPIRIDON

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

13¹⁵ – 14⁰⁰

Break

Session 4

Chair: Dr. Mariana CRISTEA

14⁰⁰ – 14⁴⁵

Plenary Conference (PC2)

ARTIFICIAL INTELLIGENCE AND THE CONSTITUTIVE RELATION THEORY – A HISTORICAL PERSPECTIVE

Diana BROBOANA, Corneliu BALAN

REOROM Group, Hydraulics Department, University Politehnica of Bucharest, Romania

14⁴⁵ – 15⁰⁰

Lecture (L9)

INFLUENCE OF PEO CONCENTRATION ON THE FILAMENT EVOLUTION

Ana-Maria BRATU, Corneliu BALAN

REOROM Group, Hydraulics Department, University Politehnica of Bucharest, Romania

15⁰⁰ – 15¹⁵

Lecture (L10)

EXPERIMENTAL OBSERVATIONS OF THE CAPILLARY FLOW OF A VISCOELASTIC PEO SOLUTION IN TANDEM WITH ANOTHER IMMISCIBLE LIQUID

Ioana RASUCEANU, Claudiu PATRASCU

REOROM Group, Hydraulics Department, University Politehnica of Bucharest, Romania

15¹⁵ – 15³⁰

Lecture (L11)

AIR – NON-NEWTONIAN FLUID INTERACTION IN CONFINED GEOMETRY

Nicoleta-Octavia TANASE, Eugen CHIRIAC, Ciprian MATEESCU,

Doru-Daniel CRISTEA

REOROM Group, Hydraulics Department, University Politehnica of Bucharest, Romania

15³⁰ – 15⁴⁵

Break

Session 5

Chair: Dr. Maria BERCEA

15⁴⁵ – 16⁰⁰

Lecture (L12)

INTRINSIC VISCOSITY METHODS BY ACACIA CAVEN GUM

Franco TONELLI¹, Martin MASUELLI²

¹ Laboratory of Chemical Reactions Engineering, FICA-UNSL, Argentina

² Physical Chemistry Research and Services Laboratory (LISEQF-UNSL), National University of San Luis-INFAP-CONICET, San Luis, Argentina

16⁰⁰ – 16¹⁵

Lecture (L13)

HYDRODYNAMIC PARAMETERS OF *CHAÑAR BREA* GUM

Fernanda TORRES, Karen GIL MILAC, Martin MASUELLI

Laboratorio de Investigación y Servicios, Universidad Nacional de San Luis, INFAP-CONICET, San Luis, Argentina

16¹⁵ – 16³⁰

Lecture (L14)

HYDRODYNAMIC PROPERTIES OF *ALCAYOTA* GUM

Federico BECERRA, Marisa ZANON, Martin MASUELLI

Laboratorio de Investigación y Servicios, Universidad Nacional de San Luis, INFAP-CONICET, San Luis, Argentina

16³⁰ – 16⁴⁵

Lecture (L15)

HYDRODYNAMIC PROPERTIES OF *CHAÑAR* GUM FROM *GEOFFREA DECORTICANS* FRUIT

Lismet LAZO¹, Martin A. MASUELLI^{1,2}

¹ Instituto de Física Aplicada, CONICET, Universidad Nacional de San Luis, Ejercito de los Andes 950, San Luis ZC: 5700, Argentina

² Área de Química Física, Departamento de Química, Facultad de Química, Bioquímica y Farmacia, Laboratorio de Investigación y Servicios de Química Física (LISeQF-UNSL), San Luis, Argentina

16⁴⁵ – 17⁰⁰

Lecture (L16)

A MICROPLATE ASSAY FOR TRACKING PEPTIDE-ALGINATE OR PROTEIN-ALGINATE GELATION ASSISTED BY GLUTARALDEHYDE

Stefania-Claudia JITARU, Alexandra LUPU, Vasile Robert GRADINARU

Alexandru Ioan Cuza University, Faculty of Chemistry, Iasi, Romania

Session POSTERS

Chairs: Dr. Andreea Irina BARZIC, Dr. Anca FILIMON, Dr. Maricel DANU

17⁰⁰ – 17⁴⁰

P1. RHEOLOGICAL INVESTIGATIONS ON 5-NITROSALICYLALDEHYDE-CHITOSAN HYDROGELS

Anda Mihaela CRACIUN, Simona MORARIU, Luminita MARIN

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

P2. RHEOLOGICAL AND MECHANICAL PROPERTIES OF XANTHAN-BASED CRYOGELS

Raluca Nicoleta DARIE-NITA, Irina Elena RASCHIP, Nicusor FIFERE, Maria Valentina DINU

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

P3. RHEOLOGICAL ASPECTS ON CELLULOSE-BASED HYDROGELS

Daniela RUSU, Raluca Nicoleta DARIE-NITA, Diana CIOLACU

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

P4. PHASE BEHAVIOR OF MIXTURES OF AMPHIPHILIC CATIONIC POLYSACCHARIDES AND ANIONIC SURFACTANTS

Marieta NICHIFOR¹, Margarida BASTOS², Antonio LOPES³

¹ "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

² Faculty of Science, University of Porto, Porto, Portugal

³ Instituto de Tecnologia Química e Biológica, Oeiras, Portugal

P5. HYBRID HYDROGELS BASED ON PEPTIDE

Alexandra CROITORIU, Loredana E. NITA, Alina G. RUSU, Alina GHILAN, Florica DOROFTEI, Maria BERCEA, Aurica P. CHIRIAC

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

P6. INVESTIGATION OF AN INTERPENETRATED POLYMER SYSTEM CONTAINING CELLULOSE NANOFIBRILS AND A COPOLYMACROLACTONE STRUCTURE

Alexandra CROITORIU, Loredana E. NITA, Alina G. RUSU, Alina GHILAN, Florica DOROFTEI, Maria BERCEA, Aurica P. CHIRIAC

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

P7. STRUCTURE AND PROPERTIES OF POLY(VINYL ALCOHOL) MODIFIED WITH PHOSPHONIC DICHLORIDES

Diana SERBEZEANU, Mihaela Dorina ONOFREI, Corneliu HAMCIUC, Ana-Lavinia VASILIU, Tachita VLAD-BUBULAC

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

P8. CORRELATION BETWEEN SOLUTION RHEOLOGY AND ELECTROSPUN FIBERS FORMATION OF NEW POLYIMIDE

Tachita VLAD-BUBULAC, Maria BERCEA, Corneliu HAMCIUC, Diana SERBEZEANU, Florica DOROFTEI

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

P9. POLYSACCHARIDE-BASED ELECTROSPUN NANOFIBERS. PREPARATION AND CHARACTERIZATION

Dana M. SUFLET¹, Irina POPESCU¹, Irina M. PELIN¹, Diana SERBEZEANU¹, Alexandru Alin ENACHE², Maria BERCEA¹

¹ "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

² Apel Laser S.A., Mogosoaia, Ilfov, Romania

P10. DYNAMIC PROPERTIES OF THE (HYDROXYPROPYL)METHYL CELLULOSE / POLY(VINYLPYRROLIDONE) / WATER SYSTEMS. INFLUENCE ON THE FORMATION OF FIBROUS MATERIALS

Mihaela Dorina ONOFREI, Diana SERBEZEANU, Alexandru ANISIEI, Anca FILIMON

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

P11. CONFORMATIONAL RESTRUCTURATIONS IN POLYSULFONIC SYSTEMS INDUCED BY TRIETHYLPHOSPHONIUM PENDANT GROUPS

Adina Maria DOBOS¹, Adriana POPA², Dumitru POPOVICI¹, Anca FILIMON¹

¹ "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

² "Coriolan Drăgulescu" Institute of Chemistry, Timisoara, Romania

P12. VISCOSITY STUDY OF PVA, PVP AND THEIR MIXTURES IN DILUTE AQUEOUS SOLUTION

Mirela TEODORESCU

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

P13. TEXTURAL AND MECHANICAL FEATURES OF POROUS CHITOSAN-BASED HYDROGELS

Ioana-Victoria PLATON, Claudiu-Augustin GHIORGHITA, Maria Marinela LAZAR, Irina Elena RASCHIP, Maria Valentina DINU

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

P14. A PH-TRIGGERED SELF-ASSEMBLING PEPTIDE STUDIED BY ATOMIC FORCE MICROSCOPY

Stefania-Claudia JITARU¹, Robert-Vasile GRADINARU¹, Brindusa-Alina PETRE^{1,2}, Laura ION¹, Iuliana STOICA³, Gabi DROCHIOIU¹

¹ Alexandru Ioan Cuza University, Faculty of Chemistry, Iasi, Romania

² TRANSCEND - Regional Institute of Oncology, Iasi, Romania

³ "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

P15. VISCOSITY OF BOVINE SERUM ALBUMIN SOLUTIONS IN PRESENCE OF NEUTRAL POLYMERS

Ioana-Alexandra PLUGARIU, Maria BERCEA

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

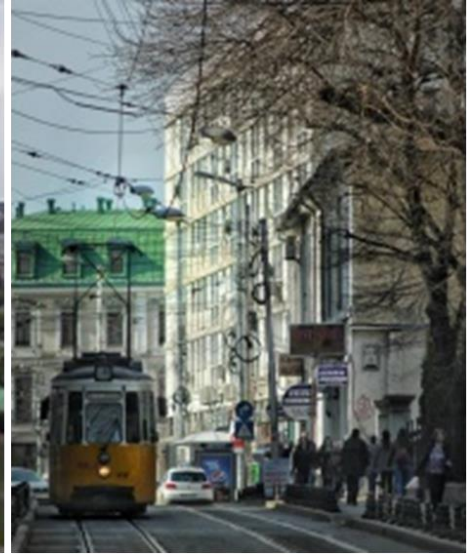


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Romanian Society
of Rheology



"PETRU PONI" Institute of
Macromolecular Chemistry
Iasi, Romania

ABSTRACTS

INTERNATIONAL CONFERENCE ON RHEOLOGY

Understanding the Viscoelastic Behavior of Materials – Progress and Challenges

Promoting excellence in rheology and science !

**Dr. Mariana CRISTEA
Dr. Anca FILIMON
Dr. Daniela IONITA
Dr. Diana CIOLACU**

**Dr. Cristina-Eliza BRUNCHI
Dr. Mirela TEODORESCU
Dr. Maricel DANU
Dr. Maria BERCEA**

IASI, ROMANIA, MAY 26th, 2022

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Plenary Conference 1

CELLULOSE NANOCRYSTALS IN SIMPLE AND NOT SO SIMPLE FLOWS

Roland KADAR

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412 96 Göteborg, Sweden
Wallenberg Wood Science Center (WWSC), Chalmers, 412 96 Göteborg, Sweden
E-mail: roland.kadar@chalmers.se*

Cellulose nanocrystals (CNCs) are 1D nanoparticles and part of the rodlike family of lyotropic materials. CNCs self-assemble and can be flow-assembled into liquid crystalline orders in a water suspension. The orders range from nano- to macroscale with contributions of individual crystals, their micron clusters and macroscopic assemblies influencing their rheological properties and flow behavior. The resulting hierarchies are optically active materials that exhibit iridescence, reflectance, and light transmission. This has inspired a number of applications in the fields of optics and electronics among others. Although these assemblies have the potential for future renewable materials, details about structures on different hierarchical levels that span from the nano- to the macroscale and the influence of flow thereon are still not unraveled. In this conference several aspects of CNCs and their assembly in flow from our recent and ongoing work will be presented. This will be centered mainly in relation to their orientation, thixotropy, nonlinear material response, phase behavior and flow stability, including elastically driven and inertia-elastic instabilities [1-4].

REFERENCES

- [1] Kádár R., Spirk S., Nypelö T. (2021). Cellulose nanocrystal liquid crystal phases: Progress and challenges in characterization using rheology coupled to optics, scattering, and spectroscopy, *ACS Nano*, 15, 5, 7931–7945
- [2] Wojno S., Fazilati M., Nypelö T., Westman G., Kádár R. (2022). Phase transitions of cellulose nanocrystal suspensions from nonlinear oscillatory shear. *Cellulose*, **29**, 3655–3673
- [3] Fazilati, M., Ingelsten, S., Wojno, S., Nypelö, T., Kádár R. (2021). Thixotropy of cellulose nanocrystal suspensions. *Journal of Rheology*, 65(5), 1035–1052
- [4] Kádár, R., Fazilati, M., Nypelö, T. (2020). Unexpected microphase transitions in flow towards nematic order of cellulose nanocrystals. *Cellulose*, 27(4), 2003–2014.



Plenary Conference 2

**ARTIFICIAL INTELLIGENCE AND THE CONSTITUTIVE RELATION THEORY –
A HISTORICAL PERSPECTIVE**

Diana BROBOANA, Corneliu BALAN*

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The paper is dedicated to the celebration of 100 years since the publishing in English of the *Tractatus Logico-Philosophicus*, by Ludwig Wittgenstein (1889-1951), today a text considered a milestone of the philosophical creation.

The theory of the constitutive relations, which describe the material behavior in the frame of continuum mechanics and thermodynamics, is based on some principles, e.g.: (i) Determinism, (ii) Fading memory, (iii) Local action, (iv) Objectivity/Frame Indifference, (v) Just setting. These principles are actually the postulates of the rheology, even if they are not always recognized or considered explicitly. The subject of axiomatic structure of rheology is not anymore in the focus of today scientific research, but the future seems to open again the interest on the topic once the artificial intelligence (AI) approaches are applied in materials modelling. AI procedures are based on languages and images recognitions techniques, which are implemented in computers by numerical codes created and organized accordingly to some logical structures. Any logical structure (generated by a human or artificial mind) is directly related to the past-history, a data base consists of sets of elements which are recomposed in a coherent picture. The paper introduces and discusses the axiomatic structure of the constitutive relations theory applied to viscoelastic materials, in particular fluids. It is a historical perspective on the subject, starting with the end of the XIXth century and continuing up to the present.



Conference 1

CHALLENGES IN THE EVALUATION OF LOSS FACTOR PROBED BY DMA VERSUS THE RELATION STRUCTURE-PROPERTY OF POLYMERS

Daniela IONITA*, Mariana CRISTEA, Constantin GAINA, Bogdan C. SIMIONESCU

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In the field of chemistry and material science the determination of the glass transition (T_g) plays a critical role in terms of engineering performance of polymers. The glass transition associated with α -relaxation is easily identified from dynamic mechanical data as the maximum of loss factor ($\tan \delta$) peak [1]. The shape and height of $\tan \delta$ peak provide an insight on the degree of molecular mobility and also supply information regarding the stiffness, damping behaviour, structural homogeneity and the range of temperature in which material can be used [2-4]. However, not every $\tan \delta$ peak or shoulder observed in DMA experiments corresponds to a relaxation.

A linear amorphous polymer like poly(methyl methacrylate) exhibits in a single frequency DMA experiment a relatively narrow $\tan \delta$ peak during the glass transition which reflects the onset of the coordinated movements of chain segments. The accurate assessment of the glass transition is rather difficult and can often lead to misinterpretation. For example, a large $\tan \delta$ peak can be defined by at least a bimodal shape. It is the case of polyurethane networks with a heterogeneous structure, polyimide or of semicrystalline polymers like poly(ethylene terephthalate) and poly(lactic acid) where the glass transition comes along or is succeeded by various processes with increasing temperature: imidization, melting/recrystallization, enthalpic relaxation – orientation/crystallization phenomena.

The present study aims to unravel how the variation of $\tan \delta$ with temperature and frequency can assess a true relaxation, how to differentiate it from a kinetic event or whether there are overlapped events in the glass transition region.

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Conference 2

**PEG NANOPARTICLE ENHANCED FLUIDS WITH Al₂O₃ AND ZnO.
VISCOSITY STUDIES**

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Fluid viscosity is essential for characterizing fluids used in practical applications. The viscosity of nanofluids depends on many factors, such as the type and shape of the nanoparticles, the particle concentration, the shear rate and the working temperature. However, until now, relatively few experimental studies have been performed on viscosity modification by the introduction of nanoparticles into polyethylene glycol PEG 400. In this paper, we experimentally investigated the effect of addition of Al₂O₃ and ZnO nanoparticles (0.25 % wt. – 5.00 % wt.) to polyethylene glycol PEG 400 on rheological behavior of PCMs. Viscosity tests were performed with a Physica MCR 501 rheometer (Anton Paar, Austria) equipped with a Peltier temperature control system. The results were recorded at the variation of the shear rate in the range 1 - 1000 1/s in rotational mode. Three types of tests were performed, namely: determination of flow curves at 288.15 K and 298.15 K, tests to check the viscosity on heating and the determination of viscosity for different successive heating-cooling regimes. For the variation of viscosity with temperature, a constant shear rate of 100 1/s was maintained while the temperature varied between 283.15 K and 333.15 K with a heating / cooling gradient of 1 K/min. Rheological tests have shown that PEG 400 and PEG 400-based nanofluids with various mass concentrations of alumina have obvious a Newtonian behavior. On the other hand, nanofluids with a mass concentration of 5 % ZnO have a non-Newtonian behavior. The viscosity clearly increases by adding nanoparticles to the base mixture, the increase being quantified between 5.78 % and 30 %. In addition, when the temperature rises, the viscosity decreases, which is a normal phenomenon for most liquids. In conclusion, because the problems facing researchers are mainly focused on methods of limiting the exaggerated increase in the viscosity of nanofluids by adding nanoparticles, detailed studies are needed on the concentration and size of nanoparticles, the working temperature of nanofluids and the shear rate.



Conference 3

HYALURONAN IN BIOLOGICAL FLUIDS AND ITS RELATED BIOMEDICAL APPLICATIONS

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Dedicated to the memory of Prof. Robert M. MORIARTY

Hyaluronic acid (HA) is one of the most simple in structure and also most fascinating naturally occurring biopolymer. HA chains consist of alternating residues of β -D-(1-3) glucuronic acid (GlcA) and β -D-(1-4)-*N*-acetylglucosamine (GlcNAc). HA is considered the largest linear unbranched non-sulfated glycosaminoglycan. At physiological pH and ionic strength, HA chain has the carboxyl groups on the glucuronic acid residues (of pK_a 4–5) negatively charged and is termed hyaluronan.

Hyaluronan molecules have random coil conformation and, depending on their molecular mass, occupy a large hydrodynamic volume. Hence, in solution hyaluronan occupies a volume approximately 1000 times greater than in dry state. The most distinctive property of HA solutions is both their viscous and elastic non-Newtonian behavior when exposed to various shear rate properties, making them excellent biological shock absorbers and lubricants. The viscoelastic rheology of hyaluronan solutions depends on the concentration and the average molecular mass, salt concentration, pH and shear rate. For instance, a 2-fold increase in concentration or molecular mass results in a 10-fold increase in bulk viscosity. The high viscosity of hyaluronan solutions is of great importance in biological fluids, as well as in its related biomedical applications. For application in body compartments, the concentration of hyaluronan cannot be increased much above 10 mg/mL due to the highly non-ideal colloid osmotic behavior. High viscosity hyaluronan solutions must therefore be based on high molecular mass. Biomedical applications are, as consequence, limited by short turnover rate and limited mechanical properties of native HA solutions, chemical modifications being required to provide stable biomaterials with enhanced or modulated properties.

The content of HA is different in different normal biological fluids. HA is a component of articular joint synovial fluid, where it provides the viscoelasticity and lubrication, in concentration of approximately 2–3 mg/mL in knee joints. HA is also a component of the vitreous body of the eye, at a concentration of approximately 200 μ g/mL, in human eye vitreous, while in the aqueous humor is only about 1 μ g/mL. Biomedical applications of hyaluronan solutions mainly consist of fillers for tissue augmentation and regeneration, due to their particular lubricant and viscoelastic properties.



Particularly, biomimetic hyaluronan solutions target viscosurgery – to protect eye tissues and provide space in ophthalmic surgery; viscoaugmentation – to fill and augment tissue spaces in skin, sphincter muscles, and vocal and pharyngeal tissues; viscosupplementation – to replace or supplement tissue fluids, such as synovial fluid; viscoseparation – to separate soft connective tissue surfaces after surgical procedures or injury, in order to prevent adhesions and excessive scar formation.



Lecture 1

**FERROFLUID BASED BIDISPERSE MAGNETORHEOLOGICAL SUSPENSIONS:
THE INFLUENCE OF PARTICLE SIZE**

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The rheological behaviour of magnetic suspensions can be maximized by using particles with different sizes. The size ratio is crucial with regard to stability and MR effect. Nine samples of ferrofluid based bidisperse magnetorheological suspensions were prepared. Iron nanoparticles (FeMNPs) with 22 nm, 65 nm and 95 nm average diameter were dispersed at 15 %, 20 % and 25 % volume fractions in a concentrated ($M_{\text{sat}} = 475$ G, i.e. 11 % magnetite nanoparticle volume fraction) transformer oil based ferrofluid (FF-UTR). The mean size of magnetite nanoparticles in the composition of the ferrofluid is approx. 7nm. The sample's flow curves were measured for shear rates in the range $10^{-2} \text{ s}^{-1} - 10^3 \text{ s}^{-1}$ and magnetic field induction in the range 0 – 0.7 T.

The magnetoviscous effect (MVE) is the same for 65 nm and 95 nm FeMNPs and stronger than 22 nm FeMNPs (Fig.1) at all three volume fractions. The MVE increases two orders of magnitude in the investigated magnetic induction range. The MVE of 65 nm and 95 nm samples is stronger than for the commercial product Lord MRF 140 CG, but weaker than extremely bidisperse ferrofluid based suspension with 10 microns Fe particles (Figure 1). The results are analyzed and discussed to explore and demonstrate the feasibility and advantages of suspensions of different sized particles finely tuned to fulfill the requirements of a large diversity of engineering applications.

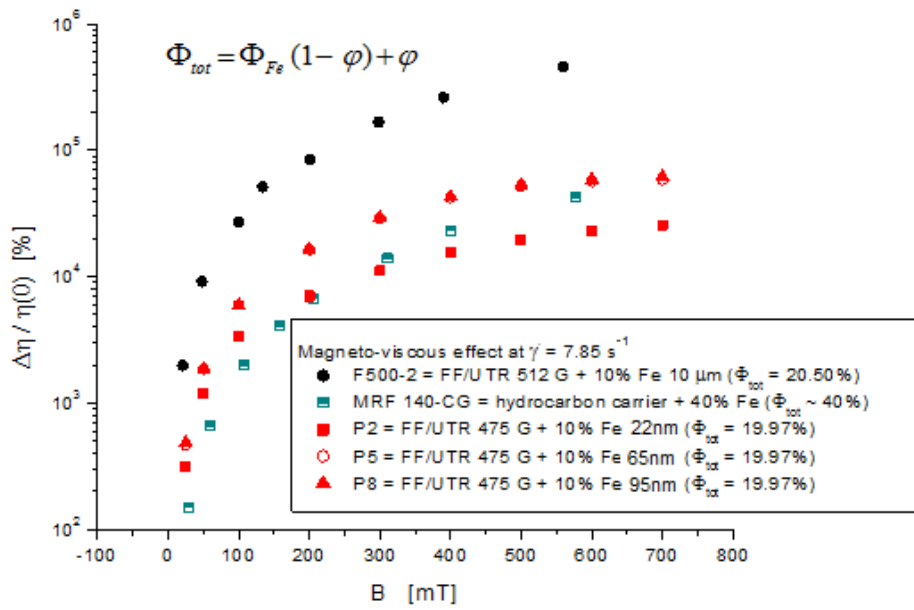


Figure 1. The magnetoviscous effect for three samples of 20 % concentration (P2, P5 and P8), commercial LORD Co. MRF 140 CG and extremely bidisperse ferrofluid suspension.



Lecture 2

FOAMABILITY OF LINEAR AND BRANCHED POLYPROPYLENES BY PHYSICAL EXTRUSION FOAMING - INPUT OF THE THERMOMECHANICAL ANALYSIS OF PRESSURE DROP IN THE DIE

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Key Words: *Physical foaming extrusion, polypropylene, modelling*

This study aims to better understand the polypropylene (PP) foamability by physical extrusion foaming comparing branched chains with strain hardening versus linear ones. Trials were conducted in a single screw extrusion equipped with a gear pump for the gas dissolution step (same extrusion parameters, 1 wt. % CO₂) and a static mixer cooler allowing to decrease the melt temperature before the final die (referred as foaming temperature). The effect of decreasing the foaming temperature on the PP foamability was analyzed.

The foam density of branched PP varies from high to low values while decreasing the foaming temperature. This foamability transition coincides with an increase of the pressure drop in the die. As reported, branched PPs depict a better foamability than linear grades. As the pressure drop in the die is responsible of the polymer foaming, a thermomechanical analysis of the polymer flow was conducted to better understand the foamability transition.

The pressure drop was calculated considering shear flow in the die using dedicated analytical expressions for the converging and capillary parts and a power law for the viscosity curve. Calculated pressures due to shear flow are lower than the measured values. The discrepancy is interpreted as an additional contribution due to the elongational flow in the converging channel, which can be estimated. The pressure drop variation with the foaming temperature follows an Arrhenius dependence in the case of linear grades. In the case of branched grades, the Arrhenius dependence is valid for large foaming temperatures but a large discrepancy is reported for low foaming temperatures. Two phenomena (presence of strain hardening for branched PP and/or of flow-induced crystallization) can be at the origin of this discrepancy. These hypotheses will be examined and discussed for the different polymer grades in order to clarify the physical scenario for the foaming process.



Lecture 3

TAILORING THE PROPERTIES OF ELECTROSPUN POLYURETHANE-BASED MAGNETIC NANOCOMPOSITES BY USING THE RHEOLOGICAL DATA

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Electrospinning of nanomaterials constitutes an interesting approach to boost and develop novel properties and applications. To this end, polyurethane-based magnetic electrospun nanocomposites were prepared and the effect of the magnetic nanoparticles (Fe_2O_3) on the various properties was evaluated. Firstly, the viscosity of polyurethane solutions in dimethylformamide was investigated over a large concentration domain in order to select the optimum polymer concentration for electrospinning (the domain of entangled macromolecules). Then, the viscosity was determined for polyurethane-based magnetic samples with different amounts of Fe_2O_3 nanoparticles, examining the stability in time of the different nanocomposites. The rheological data were further correlated with the morphology of the magnetic nanocomposite fibers obtained by electrospinning. It was observed that the mechanical, dielectric, and magnetic properties were enhanced in the magnetic nanocomposite samples when compared with the pristine polymer matrix. Moreover, the investigation of *in vitro* biocompatibility of the novel nanocomposites showed that these samples could be excellent candidates for biomedical use.

The relationship between the structure and rheological properties is demonstrated to be an efficient approach to tailor the properties of magnetic polyurethane-based nanocomposites. Thus, the current study focused on electrospun formulations based on polyurethane with magnetic behaviour that could offer perspectives on future directions in the advancement of polymeric biomedical formulations, especially in magnetic resonance imaging methods.

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Lecture 4

ANALYSIS OF *IN VITRO* RELEASE PROFILES AND RHEOLOGICAL PARAMETERS FOR SOME NAPROXEN-BASED TOPICAL SEMI-SOLID SYSTEMS

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Objectives: Naproxen, a non-steroidal anti-inflammatory drug, is generally used to alleviate pain, diminish inflammation, and bring down a high temperature. Because of its side effects on the digestive and renal systems when it is administered orally, the alternative way is the topical administration of this drug, a more advantageous and regularly used path due to its local therapeutic action. Moreover, the topical administration of naproxen improves the patients compliance and their adherence to treatment due to the decrease of dosing frequency and systemic toxicity. Therefore, the main purpose of this work was to evaluate the *in vitro* kinetics release and flow behaviour for some naproxen-based topical semi-solid systems.

Methods: Different industrial naproxen-based hydrogels with 10 % concentration were studied. The semi-solid dosage forms were assessed from kinetic and rheological point of view. The analysis of the *in vitro* release profiles from the topical systems was carried out using an immersion cell device adapted to a dissolution equipment and a Franz diffusion cell. The determination of rheological parameters was performed using a rotational viscometer at two different temperatures: 23 °C (room temperature) and 33 °C (skin temperature).



Results: The kinetic experimental data were fitted with the Higuchi model and the diffusion coefficient and time-lag were determined. The rheological profiles recorded as viscosity *versus* shear rate were examined by fitting the Power law model. The forward and backward rheograms plotted as shear stress versus shear rate were built and the thixotropic descriptors as thixotropic area and thixotropic index were evaluated.

Conclusions: All semi-solid products showed a non-Newtonian pseudoplastic behaviour, their viscosity decreasing with the increase of the shear rate at both tested temperatures. The pseudoplastic behaviour is a preferable property for the semi-solid systems because this feature improves their conditioning and spreadability on the skin surface, promoting the topical administration. The drug release transport indicated a Fickian diffusion, the relaxation rate of the polymer being much higher than drug diffusion rate. The *in vitro* naproxen release patterns and rheological parameters were strongly influenced by the excipients nature from the industrial hydrogels.

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Lecture 5

EFFECT OF CROSSLINKING DEGREE ON THE RHEOLOGY OF SALICYL-IMINE-CHITOSAN HYDROGELS

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The chitosan-based hydrogels are of interest in biochemistry and bioengineering applications due to the main properties of this natural polymer: biocompatibility and biodegradability [1]. Usually, the chitosan hydrogels are obtained by acid condensation reaction of amine groups of chitosan with dialdehyde crosslinkers. Our studies revealed the possibility of chitosan crosslinking using monoaldehydes, hydrogels with excellent properties being obtained in the case of salicylaldehyde as crosslinker [2]. This unusual chitosan gelling has been deciphered following and correlating data of NMR, FTIR, wide angle XRD and SEM measurements. FTIR and NMR spectroscopies demonstrated the formation of covalent imine bonds and physical interactions and X-ray diffraction confirmed a supramolecular ordering process at three dynamic levels, leading to conclusion that hydrogelation is the result of supramolecular ordering of salicyl-imine units. The hydrogels have a superporous morphology with a high degree of swelling in close correlation with their crosslinking degree.

The thixotropic behaviour of hydrogels based on chitosan and salicylaldehyde was evaluated by hysteresis loop tests (Figure 1).

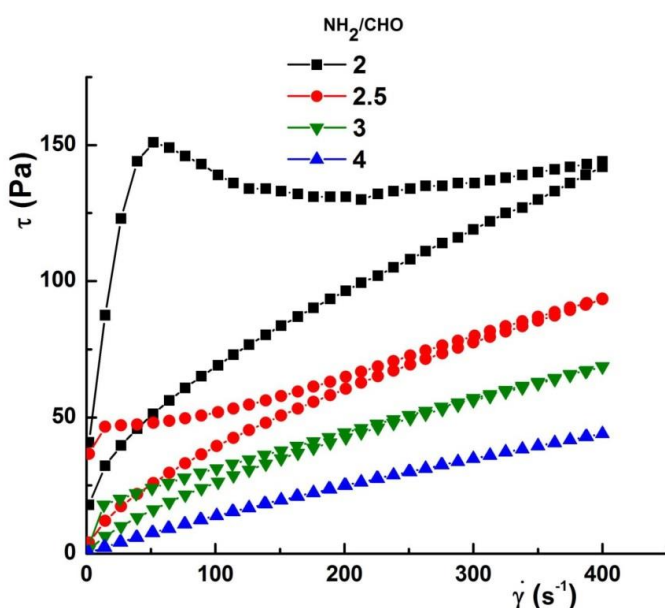


Figure 1. Hysteresis loop of the flow curves of salicyl-imine-chitosan hydrogels with various NH_2/CHO ratios.



The thixotropy of the hydrogels increases by increasing the crosslinking degree. In addition, the dynamic flow properties of salicyl-imine-chitosan hydrogels with different crosslinking degrees (NH₂/CHO ratio between 2 and 4) were investigated at temperatures in the range of 20 °C – 40 °C. The storage modulus, loss modulus and complex viscosity were determined over a wide range of oscillatory frequencies, and the experimental results were presented using master curves.

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Lecture 6

THE ROLE OF DIAMINE MOIETIES ON THE RHEOLOGICAL BEHAVIOUR OF SOME POLYIMIDES

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Dedicated to the memory of Dr. Silvia IOAN (1943-2021)

Polymers having imide rings along their backbone are widely recognized for their superior thermal, mechanical and dielectric characteristics. These features are fitting many requirements formulated by electronic applications. Nowadays, electronics business is extensively counting on rheological testing of the polymer samples for ensuring an elevated level of quality of the products. In this context, the current paper is aiming to describe the effect induced by the diamine segments on the rheological behaviour of the some polyimide structures. The flow curves are registered at several temperatures to emphasize the correlation between the activation energy and polymer flexibility. Also, the viscoelasticity is evaluated by means of oscillatory experiments that point out a transition from viscous to elastic flow. The transition point is affected by the diamine moieties length and rigidity. The rheological data are also discussed in regard to polymer processing conditions. Such investigations are paramount for producing dielectric layers for electronic circuits used in modern technologies.



Lecture 7

VISCOELASTIC PROPERTIES OF XANTHAN IN AQUEOUS SOLUTIONS

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Dedicated to the memory of Dr. Silvia IOAN (1943-2021)

Xanthan gum (XG) is a bacterial heteropolysaccharide produced by the *Xanthomonas Campestris*. The extraordinary stability to heat, acid and alkali, high viscosity and plasticity, good solubility in hot or cold water along with biological properties (e.g., nontoxicity, biocompatibility, biodegradability, etc.) and ability to modify/improve the rheological properties of the systems in which is introduced, increase its versatility for applications in food and non-food industry [1].

The aim of this study is to investigate the viscoelastic properties for xanthan gum aqueous solutions at 25 °C for different polymer concentrations (c_{XG}) and shear regimes. The rise of the polymer concentration determines the increase of the elastic (G') and viscous (G'') moduli (Fig. 1). Furthermore, a transition from the liquid-like behavior ($G' \sim \omega^2$ and $G'' \sim \omega^1$, for $c_{XG} = 0.02, 0.05$ and 0.2 wt. %) to solid-like behavior was observed: $G' \sim \omega^n$ and $G'' \sim \omega^n$ [2], where n is around 0.3 and 0.1 for $c_{XG} = 0.4$ and 1 wt. %.

The loss tangent values ($\tan \delta = G''/G'$) obtained for $c_{XG} = 1$ wt. % ($\tan \delta < 0.1$) indicate a high degree of elasticity, while for $c_{XG} = 0.4$ wt. % a constant value close to unity was obtained, suggesting a state of matter associated with the critical gel structure. Stationary shear measurements revealed that the beginning of the shear thinning zone is shifted to higher shear rates as the concentration decreases. In addition, the applicability of Cox-Merz rule was tested for xanthan gum solutions.

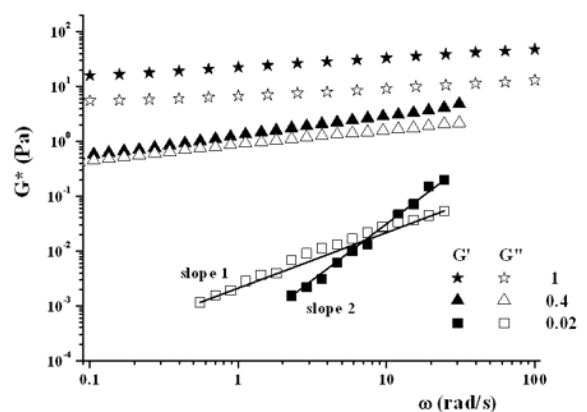


Figure 1. Evolution of viscoelastic moduli as a function of frequency for different xanthan concentrations (wt. %).



The complex viscosity (η^*) varies with the oscillation frequency as $\eta^* \sim \omega^{-0.65}$ for $c_{XG} = 0.4$ wt. % and $\eta^* \sim \omega^{-0.84}$ for $c_{XG} = 1$ wt. %.

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Lecture 8



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Instrumente Structurale
2014-2020

PARTNERSHIPS FOR KNOWLEDGE TRANSFER IN THE FIELD OF POLYMER MATERIALS USED IN BIOMEDICAL ENGINEERING - POINGBIO

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"Petru Poni" Institute of Macromolecular Chemistry Iași is implementing the project "Partnerships for knowledge transfer in the field of polymer materials used in biomedical engineering", Contract no.86/08.09.2016, ID P_40_443, SMIS 105689. The project is cofinanced by the European Regional Development (ERDF) Fund by the Competitiveness Operational Programme (OCP) 2014-2020, Axis 1 Research, Technological Development and Innovation (RDI) in support of economic competitiveness and business development, Action 1.2.3 Knowledge Transfer Partnerships. The project duration is 72 months.

The project aims to enhance the economic competitiveness of small and medium enterprises, which are partners in the project during 2016-2020, following the transfer of knowledge aimed at scientific and technological expertise in the design and development of multifunctional polymer systems that can stimulate a specific biological response and allow adherence and proliferation of a particular type of cell, depending on the tissue to be treated.

The eligible activities of the project are:

- the access of the companies to the facilities, installations, equipment of the research organizations in order to realize the analysis, tests, experiments, characteristics, quality labeling and the certification and to develop new products / technologies/ methods improved through:
- the transfer of the activities skills/competencies for research-development and for innovation support from research organization to industrial partner;



- industrial research activities and / or experimental development executed for and on behalf of the organization;
- the detachment of highly qualified personal who perform the research activities, development and innovation, from research organization to enterprises, in a newly function created within the enterprise, without replacing other personnel;
- the market research realized by the research organization for companies.



Lecture 9

INFLUENCE OF PEO CONCENTRATION ON THE FILAMENT EVOLUTION

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The paper is concerned with the experimental investigations of viscoelastic filaments breakup in air. The viscoelastic samples are polymer solutions at different concentrations of PEO ($M_w = 10^6$ g/mol) in water. The filament's profile in the vicinity of its minimum diameter is determined by the images processing of the frames using an original code developed in Matlab environment. The visualizations are performed with a fast camera in the interval 2,000 fps to 50,000 fps.

The parameters followed in our investigations are the time evolution of the filament neck and the corresponding thinning velocity before the droplet/jet breakup. Three flow regimes are observed as the relative time approach to zero (when breakup occurs): (i) an exponential increasing of the neck thinning velocity, followed by (ii) a non-monotonous variation of the thinning velocity and, (iii) the final pinch-off region, where thinning velocity is decreasing to a constant value or oscillates until the rupture of the filament.

The values of the thinning velocity are correlated with the polymer concentration and the samples' elasticity measured in oscillatory shear. The results of this experimental study have potential in developing novel techniques and more precise procedures in determining the interfacial rheology of complex fluid in dominated elongational flows.



Lecture 10

EXPERIMENTAL OBSERVATIONS OF THE CAPILLARY FLOW OF A VISCOELASTIC PEO SOLUTION IN TANDEM WITH ANOTHER IMMISCIBLE LIQUID

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We investigate the time-dependent dynamics of a polyethylene oxide solution (PEO) in a capillary tube. The setup implies another immiscible liquid as the prefilling fluid. We emphasize the prefilling liquid's influence on the dynamics of a less-viscous PEO solution in a capillary tube in contrast with the classical approach of one liquid displacing air. We find significant changes in the capillary regime as the prefilling liquid's volume increases.



Lecture 11

AIR – NON-NEWTONIAN FLUID INTERACTION IN CONFINED GEOMETRY

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The paper is concerned with the numerical simulations of the flow behavior of air and non - Newtonian fluid within a confined bifurcation. The bifurcation under consideration has one inlet, two outlets and a zone with the non-Newtonian fluid on the wall before a junction. In the bifurcation the flow rate of air is constant. The numerics is performed with the commercial software ANSYS – Fluent using the VoF code.

The goal of the paper is to determine the interface shape dynamics manifested between the air and non-Newtonian fluid.

The current numerical results will be focused for the numerical simulation of the air flow in the human trachea in the presence of mucus.



Lecture 12

INTRINSIC VISCOSITY METHODS BY ACACIA CAVEN GUM

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The *Acacia caven* gum (ACG) is an exudate from *Acacia caven* tree, this gum is dissolved in water and purified by precipitation with ethanol. In this paper, the intrinsic viscosity, $[\eta]$, is calculated by dissimilar equations, as Huggins, Kramer, Arrhenius-Rother-Hoffmann, Staudinger & Heuer, Square (S), Square root (SR), S-SR average plot, average values of S-SR, and Kraemer equation is taken as standard. The results obtained with different methods are evaluated and compared. From $[\eta]$ measurements, the molecular weight (M_v) and hydrodynamic radius (R_H) are determined, with values of 1,060 Kg/mol and 24 nm, respectively. This polysaccharide acquires a random coil conformation with Mark-Houwink parameters of $a = 0.5507$ and $k = 0.0225 \text{ cm}^3/\text{g}$. This polysaccharide can be applied as thickener, coemulsifier and gelling in different industry.



Lecture 13

HYDRODYNAMIC PARAMETERS OF CHAÑAR BREA GUM

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Chañar Brea Gum (CBG) is a hydrocolloid obtained as an exudate from the *Cercidium praecox* tree. CBG could be also used as additive or excipient for pharmacological formulations. This work reports the intrinsic viscosity, coil overlap and Mark–Houwink–Kuhn–Sakurada (MHKS) parameters of CBG solutions. Partially hydrolysed CBG solutions were analysed using intrinsic viscosity measurements, dynamic light scattering and size-exclusion chromatography (SEC). The MHKS parameters, a and k , were determined for CBG at 25 °C, with values of 0.4133 and 0.1347 cm³/g, respectively. The viscometric molecular weight of CBG was 1,890 kg/mol. The hydrodynamic parameters of CBG were indicative of a hyperbranched structure and spherical conformation. The knowledge obtained on the physicochemical properties of CBG favours its use in food and pharmaceutical applications.



Lecture 14

HYDRODYNAMIC PROPERTIES OF ALCAYOTA GUM

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The extraction of alcayota gum from *Cucurbita ficifolia* fruit was carried out by alkaline hydrolysis. The gum is purified by hydroalcoholic precipitations. This gum is characterized by intrinsic viscosity and density measurements, dynamic light scattering (DLS), and rheological investigations. The intrinsic viscosity of the gum was 149.83 cm³/g and the molecular weight of 1,867 kDa (whose Mark-Houwink parameters were $k = 0.00263$ cm³/g and $a = 0.7583$), a shape factor of 3.12 and a hydration value of 47.63 g/g. From DLS measurements, the hydrodynamic radius was determined with a value of 53 nm, a molecular weight of 1722 kDa and with Mark-Houwink parameters of $a_D = 0.5998$ and $k_D = 0.002543$ cm³/g. The rheological studies carried out for CyOH(d) showed a thixotropic behavior for the dispersed solutions that increased with the increase in hydrolysis and glycerin and decreased with the increase in temperature. The degree of thixotropy is higher for CyOH(d) compared to Cy(d). This polysaccharide can be applied in the film forming technology, as a thickening agent, etc.



Lecture 15

HYDRODYNAMIC PROPERTIES OF CHAÑAR GUM FROM GEOFFREA DECORTICANS FRUIT

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Currently, there is a growing interest in the use of natural resources in a sustainable manner. Finding the *Geoffroea decorticans* tree, popularly known as Chañar, a good target to cover this interest, since it is not cultivated or harvested, rather is little exploited in its natural habitat. Chañar gum (CHG), a polysaccharide type, is obtained from Chañar fruit flour. Two extraction methods were used, hydrothermal and acid extraction. The resulting polysaccharides (CHT and CHA) were characterized with density, viscosity, and diffusion coefficient measurements to obtain their properties in aqueous solution (intrinsic viscosity, shape factor, partial specific volume, hydration value, molecular weight, and hydrodynamic radius). From the intrinsic viscosity data, it can be concluded that both macromolecules, obtained by different extraction techniques, differ in the molecular weight, size, and shape. Both gums were quasi-spherical where the $v_{a/b}$ value of CHA is less than CHT, and M_v and R_H of CHT were greater than CHA. These data were corroborated with the intrinsic diffusion coefficient data. This phenomenon can be explained by the nature of the hydrolysis. The partial specific volume was slightly higher for CHA. Regarding the Mark-Houwink parameters, CHA presents values of $k = 0.01810 \text{ cm}^3/\text{g}$, $a = 0.5522$, which affirms its quasi-spherical shape ($v_{a/b}$ of 2.80). CHT values where $k = 0.00611 \text{ cm}^3/\text{g}$, $a = 0.6249$ which is a boundary between spheroid and ellipsoid shape ($v_{a/b}$ of 3.42). The study of these properties is critical to demonstrate the functionality of biopolymers and their application. The obtained results represent an advantage and evidence that Chañar is an interesting source for extract polysaccharides. We have not yet elucidated the structure of these polysaccharides, but it has a high molecular weight that guarantees its application in the food industry as a thickening agent, film, and gel former.

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Lecture 16

A MICROPLATE ASSAY FOR TRACKING PEPTIDE-ALGINATE OR PROTEIN-ALGINATE GELATION ASSISTED BY GLUTARALDEHYDE

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Alginate hydrogels are widely used for biomedical purposes [1-3]. Alginate bioconjugation with peptides or proteins using crosslinking agents could be applied to obtain hybrid gels. These gels are obtained by non-covalent (electrostatic interactions) or covalent crosslinking approaches [4-6].

Herein, an optical study of four alginate-polypeptide systems and their gelation in the presence of glutaraldehyde as a crosslinking agent is presented. Bovine serum albumin (BSA), γ -globulin, and two oligopeptides, FESNF and DVCYYASR, were selected as biomolecules. The kinetics of gelling was followed in a microplate reader at 600 nm at pH 7.4 (Tris 30 mM) and 21 degrees using both alginate and glutaraldehyde concentrations of around 1%. However, in order to obtain a suitable kinetic profile, the BSA content should exceed 1 mg per well. Moreover, at 3 mg BSA per well a good response was noticed within 1-2 hrs. In contrast, γ -globulin forms aggregate in the investigated systems even at smaller amounts (75-225 μ g protein). The alginate-FESNF system was distinguished by a much faster and similar gelation trend as BSA. Preliminary rheological results obtained for the alginate-FESNF system were consistent with spectroscopic studies. Overall, these results provide a simple microplate method to follow the gelation through kinetic approaches that could be expanded to other gelation systems since requires small amounts of a polypeptide as compared with the classical test-tube-inversion method. This microplate assay, proposed here, could be successfully implemented as a preliminary screening method for subsequent rheological studies.

ACKNOWLEDGMENTS. The authors wish to thank the financial support from the Romanian Government through UEFISCDI (PN-III-P2-2.1-PED2019-2484, Contract PED494/2020, BIOPASCAL).

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Poster 1

RHEOLOGICAL INVESTIGATIONS ON 5-NITROSALICYLALDEHYDE-CHITOSAN HYDROGELS

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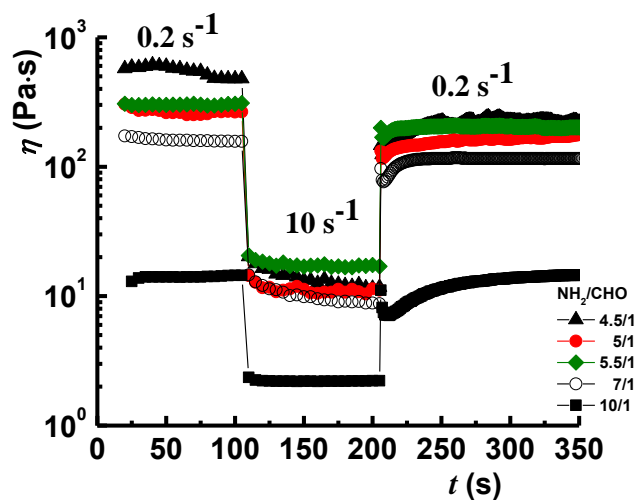
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Hydrogels are a class of soft materials with industrial and biomedical applications. An attractive direction for their bioapplications is local therapy, a particular example being cancer therapy by injecting hydrogels directly into the tumor, thus limiting side effects [1,2]. There are many examples of successful implementation of hydrogels in the treatment of heart attack, as sealing agents for severe bleeding, as easy-to-remove adhesives used in the treatment of second-degree burns, treatment of infections caused by antibiotic-resistant bacteria, loco-regional treatment of tumors, or in stem cell therapy. It has been found that the supramolecular architecture of hydrogels has a critical impact in regenerative medicine, having the ability to control cellular behavior in cell therapy [3].

Our contribution to the development of this field consists in obtaining chitosan-based hydrogels and 2-hydroxy-5-nitro-benzaldehyde, based on the supramolecular architecture of the imine units formed. By varying the ratio between the NH₂ and CHO functional groups, a series of hydrogels with different content of imine groups was obtained.

Hydrogels were characterized from a structural and supramolecular point of view, by NMR and FTIR spectroscopy, X-ray diffraction, and polarized light optical microscopy. The formation of imine bonds and their self-ordering in layered supramolecular architectures have been demonstrated. SEM images showed a porous micrometric morphology of hydrogels. Also, hydrogels were biologically tested on HeLa cells, and have shown adequate cytotoxicity *in vitro*, indicating their potential use as locally administered anticancer materials [4].

In order to apply these hydrogels as local treatment in tumors is necessary to know their rheological properties. These investigations have indicated elastic hydrogels with good resistance to continuous deformation and a high degree of recovery of mechanical properties.



The ability of the hydrogels to recover their mechanical properties after applying a high strain was not significantly influenced by the density of the imine covalent bonds.

ACKNOWLEDGMENTS. This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PD 197/2020, within PNCDI III.

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Poster 2

**RHEOLOGICAL AND MECHANICAL PROPERTIES OF
XANTHAN-BASED CRYOGELS**

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Xanthan gum (XG) is an important water-soluble anionic natural polymer, non-toxic, biodegradable and biocompatible, being recognized as a food additive by Food and Drug Administration [1,2]. In the food emulsifier list, XG is well-known as E-415. Consequently, a wide range of biomaterials based on XG in form of coatings, films, nanoparticles or hydrogels have been prepared for multiple applications including food packaging, environmental protection and drug delivery [1,2]. However, the uncontrolled swelling and rapid degradation upon storage are two major drawbacks of XG which limits its application domain. To overcome these disadvantages and to enhance its physicochemical properties and functional features, XG has been combined with other natural [3,4] or synthetic polymers [5] to design composite materials.

In this study, XG-based composite cryogels containing or not a natural polyphenol were prepared by a versatile and eco-friendly approach, namely cryogelation. The viscoelastic properties of these composite hydrogels were investigated by dynamic frequency sweep measurements comparative with those of pristine XG gels. Unconfined compressive tests were also performed to assess the mechanical stability of composite cryogels. Changes of the rheological and mechanical properties of XG-based composite hydrogels have been studied in terms of network composition, ratio between components and number of freeze/thawing cycles. It was found that G' was higher than G'' in the whole frequency range, i.e., the elastic behavior of all samples predominated over the viscous one. The values of compressive strength determined by uniaxial compression tests increased with the increase in the number of the freeze/thawing cycles, indicating the transition from a soft network to a more dense and stiff one.

ACKNOWLEDGEMENTS. The project AntoSensECOPACK, PN-III-P1-1.1-TE-2021-1683, number 6/2022 is acknowledged.

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Poster 3

RHEOLOGICAL ASPECTS ON CELLULOSE-BASED HYDROGELS

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Cellulose, the most abundant natural polymer on earth, is an inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products. Moreover, it is well known that cellulose-based hydrogels have attracted special attention, both scientifically and industrially, due to their biodegradable, biocompatible nature and their high swelling capacity. In this idea, cellulose-based hydrogels have been made in which cellulose nanocrystals have been incorporated in order to improve their mechanical properties. The hydrogels were characterized by determining the degrees of swelling, when was observed an increase of the swelling by incorporation of nanocelluloses. Rheological measurements indicated that the elastic and viscous modulus of hydrogels increased with the addition of cellulose nanocrystals, reflecting better mechanical properties of hydrogels. The structural and morphological characterization of hydrogels was performed by scanning electron microscopy (SEM) investigations and by X-ray diffractometry (XRD).



Poster 4

PHASE BEHAVIOR OF MIXTURES OF AMPHIPHILIC CATIONIC POLYSACCHARIDES AND ANIONIC SURFACTANTS

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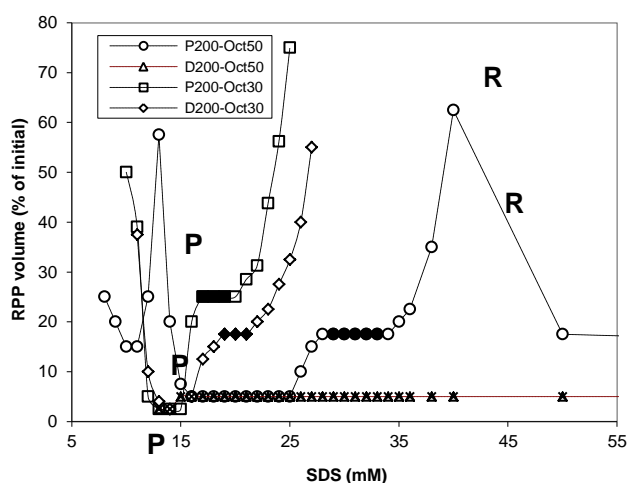
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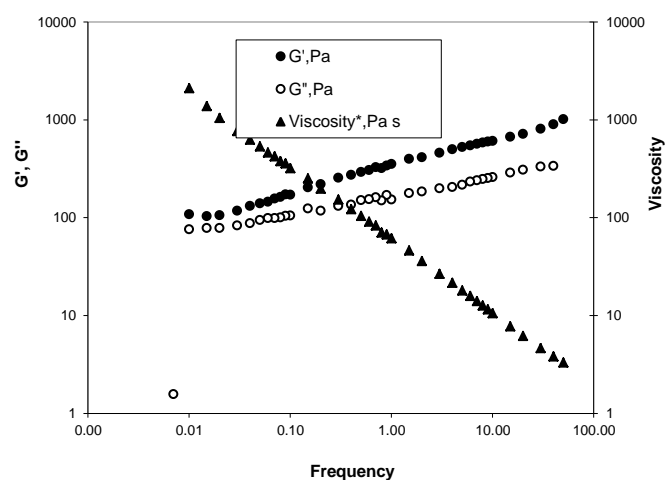
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Phase behavior in aqueous mixtures of 1 wt % of a hydrophobically modified polysaccharide (dextran or pullulan) with pendant N,N-dimethyl-N-(2-hydroxypropyl)-N-alkylammonium chloride groups) and different concentration of anionic surfactants, sodium dodecyl sulfate (SDS) or deoxycholic acid (DCA), was studied by capillary viscometry, cross-polarized light evaluation and rheology. Presence of both amphiphilic species will give rise to special aggregates with participation of unimers, self-assembled individual components, and mixed assemblies of components. Aggregates' characteristics depend on polymer properties (charge density, length of the alkyl substituent, polysaccharide molecular weight), surfactant nature and the components individual and relative concentration in the medium. At moderate polyelectrolyte concentration (1 - 5 wt %), an associative phase separation occurs when the molar ratio of the components is close to charge neutralization. The properties of the separated complex polyelectrolyte-surfactant depend also on the component characteristics. In some cases, the redissolution of the complex can occur by increasing molar ratio surfactant/polymer.



Variation of the rich polymer phase (RPP) volume with surfactant concentration. P indicates the start of phase separation, R the start of redissolution. Marks: cross-powder, open- isotropic gel, solid - birefringent gel.



Frequency dependence of the storage modulus (G'), loss modulus (G'') and complex viscosity for the birefringent swollen gel obtained by mixing P200-Oct50 with 32 mmol SDS.



Poster 5

HYBRID HYDROGELS BASED ON PEPTIDE

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Although supramolecular peptide gels and polymer gelators have different advantages and disadvantages, the combination of these two types of networks offers the possibility to significantly extend the scope of what can be achieved with gel phase materials. These types of network, called hybrid gels, can be considered as a type of multicomponent system, being composed of two independent gel networks. Also, incorporation of peptide, protein, DNA or polysaccharide can be a suitable option to improve biological performance of hydrogels. The association forces between both networks depend on the intrinsic physicochemical properties of both components. Hence, supramolecular co-assembly between distinct components could be generated by complementary chemical groups. The benefits of multi-component hydrogels include diversity in morphology, multiple bioactivity, enhanced mechanical properties.

In the present study, the hydrogels derived from amino acids or peptides and polysaccharide derivatives were obtained. A polysaccharide (agarose) was introduced in order to improve the mechanical and physical features of amino acid/peptide hydrogel. The obtained gels were characterized through rheological and morphological investigations.

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Poster 6

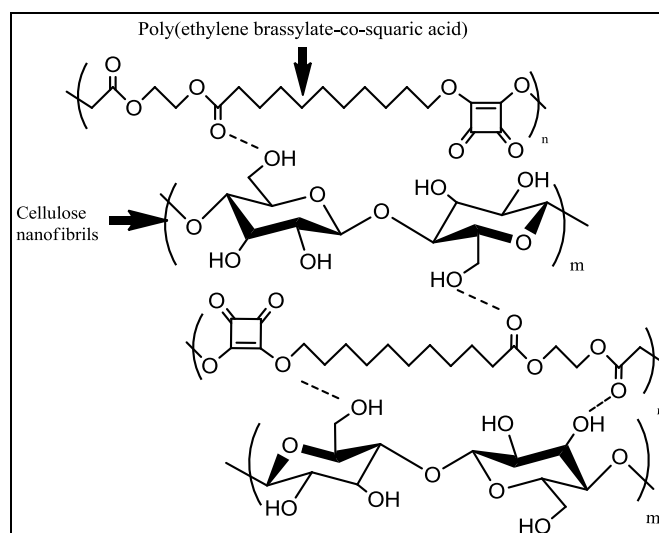
**INVESTIGATION OF AN INTERPENETRATED POLYMER SYSTEM
CONTAINING CELLULOSE NANOFIBRILS AND A
COPOLYMACROLACTONE STRUCTURE**

**Alexandra CROITORIU, Loredana E. NITA, Alina G. RUSU, Alina GHILAN,
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The physicochemical properties of hydrogels can be improved by blending specific compounds with appropriate structures. The aim of the study was to develop a system containing cellulose nanofibrils (CNFs) and a copolymacrolactone in a new interpenetrated polymer network structure with gelling ability. Due to the numerous hydroxyl groups, CNFs can form hydrogels by nanofibrils entanglements and nanofibril–nanofibril interactions, namely hydrogen and van der Waals bonds. The copolymacrolactone based on ethylene brassylate (EB) and squaric acid (SA) which will be used to form interpenetrated polymer network has already shown in previous studies the capacity to encapsulate essential oils.



This behaviour will be beneficial in the context of using the new network for the incorporation of hydrophobic compounds. In this work, we focused on investigating the compatibility between the two polymer systems, through rheological and morphological evaluation.

ACKNOWLEDGEMENTS. This work was funded by a grant of the Romanian Ministry of Education and Research, CNCS-UEFISCDI, through the research projects 562 PED/2020, PN-III-P2-2.1-PED-2019- 2743 and 339 PED/2020, PN-III-P2-2.1-PED-2019- 2743, within PNCDI III. Also, the authors thank to the group from Cellulose Lab, from Canada for offering the cellulose derivative (<https://www.celluloselab.com/>).



Poster 7

STRUCTURE AND PROPERTIES OF POLY(VINYL ALCOHOL) MODIFIED WITH PHOSPHONIC DICHLORIDES

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Phosphorylation of poly (vinyl alcohol) has been performed by nucleophilic substitution of the hydroxyl groups of the poly (vinyl alcohol) (PVA) with phenoxyphosphonic dichloride and phenylphosphonic dichloride, respectively, using DMF as reaction medium. In the electrospinning process, the viscosity of the polymer solution is considered to be the most critical factor in relation with the morphology of the obtained material, especially with the average diameter of the fibers. Fibers can be formed by controlling the viscosity of the polymer solution in a certain optimal interval during the electrospinning process. Figures 1 and 2 show the variation of the apparent viscosity and the shear stress depending on the shear rate for poly (vinyl alcohol) (PVA)/phenoxyphosphonic dichloride (PVA-OP) and poly (vinyl alcohol) (PVA)/phenylphosphonic dichloride (PVA-P) samples of different concentrations in double-distilled water at 25 °C, in stationary flow conditions.

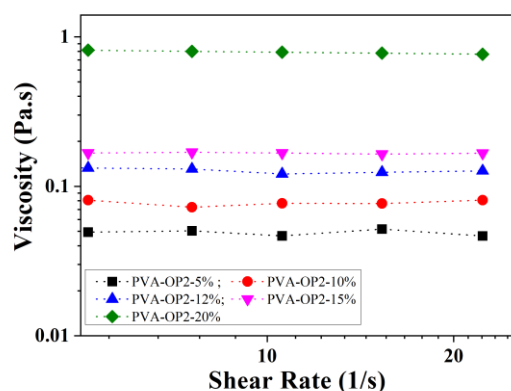


Figure 1. Apparent viscosity as a function of shear rate for PVA-OP2 sample of different concentrations in double distilled water, measured at 25 °C

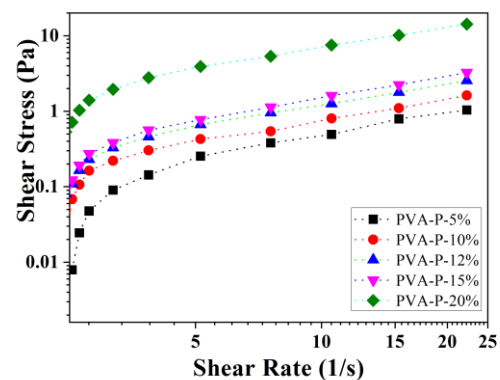


Figure 2. Shear stress as a function of shear rate for PVA-P samples of different concentrations in double distilled water at 25 °C.



The thermal stability of the PVA-OP and PVA-P was introspected through TGA analysis. Also, the microscale combustion calorimetry measurements have been conducted, in order to investigate the combustion mechanism of the synthesized PVA-OP and PVA-P samples. Thus, from the heat release capacity (HRC) point of view, the sample with the best fire behavior is the APV-OP2, with an HRC of 245.38 J/(g·K), 7.6% lower, than the highest HRC which is 265.65 J/(g·K) and is recorded in the APV-OP3.

ACKNOWLEDGMENTS: The authors gratefully acknowledge the financial support through CNCSIS–UEFISCSU, Project Number PN-III-P1-1.1-TE2019-0639 nr. 89/03.09.2020.



Poster 8

**CORRELATION BETWEEN SOLUTION RHEOLOGY AND ELECTROSPUN FIBERS
FORMATION OF NEW POLYIMIDE**

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In the present paper, the implications of the entanglements in solution (above the critical entanglement concentration, C_e) on the electrospinning process for a new polyimide (PEI) were investigated. The dependence of specific viscosity (η_{sp}) on concentration enabled the determination of the semidilute unentangled, semidilute entangled and concentrated regimes for the PEI solutions. The polyimide sample was electrospun from semidilute unentangled, semidilute entangled and concentrated solutions under identical conditions to determine the effects of concentration regime and molecular topology on electrospun fiber morphology. From the dependences of shear viscosity as a function of shear stress (Figure 1a), the yield stress (σ_0) was determined as being the shear stress value at which the viscosity decreases. The value of σ_0 is below 1 Pa for PEI concentrations between 12 % and 16 %, thus this concentration range is recommended for electrospinning process in order to minimize energy consumption. From Figure 1b it is observed that the deformation is fully recovered for $\sigma < 2$ Pa, it is 81 % recovered for $\sigma = 5$ Pa, and it remains approximately constant around 75 % for a wide range of shear stress values (10 Pa – 2,000 Pa). Over 2,000 Pa the viscous flow becomes predominant and the recovery decreases significantly to approx. 20 %. These data on the creep behavior and elastic recovery suggest that the degree of viscoelasticity of the sample remains constant for a wide range of shear stresses, corresponding to the parameters imposed in the electrospinning process.

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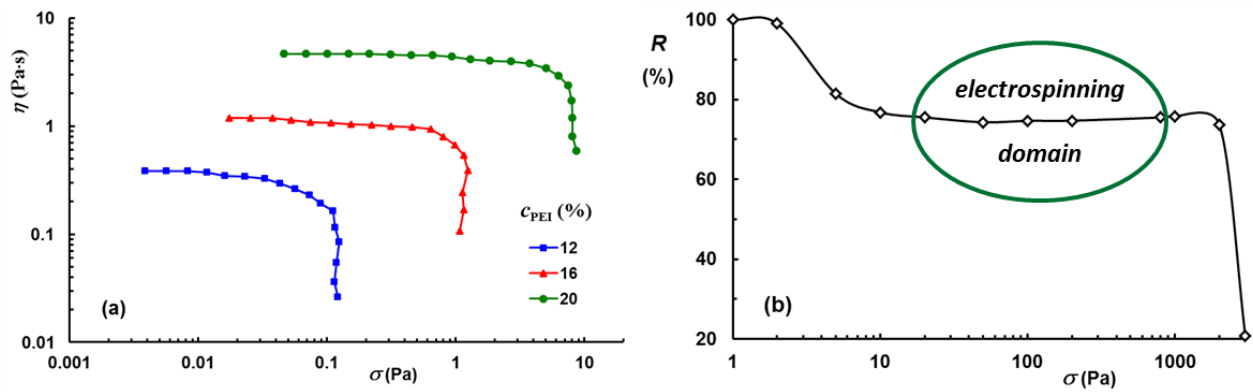


Figure 1. Evidence of yield stress for entangled solutions of PEI in DMF at 25°C (a); the total recovered deformation reported to the maximum deformation of the sample as a function of the shear stress applied during the creep test (b).



Poster 9

**POLYSACCHARIDE-BASED ELECTROSPUN NANOFIBERS.
PREPARATION AND CHARACTERIZATION**

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Nanofibers composed of phosphorylated curdlan (PCurd) and poly(vinyl alcohol) (PVA) were prepared using an electrospinning method from aqueous solutions. The optimal composition of the polymers mixture for the electrospinning process was established by viscometric and rheological studies. The electron microscopy confirmed the obtaining of well-defined and drop-free nanofibers with a diameter of 157 nm. The PCurd/PVA electrospun membrane has shown a tensile strength of 1.97 MPa and a Young modulus of 0.861 MPa. These results encourage us to continue studies regarding the use of this new membrane as a wound protection dressing.

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Poster 10

DYNAMIC PROPERTIES OF THE (HYDROXYPROPYL)METHYL CELLULOSE / POLY(VINYLPYRROLIDONE) / WATER SYSTEMS. INFLUENCE ON THE FORMATION OF FIBROUS MATERIALS

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Dedicated to the memory of Dr. Silvia IOAN (1943-2021)

Design of new fibrous polymeric materials with adapted properties and multiple functionalities has gained a great interest in various scientific fields. The physical mixing of two or more polymers represents simplest conceptual way to achieve the desired properties of new materials. In this direction, to guarantee the quality and functionality of the fibrous polymeric materials on the targeted applications, the choice of the polymers systems and used solvents plays an important role in the solutions electrospinning process. From this perspective, in the present study, (hydroxypropyl)methyl cellulose (HPMC) and poly(vinylpyrrolidone) (PVP) were selected due to their excellent physical properties for a variety of applications. Thus, the aim of this study is to analyze the rheological behavior of HPMC/PVP/water system and to acquire information about the effects of the polymers from blend at different compositions of HPMC or PVP, and also of the used solvent in electrospinning process.

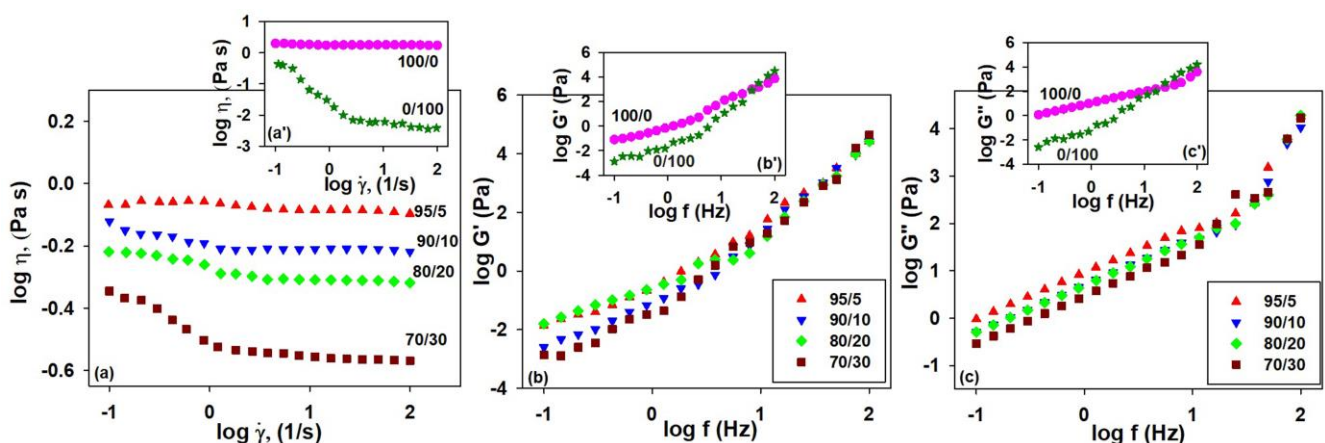


Figure 1. Rheological parameters of HPMC/PVP/water system: dynamic viscosity *versus* shear rate (a, a'), storage modulus (b, b') and loss modulus (c, c') *versus* oscillatory frequency for different compositions at 25 °C.



According to those mentioned, by evaluating the rheological parameters, namely the dynamic viscosity (Figure 1a, a') and viscoelastic moduli (Figure 1b, b' , c , c'), it was possible to establish and control the optimal concentration and compositions of the studied blends in order to obtain the continuous cylindrical and thin fibers, defect-free. Thus, the optimum composition of fibers with the best morphological characteristics corresponds to PVP content up to 30 wt.%. Therefore, the rheological properties were the key factors in electrospinning process, affecting directly the morphology of the electrospun fibers.

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Poster 11

CONFORMATIONAL RESTRUCTURATIONS IN POLYSULFONIC SYSTEMS INDUCED BY TRIETHYLPHOSPHONIUM PENDANT GROUPS

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Polysulfonic materials containing ammonium or phosphonium groups have gained attention in various technologies being applied as potential phase transfer catalysts, antistatic agents, moisture sensors or ultrafiltration membranes. Also, they are good candidates as antimicrobial agents, synthetic enzymes and can be used in non-viral gene delivery or as drug carriers. Unlike compounds containing amino groups, those with phosphonium have much improved properties. Thus, a new polysulfone was synthesized by the reaction of chloromethylated polysulfone with triethylphosphine and dioxane in order to be used in obtaining of performant materials with applicability in different fields. Study of the rheological behavior of the polysulfone with triethylphosphonium pendant groups (PSFP) solutions is of a real help considering that the conformational restructurations, generated by the specific interactions from the system, have a major impact on the processability and performance of polysulfonic materials.

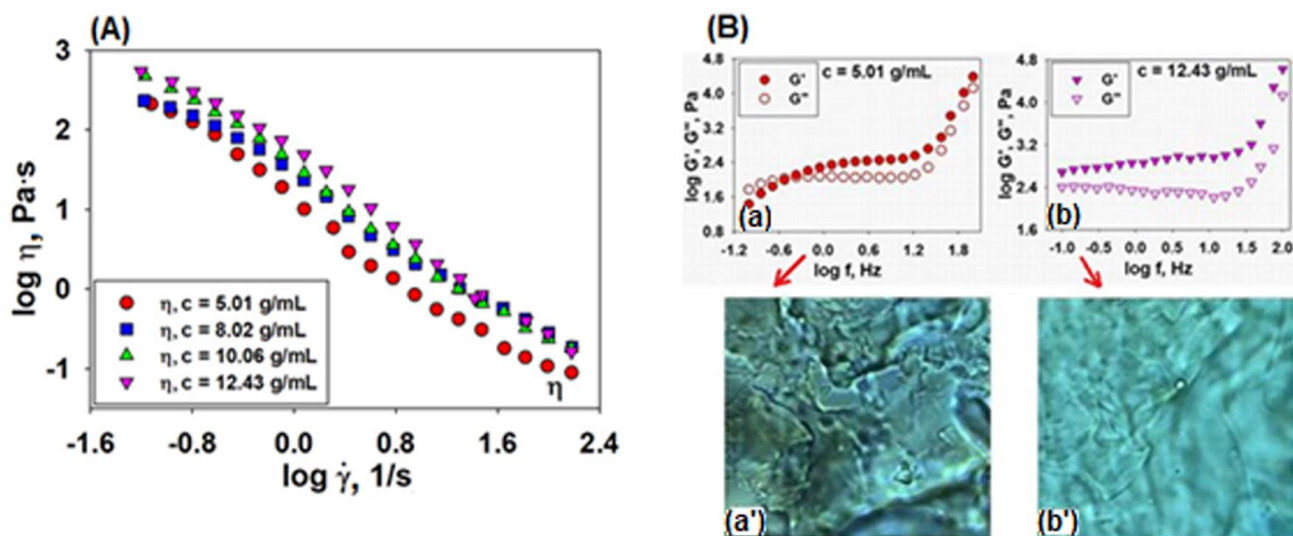


Figure 1. Variation of dynamic viscosity as function on shear rate (1A) and of viscoelastic moduli on frequency (1B (a,b)) with corresponding POM images (1B (a',b')).



As can be observed (Fig. 1A) all studied solutions exhibit a shear thinning profile, the dynamic viscosity decreasing with increasing of shear rate. Moreover, higher values of the elastic modulus (G') compared to the viscous modulus G'' (Fig. 1B (b)) but also the fine texture with bands characteristic of the layered architectures (Fig. 1B (b')) highlights the transition from sol state to a compact gel structure, as the concentration increases.

Rheological data suggest that polysulfone with triethylphosphonium pendant groups can be successfully used as gel matrices in obtaining materials with applicability in various fields designed to improve the life quality.



Poster 12

**VISCOSITY STUDY OF PVA, PVP AND THEIR MIXTURES
IN DILUTE AQUEOUS SOLUTION**

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For the present study, there have been selected a pair of polymers with high applicability in biomedical field, namely: poly(vinyl alcohol) (PVA) and poly(vinylpyrrolidone) (PVP). The viscometric investigations were performed in order to determine the hydrodynamic properties of this polymer mixture as compared with the corresponding single polymer solutions at storage temperature (i.e., 25 °C). The main interest is a better understanding of the polymer-polymer interactions and to identify the synergistic behavior in order to design multicomponent biomaterials with targeted properties. In this context, PVA and PVP are of interest in a large area of biomedical applications (tissue engineering, drug delivery, contact lenses, etc.).

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Poster 13

**TEXTURAL AND MECHANICAL FEATURES OF POROUS
CHITOSAN-BASED HYDROGELS**

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Hydrogels are three-dimensional polymeric systems constructed using synthetic or natural polymers and stabilized through chemical and/or physical cross-links. Characteristics such as high-water absorbency and structural similarity to biological tissues recommend them for many healthcare and environmental end-uses. Chitosan (CS), the only natural cationic polymer, has harnessed a great amount of attention as building-block for the design of multifunctional hydrogels because of its bioavailability, high number of functional groups, pH-responsiveness, biocompatibility and antibacterial activity. Consequently, CS-based hydrogels have been deeply investigated as potential drug delivery devices, actuators, insulators or sorbents for water purification [1-4].

In this work, information on the textural and mechanical properties of CS hydrogels prepared by formaldehyde cross-linking through the cryogelation technique are presented. Because formaldehyde's high reactivity towards amino groups through Schiff base chemistry, the possibility to functionalized the CS hydrogels with thiourea is also described. The CS-based hydrogels were highly porous with a honey-comb morphology having interconnected pores in the range of tens of micrometers. The uniaxial compression measurements performed on swollen hydrogels revealed typical compressive stress-strain profiles for porous polymeric materials. In addition, to evaluate the resilience and robustness of the interconnected macroporous hydrogels, the dynamic stress-strain behavior of the hydrogels was performed for 12 cycles by applying a strain of 90 %. A remarkable elasticity and toughness with no obvious recovery loss was registered for the CS-based hydrogels prepared at an amine/aldehyde molar ratio of 1:10.

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Poster 14

**A PH-TRIGGERED SELF-ASSEMBLING PEPTIDE
STUDIED BY ATOMIC FORCE MICROSCOPY**

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Peptide-based hydrogels have received a lot of interest in recent years considering their remarkable biocompatibility and potential biomedical advantages [1]. The FESNF peptide sequence (where F-phenylalanyl, E-glutamyl, S-seryl, N-asparaginy) is found in the structure of lysozyme, a naturally occurring enzyme that modulates immune response to infection and is characterized by antimicrobial properties [2].

The FESNF peptide was synthesized by the solid phase peptide synthesis (SPPS) method using Fmoc-strategy. Separation and purification were carried out by reverse phase high-performance liquid chromatography. The peptide's molecular weight was confirmed by MALDI-ToF mass spectrometry and the primary structure was determined by tandem mass spectrometry. In this study the peptide was investigated using atomic force microscopy (AFM) under different pH conditions.

The peptide fibrillation was studied in methanol and two buffer solutions, at pH 5.5 and 8.2. In buffered solutions, the ability of peptide to self-assemble into long, uniform, clear and distinct fibrils was observed. In both ammonium acetate and methanol, fibrillar aggregates were identified. Surprisingly, at a physiological pH of 7.4, near the isoelectric point, a porous 3D structure was formed.

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Poster 15

**VISCOSITY OF BOVINE SERUM ALBUMIN SOLUTIONS
IN PRESENCE OF NEUTRAL POLYMERS**

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Dedicated to the memory of Dr. Silvia IOAN (1943-2021)

The paper discusses the viscosity of bovine serum albumin (BSA) solutions in presence of two water soluble polymers, poly(vinyl alcohol) (PVA) and pullulan (PULL), over a large range of concentrations, at 37 °C and pH = 7.4 (above the isoelectric point of BSA).

For dilute solutions, different models were applied to viscometric data in order to determine the hydrodynamic specific volume at infinite dilution, known as intrinsic viscosity, and parameters correlated with polymer/solvent interactions. The viscometric parameters were used to discuss the miscibility between BSA and neutral polymers [1,2].

For concentrated polymer/protein solutions, the shear viscosity was measured in steady shear conditions, by using an Anton Paar rheometer with different geometries.

The experimental data suggest that BSA/PULL complexes are formed in excess of Na⁺ ions due to attractive interactions mediated by the presence of cations [2]. Membrane osmometry was used to determine the apparent molecular weight of PULL/BSA complexes and the interactions between the macromolecules and the solvent. These structures are stable in time and in conditions of high shear forces. PVA/BSA mixtures presented an ideal behavior in dilute solutions and time dependent viscosity in concentrated solutions. The macromolecular crowding influences the overall behavior and it can be evidenced from the viscosity dependence on reduced concentration.

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IASI, ROMANIA, MAY 26th, 2022



HYALURONAN IN BIOLOGICAL FLUIDS AND ITS RELATED BIOMEDICAL APPLICATIONS

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Dedicated to the memory of Prof. Robert M. Moriarty

ABSTRACT

Hyaluronic acid (HA) is one of the most simple in structure and also most fascinating naturally occurring biopolymer. HA chains consist of alternating residues of β -D-(1-3) glucuronic acid (GlcA) and β -D-(1-4)-*N*-acetylglucosamine (GlcNAc). HA is considered the largest linear unbranched non-sulfated glycosaminoglycan. At physiological pH and ionic strength, HA chain has the carboxyl groups on the glucuronic acid residues (of pKa 4–5) negatively charged and is termed hyaluronan.

Hyaluronan molecules have random coil conformation and, depending on their molecular mass, occupy a large hydrodynamic volume. Hence, in solution hyaluronan occupies a volume approximately 1000 times greater than in dry state. The most distinctive property of HA solutions is both their viscous and elastic non-Newtonian behavior when exposed to various shear rate properties, making them excellent biological shock absorbers and lubricants. The viscoelastic rheology of hyaluronan solutions depends on the concentration and the average molecular mass, salt concentration, pH and shear rate. For instance, a 2-fold increase in concentration or molecular mass results in a 10-fold increase in bulk viscosity. The high viscosity of hyaluronan solutions is of great importance in biological fluids, as well as in its related biomedical applications. For application in body compartments, the concentration of hyaluronan cannot be increased much above 10 mg/mL due to the highly non-ideal colloid osmotic behavior. High viscosity hyaluronan solutions must therefore be based on high molecular mass. Biomedical applications are, as consequence, limited by short turnover rate and limited mechanical properties of native HA solutions, chemical modifications being required to provide stable biomaterials with enhanced or modulated properties.

The content of HA is different in different normal biological fluids. HA is a component of articular joint synovial fluid, where it provides the viscoelasticity and lubrication, in concentration of approximately 2–3 mg/mL in knee joints. HA is also a component of the vitreous body of the eye, at a concentration of approximately 200 μ g/mL, in human eye vitreous, while in the aqueous humor is only about 1 μ g/mL. Biomedical applications of hyaluronan solutions mainly consist of fillers for tissue augmentation and regeneration, due to their particular lubricant and viscoelastic properties. Particularly, biomimetic hyaluronan solutions target viscosurgery – to protect eye tissues and provide space in ophthalmic surgery; viscoaugmentation – to fill and augment tissue spaces in skin, sphincter muscles, and vocal and pharyngeal tissues; viscosupplementation – to replace or supplement tissue fluids, such as synovial fluid; viscosseparation – to separate soft connective tissue surfaces after surgical procedures or injury, in order to prevent adhesions and excessive scar formation.

Keywords: *hyaluronic acid, hyaluronan, non-Newtonian solution, viscoelastic fluid*



HYALURONAN STRUCTURE AND MOLECULAR INTERACTIONS

HA chain in aqueous solutions, such as in biological fluids, has the carboxyl groups of the glucuronic acid residues negatively charged, and is termed hyaluronan. The anionic nature of hyaluronan with sterical restrictions and hydrogen bonding give a relatively stiff, random coil structure, counterbalancing the electrostatic repulsion and generating a stiffened helical configuration. Hyaluronan chain is amphiphilic, the axial hydrogen atoms form non-polar hydrophobic patches, while the equatorial side chains form polar hydrophilic patches. The tape-like secondary structural identical sides and hydrophobic patches may associate and form double antiparallel helices related to each other. HA hydrophobic patches of different HA large molecules may also self-assemble in honeycomb network structures. As consequence, the longer the HA molecule, the more extensive and coherent the network even at low HA concentration ($< 1 \mu\text{g/mL}$) [1]. The numerous hyaluronan electronegative and $-\text{OH}$ polar groups bind water molecules.

HYALURONAN PROPERTIES IN AQUEOUS SOLUTIONS

Despite its apparently very simple structure, the conformation of HA in solution has been difficult to determine [2]. HA secondary structures containing water bridges restrict rotation and flexion at the glycosidic bonds and create a stiffened, yet mobile polymer chain [3]. Experimentally, it was shown that a 2-fold increase in concentration or molecular mass results in a 10-fold increase in bulk viscosity. The high viscosity of HA solutions is of great importance in vitreous humor of the eye, synovial fluid, skin connective tissues, as well as in related medical applications. For application in body compartments, the concentration of hyaluronan cannot be increased above 10 mg/mL , due to its high non-ideal colloid osmotic behavior. High viscosity hyaluronan solutions can therefore be obtained from high molecular masses [4].

The most distinctive properties of HA solutions are their viscoelastic and non-Newtonian behavior, when exposed to various regimes of deformations, making them excellent biological shock absorbers and lubricants. The viscoelastic rheology of hyaluronan solutions depends on the average molecular mass and source of the hyaluronan, concentration and ionic strength, pH and shear rate [5]. Hyaluronan in aqueous solution exhibits non-Newtonian behaviour, with viscosity dependence upon the applied shear conditions, the most common type being shear-thinning, where viscosity decreases with increasing shear rate. The time-dependent behaviour results from elastic dominance ($G' > G''$) at high frequencies, while viscous dominance ($G'' > G'$) at low frequencies, as consequence of macromolecular entanglements. This characteristic is beneficial as it allows to be



pumped and filled in manufacturing processes or injected by a surgeon, but once at rest the product regains its viscosity and maintain its position.

As the hyaluronan physiological life time usually takes 48-72 h, it is necessary to improve its persistence by chemical modifications, usually by controlled crosslinking reaction [6]. Both cross- and non-crosslinked products demonstrate elastic-dominant behavior at high oscillation frequencies, G' , the storage modulus being higher than G'' . However, the noncrosslinked product, typical as an ophthalmic viscosurgical or a viscosupplementation injectable gel, shows a clear trend to a viscous behavior as the oscillatory frequency decreases, whereas the crosslinked product, typical to dermal filler, maintains a solid-like behavior even down, at very low frequencies.

HYALURONAN IN BIOLOGICAL FLUIDS AND RELATED BIOMEDICAL APPLICATIONS

Due to its hydrophilicity and viscoelastic behavior, the hyaluronan based biological fluids have physical functions in hydration, space filling, lubrication and shock absorption. HA solutions also exhibit osmotic buffering capacity regulating the water content in extracellular spaces due to their non-ideal osmotic pressure behavior. At the same time, intermolecular networks generated by self-associations of hydrophobic patch sites represent a size-selective diffusion barrier in which small molecules can diffuse freely, whereas larger molecules are partially or completely excluded. The biological functionality of hyaluronan appears to be dependent on polymer size, with small and high molecular mass chains exhibiting opposite effects. While high molecular mass HA possesses anti-angiogenic, antiinflammatory, and immunosuppressive properties, smaller HA fragments act predominantly in an opposite manner, being angiogenic, pro-inflammatory and immunostimulating.

The idea of utilizing HA aqueous solutions in medicine is dated back to 1960s with the first use of HA as a viscous material for replacing vitreous of the eye. The first commercial usage of HA was in 1980s as an ophthalmic viscosurgical device solution; since then, HA has been applied to the fields of ophthalmology, rheumatology and dermatology, etc., due to viscoelastic properties and hydration capacity of high molecular mass HA.

The therapeutic classification of hyaluronan aqueous solutions applications, according to their primary mode of action, is based on the viscous and elastic properties, similar to the corresponding biological fluids: viscosurgery, used in ophthalmic surgery; viscoaugmentation, to fill and augment the intercellular spaces in connective tissues; viscosparation, to separate connective tissue surfaces; viscosupplementation, to supplement or replace tissue fluids such as synovial fluid; viscoprotection, to protect healthy, injured or wounded tissue surfaces or promote the wound healing [7].



Hyaluronan in Eye Humors and Viscosurgery

The viscosity of hyaluronan aqueous solution is dependent on the shear rate (non-Newtonian viscosity) and decreases rapidly as the shear force increases, behaviour named pseudoplasticity. Hyaluronan solutions possess the highest degree of pseudoplasticity of all the viscoelastic substances. The pseudoplasticity of a hyaluronan solution explains the blinking process. Hence, between blinks (at low shear rate), the hyaluronan macromolecules assume a randomly coiled structure that offers protective elastic properties. As the eye blinks, the shear rate increases and the macromolecules of hyaluronan tend to align and can freely move past one another. As a consequence, the solution becomes less viscous, allowing the eyelids to move easily over the corneal surface. Under blinking compression, hyaluronan acts like a sponge that releases water into its surrounding environment; when the compressive force is removed, osmotic pressure draws water back into the structure.

Ophthalmic lubricants incorporating hyaluronic acid are used for its excellent lubrication, especially in dry eyes, where the combination of high zero-shear viscosity, low high shear viscosity and viscoelastic behaviour ensure a comfortable cushion of liquid sits between the eyelid and cornea.

In ophthalmic viscosurgical gels (OVDs), the rheology determines whether the gel exhibits dispersive or cohesive characteristics, offering surface protection and film-forming or rigid structuring in use, and easy aspiration upon completion of a surgical procedure.

Hyaluronan in Synovial Fluid and Viscosupplementation – Hylans

Synovial joints are remarkable biotribosystems with unique properties. The rapid transition of the hyaluronan aqueous solutions from a viscous to an elastic state occurs at a frequency that is typical in normal joints under various types of movements. Hence, when the knee joint is flexed under no load or on jumping, the deformation is slow and the synovial fluid behaves as a viscous solution, hyaluronan macromolecules adopting a coil conformation. When the joint supports walking or running, the frequency becomes faster and faster and the fluid behaves as an elastic body, hyaluronan macromolecules tend to align and freely move past one another, dropping down the friction coefficient. These are briefly the experimental considerations that represent the foundation of the therapeutic use of hyaluronan solutions and gels as elastoviscous formulations.

Osteoarthritis (OA) is a degenerative joint disease that is characterized by the gradual erosion of articular cartilage causing pain and swelling, limiting the mobility in the joint. In healthy individuals, articular cartilage and a thin film of synovial fluid are closely linked in, providing a



protective barrier between the ends of the bones and lubricating the joint [8]. In osteoarthritic joint, damage of articular cartilage results in degradation in rheological properties of the synovial fluid, that becomes less viscous and less effective in joint lubrication. One of the non-surgical treatments for OA is intra-articular injections of hyaluronic acid formulations – viscosupplementation [9].

Hyaluronan in Viscoaugmentation – Dermal Fillers

Injectable dermal fillers based on hyaluronan have been developed for facial correction or volumizing, especially in the nasolabial fold, lips, forehead, nose, chin, and infraorbital area.

The rheology of dermal fillers is critical, with properties such as rigidity (elastic modulus, G'), zero-shear viscosity, viscoelastic relaxability, cohesivity and viscosity under shear, all contributing to their handling, injection, volumizing and persistence in time [10,11]. A dermal filler that dispenses easily and smoothly from the syringe is vital to the clinicians.

In order to maximize their efficacy, it is necessary to understand the specific properties of different fillers, mainly their rheologic properties. For instance, for a volumizing filler, a relatively high G' is recommended as the filler must lift up the soft tissue, under a lower extent of deformation. For nose and chin, the augmentation should persist for long time under high compression and shearing forces in these areas, so the filler should have a high G' . On contrary, fine wrinkles need a fine filler, with a smooth behavior to spread easily under the surface, with a low G' . To improve nasolabial folds, a moderate to high G' dermal filler is needed, corresponding to the area to be volumized, in order to prevent negative effects from compression and shear force. Immediately after its injection and during its placement into the soft tissues of the face, the HA filler is subjected both to shear stress, vertical compression and stretching forces, which lead to filler deformation. These forces also influence the fillers capability to correct volume loss and also long-term tissue integration. The elastic modulus indicates the ability of HA fillers to recover to their initial configuration, after being altered by dynamic forces. The viscous modulus G'' is a key parameter that characterizes HA resistance to these dynamic forces. The complex modulus (G^*) measures the overall resistance to deformation of a gel, which comprises a recoverable component from the gel's elasticity (G') and a non-recoverable component from the gel's viscosity (G''). In general, the higher the G' , the higher is the elasticity and resistance to deformation and, ultimately, its capability to restore the soft tissue volume [12]. G' also indicates filler stiffness or hardness and determines the injection at the appropriate anatomical level. HA fillers with higher G' are designated to be injected into the deep fat compartments or the pre-periosteal plane. These fillers give good volume restoration and can be injected deep into the soft tissue where they are neither



palpable, nor visible. A potential advantage of high G' is the capability to obtain a good prominent tissue projection with minimal amount of product. The loss tangent ($\tan \delta$) of HA fillers is always less than 1 and this indicates a predominance of an elastic behavior [13].

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VISCOELASTIC PROPERTIES OF XANTHAN AQUEOUS SOLUTIONS

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Dedicated to the memory of Dr. Silvia IOAN (1943-2021)

INTRODUCTION

Xanthan gum (XG) is a bacterial heteropolysaccharide produced by the *Xanthomonas Campestris*. Its primary structure consists by β -(1-4)-D-glucose cellulose backbone with a trisaccharide side chain linked at every second glucose residue. The side chain is formed by a glucuronic acid unit between two mannose units; a mannose unit is linked to the main chain and contains an acetyl group and the other one contains a pyruvic acid residue. Electrostatic repulsion interactions between negative charges stabilize the helical secondary structure of xanthan and make xanthan a rigid rod-like polymer. The extraordinary stability to heat, acid and alkali, greater viscosity and plasticity, good solubility in hot or cold water along with biological properties (*e.g.*, nontoxicity, biocompatibility, biodegradability, etc.) and its ability to modify/improve the rheological properties of the systems in which is introduced, increase the versatility of xanthan for applications in food and non-food industry [1].

Knowing that the rheological properties are influenced of both the environmental conditions (solvent quality, temperature, ionic strength, shear and pH [2]) and polymer characteristics in solution (for example, molecular weight or chain conformation), the present study aims to evaluate the viscoelastic properties of the XG aqueous solutions with different concentrations at 37 °C.

EXPERIMENTAL

Xanthan gum (XG) was purchased from Sigma-Aldrich (Germany) and used without further purification. XG sample is characterized by a viscometric molar mass of 1.165×10^6 g/mol [3] and acetate/pyruvate ratio of 6/5 [4]. Solutions of various XG concentrations ($c_{XG} = 0.02, 0.05, 0.2, 0.4$ and 1 wt%) were prepared in Milli-Q PF water (Millipore, Switzerland) at room temperature under gentle stirring. Rheological investigations were performed at 37°C by using a stress controlled CVO Rheometer with parallel plate geometry (60 mm diameter and 500 μ m gap) and thermal control by Peltier effect.



The measurements in the oscillatory flow regime were carried out in the frequency (ω) range of 10^{-1} - 10^2 rad/s. The flow curves were determined under stationary continuous shear conditions, by increasing the shear rate from 10^{-3} 1/s to 10^3 1/s.

RESULTS AND DISCUSSION

Prior to study the dynamic behavior of the xanthan solutions, the linearity tests were performed at 1 rad/s. The shear stress dependence of G' and G'' moduli obtained in the amplitude sweep tests shows that the strain of 1 % is suitable for all concentrations in frequency sweep tests. In oscillatory deformation tests, the complex modulus (G^*) can be analyzed by means of its real and imaginary components as follows:

$$G^*(t) = G'(t) + iG''(t) \quad (1)$$

where: G' is the elastic or storage modulus and represents a measure of the reversibly stored deformation energy, while G'' is the viscous or loss modulus and represents a measure of the irreversibly dissipated energy during one cycle.

Figure 1 presents the evolution of the viscoelastic moduli obtained for XG solutions with $c_{XG} = 0.02, 0.4$ and 1 % in frequency sweep tests at 37 °C.

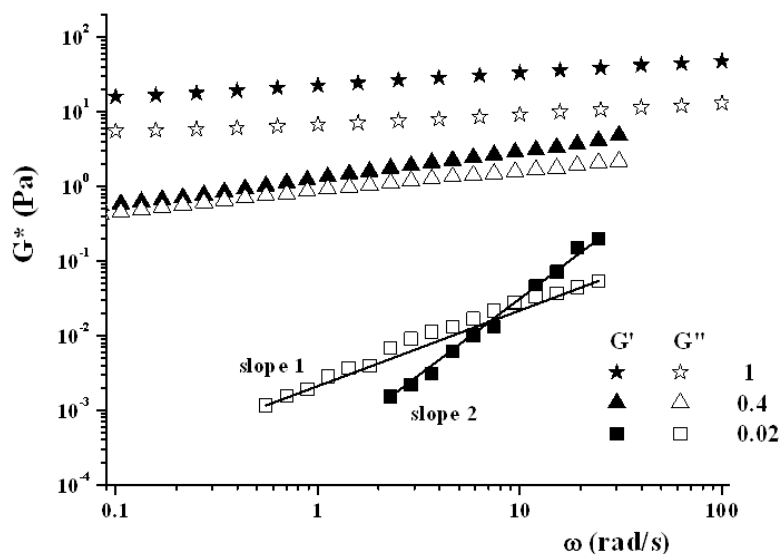


Figure 1. Evolution of viscoelastic moduli as a function of oscillation frequency for xanthan solutions with various concentrations (wt. %).

The XG solution with $c_{XG} = 0.02$ % exhibits a behavior of Maxwellian fluids with $G' \sim \omega^2$ and $G'' \sim \omega^1$. The same behavior showed also solutions with $c_{XG} = 0.05$ and 0.2 %. As the polymer concentration increase (*i.e.*, $c_{XG} = 0.4$ and 1%), the intermolecular interactions (*e.g.*, H-bonding, cation-mediated interactions or hydrophobic interactions induced by pyruvate-substitutes side chains [5]) determine the macromolecular chains to self-associate.



As a result, the values of elastic (G') and viscous (G'') moduli increased and G' become higher than G'' over the investigated frequency range indicating an elasticity degree higher than of the solutions with $c_{XG} \leq 0.2$ %. In addition, the scaling exponent of both moduli showed close values as predicted for the gel state: $G'(\omega) \sim G''(\omega) \sim \omega^n$ (i.e., $n \sim 0.3$ and 0.1 for $c_{XG} = 0.4$ and 1%). The loss tangent ($\tan\delta = G''/G'$) is another viscoelastic parameter of which magnitude indicates the response of a material during the cyclic stress in the oscillatory test.

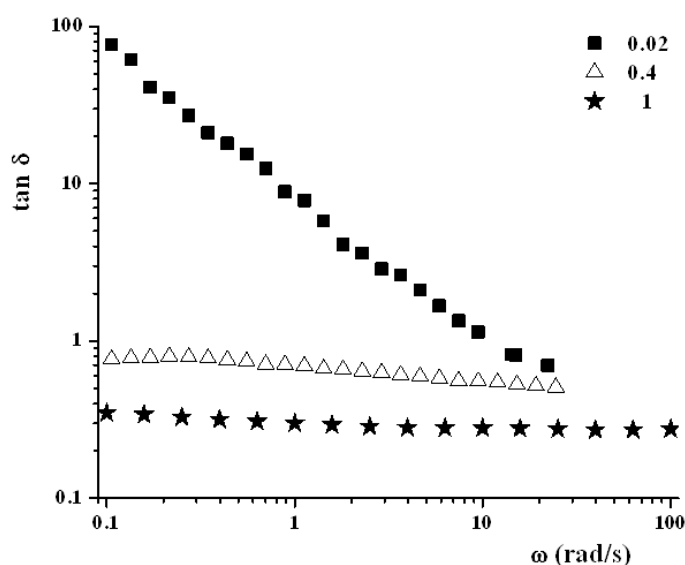


Figure 2. Loss tangent as a function of oscillation frequency for all studied xanthan solutions at 37°C.

The values of $\tan\delta$ in the studied oscillation frequency range revealed for xanthan solutions with $c_{XG} \leq 0.2$ % a behavior liquid-like materials; $\tan\delta > 1$ because both solvent and polymer contribute to G'' and only the polymer contributes to G' value. Favourable interactions among chains reduce free volume, the system behavior becomes more elastic and the magnitude of loss tangent decreases and becomes smaller than 1. The latter defines the solid-like materials, as the XG solutions with $c_{XG} = 1$ % (Figure 2). For $c_{XG} = 0.4$ %, constant and close with unity values were obtained for $\tan\delta$. The behavior was assigned to *critical gel structure*, which represents a state of matter between viscous-liquid and solid-like [6].

For more information about the effect of concentration on viscoelastic properties of xanthan solutions, the viscosity profile in oscillatory frequency domain (the complex viscosity, η^*) was compared with that obtained in continuous shear regime (shear viscosity, $\eta(\dot{\gamma})$) (Figure 3).

For fluids without a “structure” that can be disrupted by large strain, the two curves are approximately identical demonstrating the validity of the Cox-Merz rule, as follows:



$$\eta(\dot{\gamma}) = |\eta^*(\omega)| \quad (2)$$

where: $\dot{\gamma}$ is the shear rate.

The Cox-Merz rule has important practical applications as it is easier to acquire data over a wide range of oscillation frequencies; for example, biomedical studies involving high velocities and deformities, as the case of the swallowing process required the application of this rule.

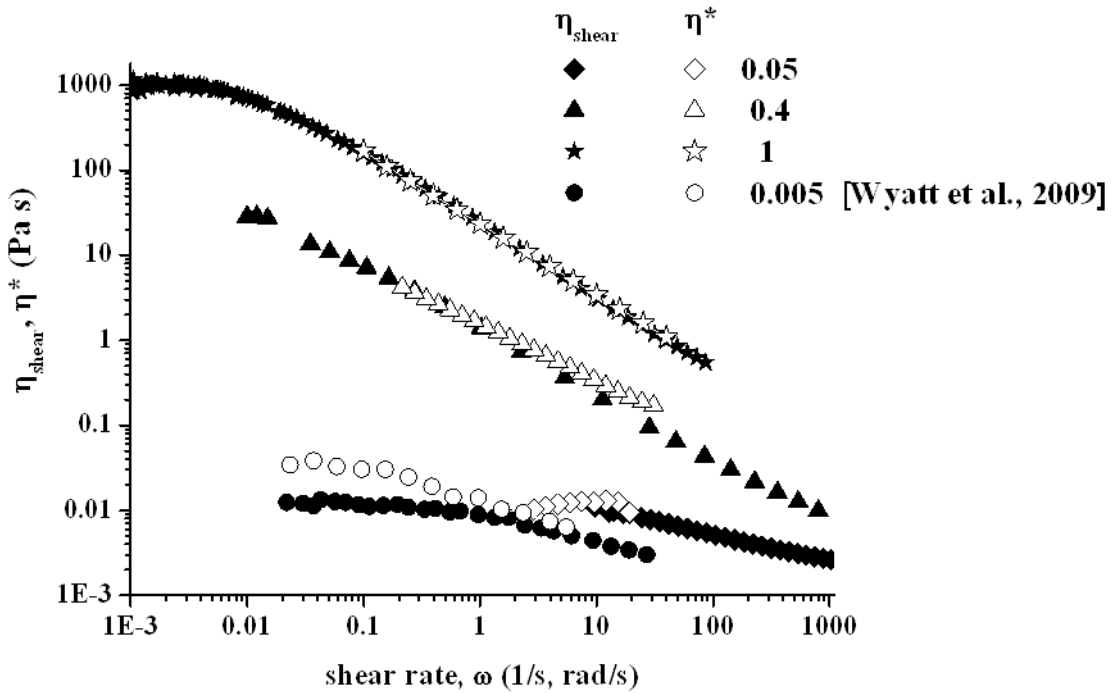


Figure 3. Comparison between the complex and stationary share viscosity profile for xanthan solutions with various concentrations (wt. %) at 37 °C and for 0.005% at 25 °C [7].

The validity of the Cox-Merz rule for the investigated XG solutions is in accordance with Wyatt et al. [7]. They found that for highly dilute xanthan solution (for example, the data for $c_{XG} = 0.005$ % included in Figure 3) the applicability of this rule was not possible. In previous studies, Lee et al. [8, 9] has shown for XG solutions that the absence of any crossover in plots of G' and G'' against ω and adherence to the Cox-Merz rule throughout the accessible range of ω imply that long-lived entanglements with relaxation times ≥ 0.01 s are absent in these rather concentrated systems of rigid rods.

Also, it can be noted that the dependence of $\eta(\dot{\gamma})$ as a function of shear rate presents a non-Newtonian domain for all xanthan solutions, regardless of concentration. As the polymer concentration increases, the Newtonian behavior occurred at lower shear rates.



CONCLUSIONS

The viscoelastic properties of xanthan aqueous solutions were investigated as a function of concentration at 37 °C. The systems with $c_{XG} \leq 0.2$ % showed liquid-like properties with $\tan \delta > 1$. The increase of elastic modulus over loss modulus led to decrease of $\tan \delta$ below unity.

All xanthan solutions present a Non-Newtonian domain regardless of concentration, while the Newtonian plateau emerged from lower shear rates as polymer concentration increased.

ACKNOWLEDGEMENTS. This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS-UEFISCDI, and project number PN-III-P2-2.1-PED-2019-2484, contract 494 PED/2020.

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PARTNERSHIPS FOR KNOWLEDGE TRANSFER IN THE FIELD OF POLYMER MATERIALS USED IN BIOMEDICAL ENGINEERING - POINGBIO

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"Petru Poni" Institute of Macromolecular Chemistry Iasi is implementing the project "Partnerships for knowledge transfer in the field of polymer materials used in biomedical engineering", Contract no.86/08.09.2016, ID P_40_443, SMIS 105689. The project is cofinanced by the European Regional Development (ERDF) Fund by the Competitiveness Operational Programme (OCP) 2014-2020, Axis 1 Research, Technological Development and Innovation (RDI) in support of economic competitiveness and business development, Action 1.2.3 Knowledge Transfer Partnerships. The project duration is 72 months.

The project aims to enhance the economic competitiveness of small and medium enterprises, which are partners in the project during 2016-2020, following the transfer of knowledge aimed at scientific and technological expertise in the design and development of multifunctional polymer systems that can stimulate a specific biological response and allow adherence and proliferation of a particular type of cell, depending on the tissue to be treated.

The eligible activities of the project are:

- the access of the companies to the facilities, installations, equipment of the research organizations in order to realize the analysis, tests, experiments, characteristics, quality labeling and the certification and to develop new products / technologies/ methods improved through:
- the transfer of the activities skills/competencies for research-development and for innovation support from research organization to industrial partner;
- industrial research activities and / or experimental development executed for and on behalf of the organization;



- the detachment of highly qualified personal who perform the research activities, development and innovation, from research organization to enterprises, in a newly function created within the enterprise, without replacing other personnel;
- the market research realized by the research organization for companies;

Knowledge transfer Contracts with SMEs:

- 2 contracts type B. Access of SMEs to facilities, installations, equipment;
- 1 contract type C. Activities of skills transfer/ competencies and innovation support RD;
- 8 contracts type D. Research and Development in effective collaboration with:

- S.C. Centrul Medical Domenico S.R.L. Iasi 
- S.C. Sanimed International Impex S.R.L. Bucharest 
- S.C. Polymer Adhesive Tapes S.R.L. Bucharest
- S.C. Intelectro Iasi S.R.L. 
- S.C. All Green S.R.L. Iasi 
- S.C. Apel Laser S.R.L Bucharest. 
- S.C. Innovative Green Power S.R.L Iasi. 

POINGBIO project contributes significantly to the objectives undertaken by Romania in 2014-2020 POC program, facilitating the use of eco- nano- technology economy by transfer of scientific knowledge and technical means to top fields in biomedical science, so that interested economic partners with the POINGBIO team can conceive or improve technologies for high performance, non-polluting, long-lived, with scientific and economic importance for the production of advanced materials.

Other expected results: 40 papers published in collaboration with SMEs; 4 patents in collaboration with SMEs; 1 new research position in the project.



Article
Eco-Friendly Method for Tailoring Biocompatible and Antimicrobial Surfaces of Poly-L-Lactic Acid

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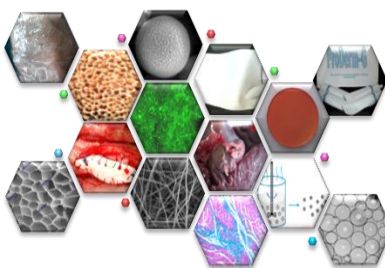
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The scientific subjects of the contracts are:

- Polymeric materials for transepidermal therapy
- Bioactive multilayer hemostatic polymer membranes
- Collagen-based micro- and nano-fibrillar structures with biomaterial characteristics for biomedical applications
- Protocols and framework technologies for obtaining innovative biomaterials based on (bio) macromolecular compounds
- Printable nano-sensors on biocompatible flexible support for medical applications
- Polymeric materials containing phytotherapeutic extract for biomedical applications
- The microwave devices utilization for the improvement of polymeric materials with applications in biomedical engineering
- Polymeric materials obtained by conventional and unconventional methods for biomedical applications
- Flexible biocompatible nano-conductive composite materials, with pre-defined multilayer architecture for increasing the quality, sensitivity and selectivity of images obtained by magnetic resonance.

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POLYSACCHARIDE-BASED ELECTROSPUN NANOFIBERS. PREPARATION AND CHARACTERIZATION

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ABSTRACT

Nanofibers composed of phosphorylated curdlan (PCurd) and poly(vinyl alcohol) (PVA) were prepared using an electrospinning method from aqueous solutions. The optimal composition of the polymers mixture for the electrospinning process was established by viscometric and rheological studies. The electron microscopy confirmed the obtaining of well-defined and drop-free nanofibers with a diameter of 157 nm. The PCurd/PVA electrospun membrane has shown a tensile strength of 1.97 MPa and a Young modulus of 0.861 MPa. These results encourage us to continue studies regarding the use of this new membrane as a wound protection dressing.

INTRODUCTION

Electrospinning technology can be considered as a simple and low cost procedure for generating ultra-fine fibers with some unique properties, including high surface-to-volume ratio, great mechanical properties, high porosity and homogeneous morphology compatible with natural extra cellular matrix. Electrospun nanofiber membranes from natural or synthetic polymers have many biomedical applications including wound dressing materials [1].

Natural biopolymers such as polysaccharides and their derivatives have attracted and given more attention for wound dressing preparation due to biodegradability, biocompatibility, haemostatic and non-toxicity. Phosphorylated curdlan (PCurd), an anionic derivative of curdlan with a linear structure composed of D-glucose units linked by β -(1 \rightarrow 3) glucosidic bonds and monobasic phosphate groups was found to be non-toxic and biocompatible [2]. On the other hand, biomaterials made from natural polymers have a limited applicability due to their poor mechanical properties. Therefore, in order to improve these properties, natural biopolymers are often blended with other synthetic materials or polymers.

Poly(vinyl alcohol) (PVA) is synthetic polymer mostly used for electrospun nanofibrous wound dressings obtaining by electrospinning technique. Even if it can be electrospun alone and used as wound dressings, this material has a major disadvantage such as an inappropriate hydrophilicity.



This inconvenience can be avoided by blending PVA with polysaccharides or other hydrophilic polymers.

The processability of the polymeric solution and the morphology of the obtained fibers are correlated with the rheology of the polymeric solution [3]. When composite nanofibers are envisaged, the miscibility between the components, which can be studied by viscometry and rheology, is also very important.

In this study, electrospinning technique was used to obtain a nanofibre membrane from aqueous solution of PCurd and PVA. Studies regarding the viscosity and rheological behaviour of the precursors and of their mixture in solution were performed in order to obtain information about the optimal mixture. The morphology of the fibers was investigated by scanning electron microscopy (SEM) and the mechanical properties of electrospun membranes were studied by tensile tests.

EXPERIMENTAL

The PCurd solution with 6 % concentrations (w/v) was obtained by dissolving monobasic phosphate curdlan at room temperature under magnetic stirring. The 10 % (w/v) PVA solution was prepared by dissolving PVA in distilled water at 90 °C with stirring. The PCurd and PVA solutions were mixed in 50:50 and 25:75 volumetric ratios and the viscometric and rheological behaviour were studied in order to optimize the electrospinning process. Viscometric measurements were performed with an Ubbelohde capillary viscometer for dilution series (type 0a, K constant of 0.005) at 25 ± 0.1 °C using an AVS 350 Schott automatic viscosity measuring system (Schott, Germany). The shear flow curves of PCurd and PVA based solutions were obtained at 25 °C by using the MCR 302 Anton Paar rheometer equipped with plate-plate geometry and Peltier device for temperature control.

The polymer solutions were electrospun using a Fluidnatek® LE-50 laboratory line from Bioinicia S.L. (Valencia, Spain) using a voltage of 22.7 kV. The distance between the tip of the needle and the collector was adjusted to 14 cm, and the flow rate of the solution was set at 10 μ L/min. The fibers were collected on a backer foil sheet attached to a copper grid used as collector.

The tensile tests of rectangular samples (10 mm length, 6 mm width and 0.06 mm thick) were performed using a Texture Analyser (Brookfield Texture PRO CT3®, USA) with a trigger load of 0.067 N and a tensile rate of 0.1 mm/s.



RESULTS AND DISCUSSION

Viscometry is one of the most popular techniques used to study the compatibility of polymer-polymer in solution. The Huggins plots for precursor solutions (PCurd and PVA) and PCurd/PVA mixtures with various weight ratios, in pure water and 25 °C are presented in Fig. 1a. Typical polyelectrolyte behaviour was observed when the reduced viscosity increases exponentially with decreasing polymer concentrations, due to the uncoiling of the charged chains in the dilute medium [4]. In order to obtain the intrinsic viscosity, the non-linear Wolf equation was used [5, 6]. This equation can be applied to both polyelectrolytes and binary mixtures of polyelectrolyte/neutral polymer in aqueous solution in the absence of salts [7, 8]. According to Wolf approach, the intrinsic viscosity ($[\eta]$) values of 26, 9.8, and 5.22 dL/g were determined for PCurd, PCurd/PVA (25:75, v/v), and PCurd/PVA (50:50, v/v) mixtures, respectively.

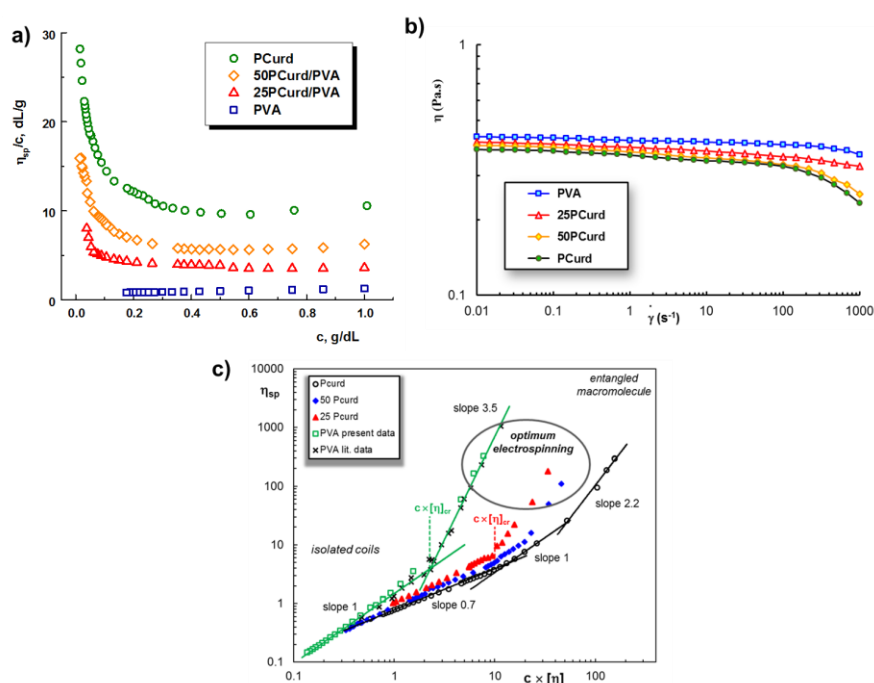


Figure 1. Dependence of reduced viscosity as function of polymer concentration (a); Shear viscosity of 10 % PVA solution, 6 % Pcurd solution and their mixture as a function of shear rate at 25 °C (b); Specific viscosity as a function of $c[\eta]$ at 25 °C (c).

The shear flow curves of the investigated systems at 25 °C are presented in Fig. 1b. The Newtonian behavior is observed at low shear rates and the viscosity values for PVA and PCurd are closed, facilitating the homogenization and stability of the PVA/PCurd mixtures. The viscosity starts to decrease at high shear rates ($\dot{\gamma} > 100$) and non-Newtonian behaviour appears for the solutions containing PCurd at lower shear rates compared to PVA, suggesting higher relaxation times for polysaccharide solutions.



The viscosity data allow the delimitation between entangled and non-entangled states of polymers in solution. Fig. 1c shows the dependence of the specific viscosity for polymers in aqueous solutions at 25 °C, as a function of the dimensionless parameter $c[\eta]$. Based on the dependences shown in Fig. 1c, the sample 25:75 volume ratio (25PCurd/PVA) was selected for preparing the composite fibres, because the polymers of this composition are in entangled state at $c[\eta] > 10$. This sample preserves the high stability of PVA in continuous shear conditions.

SEM images of PVA and 25PCurd/PVA electrospun membranes (Fig. 2) showed well-defined nanofibers without droplets and with an average diameter which decrease from 238 nm for PVA membrane (Fig. 2a) to 157 nm for PCurd/PVA (Fig. 2b).

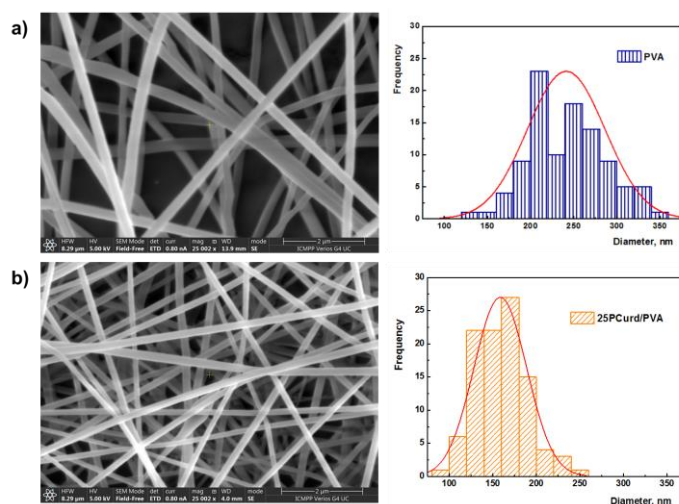


Figure 2. Scanning electron micrographs of the PVA and 25PCurd/PVA electrospun nanofibers and their size distribution.

The investigation of the mechanical properties is a key-test for electrospun membranes. The mechanical behaviour of the developed nanofibers membranes are shown in Fig. 3. The stress-strain curves of membranes present three distinguished zones: the first zone starts with the fibres straightening and reorienting towards the direction of the applied load without fibre breakage, followed by fibres breakage and slippage till the membrane reaches the maximum stress, and finally, the residual area when the fibres slip till the final failure of the whole sample.

The presence of PCurd in the polymer mixture induced a decrease in the second area, probably due to a decrease in fibre diameter and to a reduction in the contact area between the fibres that lead to a decrease of the frictional force. Most likely this is why the elongation at break of 25PCurd/PVA is smaller (7.6 %) compared with PVA membrane (16.1 %). However, the first zone where the fibres stretched and reoriented is larger for 25PCurd/PVA, showing that PCurd increased



the elasticity and the tensile strength of the fibres. As a result, the tensile strength of the membrane increased from 1.63 MPa to 1.97 MPa by the introduction of the PCurd in the electrospun mixture.

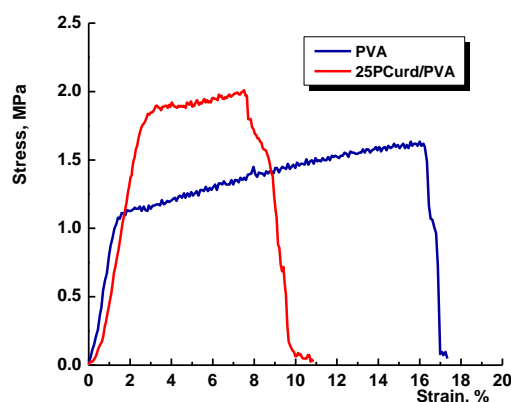


Figure 3. Stress–strain curve for PVA and 25PCurd/PVA nanofiber membranes.

The Young moduli of the two membranes are relatively closed: 0.924 MPa for PVA and 0.861 MPa for 25PCurd/PVA.

CONCLUSIONS

New nanofiber membranes based on monobasic phosphate curdlan and PVA were obtained by the electrospinning process from aqueous solution. The optimal composition of PCurd/PVA mixture of 25:75 (volumetric ratio) was established by rheological studies. SEM analysis showed an average nanofiber diameter of 157 nm. The mechanical tests confirmed the obtaining of a flexible and soft membrane.

ACKNOWLEDGEMENTS. This work was financially supported by a grant of Ministry of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P4-ID-PCCF-2016-0050-P3, within PNCDI III and project “Partnerships for knowledge transfer in the field of polymer materials used in biomedical engineering” ID P_40_443, Contract no. 86/8.09.2016, SMIS 105689, co-financed by the European Regional Development Fund by the Competitiveness Operational Program 2014–2020, Axis 1 Research, Technological Development and Innovation in support of economic competitiveness and business development, Action 1.2.3 Knowledge Transfer Partnerships.

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VISCOSITY OF BOVINE SERUM ALBUMIN SOLUTIONS IN PRESENCE OF NEUTRAL POLYMERS

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Dedicated to the memory of Dr. Silvia IOAN (1943-2021)

ABSTRACT

The viscosity of bovine serum albumin (BSA) was investigated in presence of two neutral polymers, poly(vinyl alcohol) (PVA) and pullulan (PULL), in physiological serum, over a large range of concentrations at 37 °C and pH = 7.4 (above the isoelectric point of BSA). The experimental data suggest that BSA/PULL complexes are formed in excess of Na⁺ ions due to attractive interactions triggered by the cation presence. Membrane osmometry was used to determine the apparent molecular weight of PULL/BSA complexes and the interactions between the macromolecules and the solvent. These structures are stable in time and in conditions of high shear forces. PVA/BSA mixtures presented an ideal behavior in dilute solutions and time dependent viscosity in shear conditions. The macromolecular crowding influences the overall behavior and it can be evidenced from the viscosity dependence on reduced concentration.

INTRODUCTION

The serum albumins are the essential components of the blood that is a complex fluid from rheological point of view. The rheology of globular proteins was investigated in detail and the viscosity increase at high concentrations was attributed to the formation of a viscoelastic film at the liquid–air interface [1]. Bovine serum albumin (BSA) is used as a model protein in many biomedical applications [2]. The use of high purity protein samples is important in studying rheology and surface properties of protein solutions [1,3,4]. The rheological errors can be avoided by using standard glass capillary or by addition of very small amount of surfactant; at higher shear rates, the air/water interface gives a small resistance to the fluid flow (as for example during syringe injections of BSA based biomaterials). In BSA based formulations, the film formed at the air/water interface can alter the flow properties [4].

The viscosity of protein/polymer systems is important for the pharmaceutical and biomedical applications that use frequently solutions of different concentrations. High viscosity and poor flow properties observed for increasing concentration of macromolecules in solution can be due to aggregation process that influences the stability of systems with negative consequences on the biomaterial performances. The presence of neutral polymers or a small amount of surfactants in protein solutions can avoid the occurrence of this phenomenon.



In the present paper we continued the previous investigations on the viscosity of BSA solutions in presence of two neutral water soluble polymers: a synthetic polymer - poly(vinyl alcohol) (PVA) [5,6], and a polysaccharide - pullulan (PULL) [6,7], exploring the domain of concentrated solutions.

EXPERIMENTAL

Bovine serum albumin with the molecular weight (M) of 66,104 kg/mol was purchased from Sigma Aldrich (Taufkirchen, Germany). The pullulan (PULL) sample with M = 300 kg/mol was purchased from TCI Europe N.V. and dialyzed at room temperature for 24 h against deionized water. Physiological saline solution of pharmaceutical use (sterile solution of 0.9 g NaCl in 100 ml pure water, i.e., 0.15 M NaCl) was used as solvent.

For polymer/protein solutions, the viscosity was measured by using a MCR 302 Anton Paar rheometer with different geometries.

RESULTS AND DISCUSSION

For dilute solutions, the hydrodynamic specific volume at infinite dilution (known as intrinsic viscosity, $[\eta]$) was determined by using different models applied to viscometric data. Other parameters correlated with polymer/solvent interactions were analyzed and the miscibility between BSA and neutral polymers was discussed in correlation with the phase behavior observations [5-7].

PVA/BSA mixtures showed an ideal behavior and, at low concentrations, the hydrodynamic volume obeys the additive rule as a function of macromolecules concentration [5]. By increasing the concentration, the intermolecular PVA/protein interactions in solution become unfavorable. Above a certain concentration, a demixing occurs in the PVA/BSA solutions, being accompanied by a sharp decrease of viscosity. In the case of PULL/BSA solutions, intermolecular complexes are formed in NaCl solutions [7].

An inconsistency between the viscosity in dilute and concentrated BSA solutions was observed [3]. The flow behavior of BSA in dilute solutions is governed by the electroviscous effect and the viscosity is influenced by net charges that depend on pH value [8,9], the effect of attractive interactions are negligible. The viscosity is minimal at isoelectric point (pH ~ 4.95), where the molecular charge is zero, and it increases for pH = 7.4 (as in the present study). The shear behavior of 5 g/dL BSA solutions in presence of PVA and PULL is Newtonian and the viscosity of polymer/protein mixtures deviates from the additive rule (Figure 1).

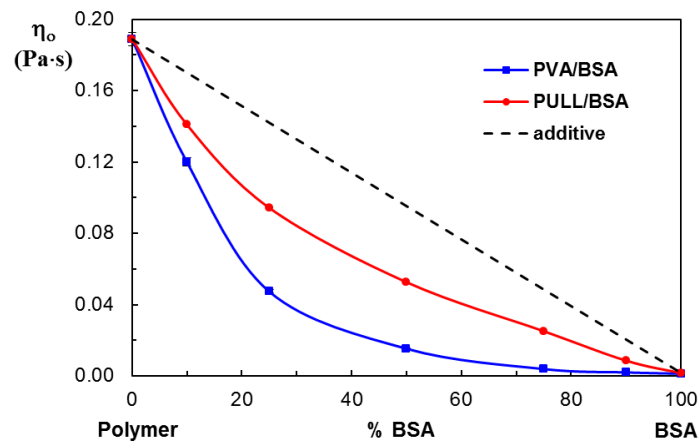


Figure 1. The viscosity dependence on polymer/BSA composition in physiological serum at 37°C and pH = 7.4 (the total concentration of macromolecules is 5 g/dL).

When the protein concentration increases, a macromolecular crowding occurs due to the excluded volume effect [6] and the protein functionality is affected. For polymer/BSA solutions, we evidenced the macromolecular crowding by analyzing the plots of the specific viscosity as a function of a dimensionless parameter, $c \times [\eta]$, defined as reduced concentration [10]. For solutions of isolated macromolecules, the slope of this dependence is close to 1 and its value increases above 3, when the macromolecular crowding occurs (Figure 2).

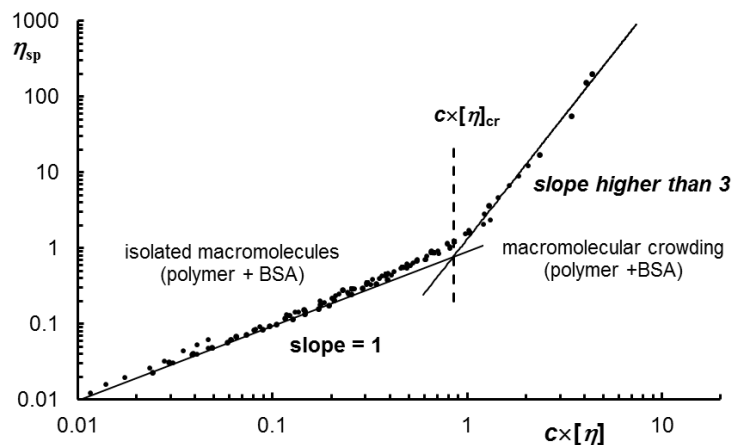


Figure 2. The evidence of macromolecular crowding by using the viscosity data obtained by capillary viscometry and rheological measurements [5-7].

During the continuous shear, it was shown that the size of BSA aggregates increase and the shear forces favors the formation of a high proportion β -sheet structure [11].



For PULL/BSA mixtures, we determined the number average molecular weight, M_n , with an absolute method, *i.e.*, membrane osmometry, by using the following virial equation:

$$\frac{\pi}{c} = RT \left(\frac{1}{M_n} + A_2 c + A_3 c^2 + \dots \right) \quad (1)$$

where π/c is the reduced osmotic pressure; R - the gas constant, $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$; T - the absolute temperature; A_2 , A_3 - the second and the third virial coefficients, respectively, taking into account the deviations from the ideal behavior of solutions.

Due to aggregates formation for all PULL/BSA mixtures, the apparent molecular weight values are higher than the additive rule (Figure 3). This was attributed to BSA/PULL complexes formed in excess of Na^+ ions due to the attractive interactions triggered by the cation presence. Furthermore, the virial coefficients A_2 and A_3 showed also higher values than expected from additive rule for the polymer/protein mixtures [7].

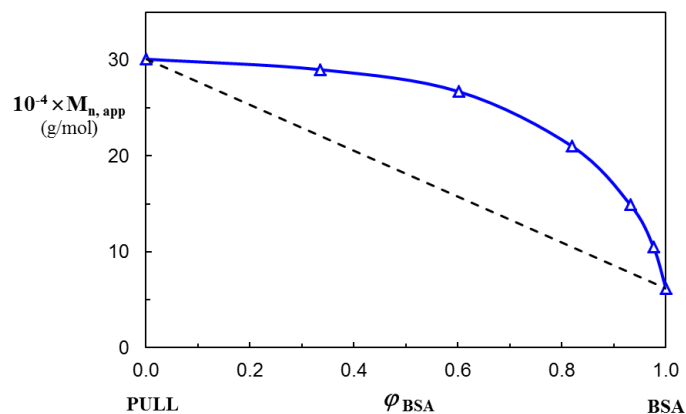


Figure 3. The apparent molecular weight of the PULL/BSA mixtures (pH = 7.4).

The attractive interactions between the BSA macromolecules increase the self-assembling probability and a transient network is formed, determining an increase of the resistance to flow (a higher viscosity value than expected). BSA solutions have shown time dependent viscosity profiles by rotational rheometry, even at low shear rates. The aggregates removal did not significantly change the rheology of BSA solutions [12]. The shear history or the presence of other macromolecules can control the BSA aggregates size.

We tested concentrated polymer/BSA solutions, when the competition between different intermolecular interactions determines an increase of solution viscosity. Viscosity profiles as a function of time in conditions of steady shear for different BSA concentrations showed time-dependent profiles.



The addition of neutral polymers determines the non-Newtonian flow as the shear rate increases. However, an increase of the viscosity in time was observed for PVA/BSA solutions submitted to successive cycles of low and high shear rates (Figure 4). At the end of experiment, the elastic modulus (G') becomes higher than the viscous modulus (G''), due to the formation of network-like structure. The high shear forces improve the PVA/protein miscibility in solution.

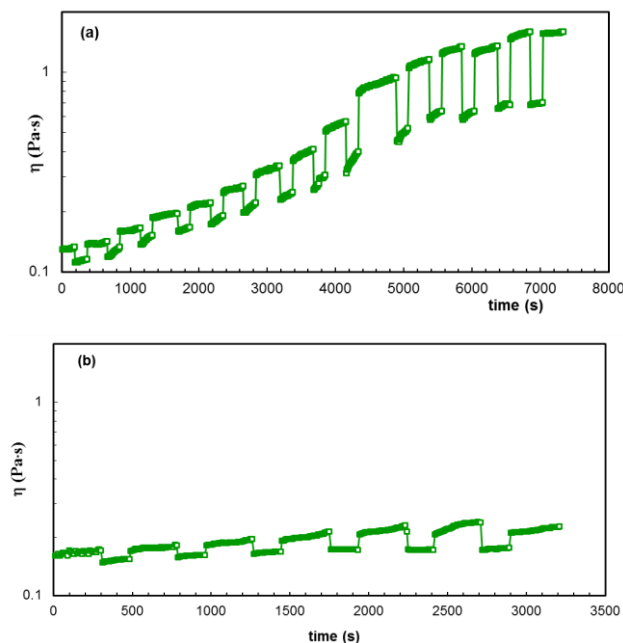


Figure 4. Time dependent viscosity for (a) PVA/BSA, (b) PULL/BSA, submitted to successive cycles of low (1 s^{-1}) and high ($1,000 \text{ s}^{-1}$) shear rates.

The investigations are now in progress and we try to understand the rheological properties in correlation with thermodynamic interactions and phase behavior of polymer/protein solutions. These systems are further used to design biomaterials for medical or pharmaceutical applications.

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