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The BRANCUSI Program is a French-Roumanian program for integrated actions in the field of scientific and technological cooperation managed by Egide (France) and Romanian Ministry of Education and Research

A Brancusi Project:

Autoassembled thin layers from polyelectrolytes based on maleic anhydride copolymers for managing the metal-polymer interfaces in organic diodes for polymeric stable and performant photovoltaic solar cells

Partners:

French Partner:
University of Angers
Department of Optical Properties of Materials and Their Applications

Romanian Partner:
"Petru Poni" Institute of Macromolecular Chemistry, Bioactive and Biocompatible Polymers Department

Teams:

French Team:
Prof Jean Michel NUNZI.
Director of project
S. Dabos-Seignon
B. Sahraoui

Romanian Team:
Dr. Gabrielle Charlotte CHITANU,
Director of project
G. Aldea
Prof. B. C. Simionescu

Scientific Objectifs/Activities:

· Synthesis of maleic anhydride copolymers with hydrophobic or hydrophilic comonomers suitable for intended applications
· Characterization of copolymers by electrochemical titration, NMR and FTIR spectra, viscometry, size exclusion chromatography, MALDI-TOF
· Preparation of polyelectrolytes from maleic anhydride copolymers
· Study of interaction between maleic polyelectrolytes and commercial cationic polyelctrolytes
· Preparation, characterization and application in the photovoltaic cell fabrication of thin layers based on maleic polyelectrolytes

Romanian - French cooperation on polymer rheology

Partners:
· "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania (Dr. Maria Bercea, Prof. Bogdan C. Simionescu)
· "Gh. Asachi" Technical University, Department of Machine Design and Tribology, Iasi, Romania (Prof. Dumitru Olaru, Prof. Ioan Bercea, Dr. Viorel Paleu)
· Ecole Nationale Supérieure des Mines de Paris, Centre de Mise en Forme des Matériaux Sophia Antipolis, France (Dr. Patrick Navard)
· Institut Européen de Tribologie, INSA Lyon, France (Dr. Daniel Nélias)

Projects:
· Rheological Constitutive Equation for Polymers in Processing Conditions: Synthesis and Characterization of Very High Molecular Weight PMMA - European Commission - Human Capital and Mobility Program (PECO ERB-CIPDCT940605).
· Surfaces, interfaces et conception de nouveaux matériaux, project ACI 2000 (Action Concertée Incitative): Influence de la composition en additifs d'un lubrifiant sur le coefficient de frottement local, en régime de lubrification limite, et effet sur la durabilité des surfaces métalliques en contact - supported by Ministère de la Recherche (France)

The research focused on understanding and predicting the flow behaviour of rheologically complex materials, i.e., polymer solutions and suspensions. The shear flows are present in nearly all practical applications and the formulation of polymeric materials should be realized in a manner that ensures an optimal processing behaviour.The rheological investigations concentrated on:

· Very high molecular weight polymer solutions

Semidilute solutions of very high molecular weight polymers (M/Me > 100) provide good model materials for evaluating new concepts on polymer dynamics in shear flow and for quantitatively supporting the existing constitutive theories. Measurements of the viscosity and first normal stress difference (N1) of these systems revealed an unusual behaviour, with steady-state shear stress (sxy) and N1 displaying a plateau at shear rates in the range < < , i.e., intermediate between the reciprocal tube disengagement time and reciprocal longest Rouse relaxation time (Figure 1). A thorough study of the transients (step-up, step-down, start-up and relaxation) shows that several flow regimes can be distinguished depending on the flow rate, which is not fully in agreement with the Doi-Edwards theory. Some of the results can be interpreted in the light of the modified Doi-Edwards theory (Cates, McLeish and Marrucci) that predicts that long polymer chains experience different shear rates during flow. The theory - experiment comparison points to the need for more accurate equations for polymer contour length dynamics in flow.

· Cellulose suspensions

The rheology of rigid rod cellulose suspensions has been investigated. They can be easily oriented and the flow properties in the disordered or ordered states can be compared. The isotropic-at-rest suspension flow curves show two plateaus, one at low and another at high shear rates, that reflect the flow of isotropic (at low shear rates) or oriented (at high shear rates) suspensions. From the low shear rate viscosity plateau vs concentration a maximum packing concentration of rigid rods was estimated, this corresponding to the experimentally measured isotropic-to-anisotropic transition. The viscosity vs concentration curve has a maximum that vanishes at high shear rates as for liquid crystalline polymer solutions. Rheological and rheo-optical observations show fast inception and relaxation of both the rheological functions and the texture, in total contrast with liquid crystalline polymer solutions.

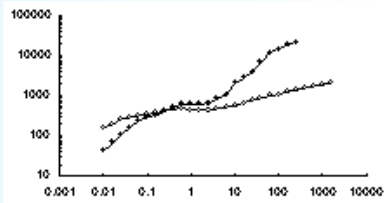

Figure 1. Shear stress (sxy) and first normal stress difference (N1) vs shear rate ( ) for very high molecular weight poly(methyl methacrylate) in toluene

· Polymer chains submitted to large deformations

In many tribological systems, base oils are not able to separate totally the contact surfaces. In these cases, important performances can be obtained by introducing macromolecular additives. As oil-in-oil emulsions or polymer-in-oil dispersions, they have demonstrated a high efficiency as viscosity index improvers in order to minimize the variation of the viscosity with temperature or to increase the lubricant film thickness.

By adsorption of polymer chains on solid surfaces, very viscous layers can be formed. These adsorbed boundary films are able to prevent the scuffing, to reduce the wear, to modify the friction or to withstand very high contact pressures. In these severe conditions of exploitation, it is difficult to evaluate the effective lubricant rheological parameters. Therefore, semi-empirical approaches are being developed to determine the elastic shear modulus, the viscosity of the lubricant and the limiting and Eyring stresses in different pressure and temperature conditions.

Representative papers published in cooperation:

· M. Bercea, C. Peiti, B.C. Simionescu, P. Navard, Shear Rheology of Semidilute Poly(Methyl Methacrylate) Solutions, Macromolecules, 26, 7095-7096 (1993)
· M. Bercea, I. Bercea, D. Nélias, D.N. Olaru, Tribological Behavior of Mineral Oils Additived with Polyethylene, Lubrication Science, 11 (3), 247-270 (1999)
· M. Bercea, I. Bercea, D. Nélias, D.N. Olaru, Polyethylene as Additive for Mineral Oils. Part I. Influence of the Polymer Concentration on the Film Forming Properties in Rolling Bearing, Trib. Trans., 42 (4), 851-859 (1999); Part II. EHD Traction Behavior, Trib. Trans., 45 (2), 145-152 (2002)
· M. Bercea, P. Navard, Shear Dynamics of Aqueous Suspensions of Cellulose Whiskers, Macromolecules, 33, 6011-6016 (2000)
· M. Bercea, L. Flamand, D. Nélias, V. Paleu, P. Vergne, I. Bercea, Comportement Rhéologique et Tribologique de Lubrifiants avec Additif Polymère, Matériaux & Technique, 3-4, 21-28 (2001)