

CPP 64: Flow-Induced Structures in Complex Fluids (with DRG, Deutsche Rheologische Gesellschaft, and DY)

Time: Thursday 9:30–12:00

Location: C 264

CPP 64.1 Thu 9:30 C 264

Rheology of PMMA solutions - the role of maximum stretch ratio in the nonlinear regime — ●SARA L. WINGSTRAND¹, QIAN HUAN¹, NICOLAS J. ALVARES², and OLE HASSAGER¹ — ¹Technical University of Denmark, Kgs Lyngby, Denmark — ²Drexel University, Philadelphia, USA

This work concerns linear and nonlinear rheology of poly(methyl methacrylate) (PMMA) solutions. Oligomeric methyl methacrylate is used as solvent. The concentration of polymer in solution has been adjusted, such that the maximum stretch ratio (λ_{max}) is equal to that of a polystyrene melt of 285 kg/mol (PS-285k). Accordingly, the molar mass of PMMA has been selected to obtain the same number of entanglements (Z) as the PS-285k. The solutions are characterized both in small amplitude oscillatory shear and in uniaxial extension, where the influence of λ_{max} and Z is investigated. It is found that the linear behavior of the PMMA solutions obey the tube model with a dilution exponent of 1. Consequently, as intended, the normalized dynamic moduli of the solutions overlap those of PS-285k. In the nonlinear regime the PMMA solutions exhibit a greater resemblance with PS-285k, than other polymers having same Z but significantly different values of λ_{max} . Nevertheless, the observed trend in extensional steady state viscosity vs. strain rate differs. Consequently we conclude that introducing λ_{max} in the tube model to enable application in the nonlinear regime, is not sufficient for obtaining a unifying model valid for polymer melts and solutions together.

CPP 64.2 Thu 9:45 C 264

Linear and Nonlinear Rheological Behavior of Carboxymethyl Hydroxypropyl Guar Gum — ●DANIEL SZOPINSKI¹, ULRICH A. HANDGE², WERNER-MICHAEL KULICKE¹, VOLKER ABETZ^{2,3}, and GERRIT A. LUINSTRAL¹ — ¹Institute of Technical and Macromolecular Chemistry, University of Hamburg, Hamburg, Germany — ²Institute of Polymer Research, Helmholtz-Zentrum Geesthacht, Geesthacht, Germany — ³Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany

Guar gum is a natural non-ionic polysaccharide from the endosperm of the guar bean (*Cyamopsis tetragonoloba*), which primarily grows in India and Pakistan. The water-thickening property is the main driver for its industrial application, which is resulting from the high molecular weight (1000-2000 kg/mol) and the formation of superstructures. Guar gum may be chemically modified with carboxymethyl (CM) and/or hydroxypropyl (HP) entities to enhance the thermal stability and solubility in water. A comprehensive rheological characterization of carboxymethyl hydroxypropyl guar gum (CMHPG) will be presented. Material functions were determined in experiments under steady state shear flow, small amplitude oscillatory shear flow (SAOS) and extensional flow (CaBER). The flow behavior at the application relevant nonlinear viscoelastic region was mapped in large amplitude oscillatory shear (LAOS) experiments. Structure-property relationships were established for dilute and more concentrated solutions as function of concentration and molecular weight. It is a basis for a description of the superstructures that guar gum and its derivatives form in water.

CPP 64.3 Thu 10:00 C 264

Relation between rheological and GPC triple detection characterization of photo-oxidated LDPE — ●VÍCTOR HUGO ROLÓN-GARRIDO, MATTHIAS KRUSE, and MANFRED H. WAGNER — Chair of Polymer Engineering/Polymer Physics Berlin Institute of Technology (TU Berlin), Fasanenstr. 90, D-10623, Berlin

Sheets of low-density polyethylene (LDPE) were subjected to photo-oxidation in the presence of air using a xenon lamp to irradiate the samples for times between 1 day and 6 weeks. The formation of long-chain branching up to 1 week of degradation and the competition between chain scission and crosslinking at longer periods of radiation were investigated by rheological characterization, Fourier transform infrared spectroscopy, and the solvent extraction method (Rolón-Garrido and Wagner. *Polym Degrad Stabil* 2014, 99:136, Rolón-Garrido and Wagner. *J Rheol* 2014, 58:199). The same samples are studied here by size exclusion chromatographic characterization using triple detection (concentration, light scattering and viscosity). The results are corre-

lated with the model parameters (beta and f_{2max}) of the MSF model. It is confirmed that the parameter beta correlates with the gel content, while f_{2max} is found to correlate with the experimentally determined contraction factors. By comparing the data of this study with those obtained earlier for polystyrene comb melts with well defined structure, the influence of the branching frequency on f_{2max} becomes evident.

CPP 64.4 Thu 10:15 C 264

Relaxation Mechanism and Molecular Structure Study of Polymer Blends by Rheological and SANS experiments — ●LUDOVICA HENGELLER¹, QIAN HUANG¹, NICOLAS J. ALVARES², ANDRIY DOROKHIN¹, JACOB KIRKENS GAARD³, KRISTOFFER ALMDAL¹, KELL MORTENSEN³, and OLE HASSAGER¹ — ¹Technical University of Denmark, Kgs. Lyngby, Denmark — ²Drexel University, Philadelphia, USA — ³Copenhagen University

Industrial polymers are largely polydisperse systems. One step towards understanding polydisperse polymers is the characterization of bi-disperse blends. Even though linear viscoelastic properties of bi-disperse polystyrene blends have been investigated thoroughly both theoretically and experimentally in recent years, both nonlinear shear and extensional flow properties are lacking. The purpose of the present study is to investigate the nature of interactions, namely polymer-polymer, in strong elongational flow using a bi-disperse polystyrene blend of 95 K and 545 K Mw with 50% weight ratio. We present both uniaxial extension and stress relaxation experiments to determine if orientation and extension of long PS chains induce orientation and extension in shorter chains. The extensional viscosity of systems investigated, provides only indirect evidence about the extent to which the molecules have been unraveled and stretched by the flow field. More directed information is obtained by neutron scattering on quenched liquid bridges of polystyrene. The results of such experiments will be discussed.

CPP 64.5 Thu 10:30 C 264

Flow-induced crystallisation of polylactides — ●DIETMAR AUHL, NILS LEONE, YOGESH DESHMUKH, and SANJAY RASTOGI — Maastricht University, Maastricht, The Netherlands

Polylactides (PLA) obey like many biopolymers a relatively poor crystallisation behaviour and are therefore difficult to process. In addition, PLA grades may vary in D,L-enantiomer distribution and form a stereocomplex, which significantly affects the crystallisation as well as final properties or product performance. Therefore, various routes are employed to control and improve the formation of crystal domains further to optimisation of processing conditions, e.g. chain modifications, addition of plasticisers or nucleating agents [1]. In this study, the crystallisation behaviour and morphology of such different PLA grades has been investigated in detail by rheo-microscopy with polarised light imaging as well as rheo-scattering for a broad range of thermo-mechanical histories and superposed to calorimetric data from thermal analysis. The comparison of experiments and molecular theory both highlight the flow-induced effects on polymer chains of initially equilibrated Gaussian conformation that enhance the crystallisation process, for which the total deformation and rate in relation to the time scales of molecular motions are decisive. [1] Saeidlou, S.; Huneault, M. A.; Li, H.; Park, C. B. *Prog. Polym. Sci.* (2012) 1657.

15 min. break

CPP 64.6 Thu 11:00 C 264

Rheological and SEC characterization of long-chain branched poly(ethylene terephthalate) — ●MATTHIAS KRUSE, VÍCTOR HUGO ROLÓN GARRIDO, and MANFRED H. WAGNER — Chair of Polymer Engineering/Polymer Physics, Berlin Institute of Technology (Berlin), Fasanenstrasse 90, D-10623 Berlin, Germany

Reactive processing is an effective and economic method to produce customized polymers fulfilling improved or additional properties. We report on reactive extrusion of poly(ethylene terephthalate) (PET) and demonstrate that linear PET can be converted into long-chain branched (LCB) PET via chain extension thereby broadening the range of possible applications. An anhydride and an epoxy based chain extender were employed, which react with the functional end groups

of linear PET. Different concentrations of the two tetrafunctional coupling reagents were used to achieve different degrees of branching and to compensate for the degradation of the polymer during extrusion. The formation of LCB was proven by dynamic plate-plate rheometry and leads to a more pronounced shear thinning behavior and an increase in the complex viscosity. The increase of molecular weight and polydispersity are also confirmed by size exclusion chromatography using triple detection (concentration, light scattering and viscosity). The elongational viscosity measurements conducted with a SER device show an unexpected influence of the chain extender on the type of sample rupture at larger extensions, and give clear evidence of different levels of strain hardening with respect to the chain extender content, as quantified by the molecular stress function (MSF) model.

CPP 64.7 Thu 11:15 C 264

Foaming of polystyrene-block-poly(4-vinyl pyridine) diblock copolymers: Thermal, rheological and processing properties — MARIA SCHULZE¹, •ULRICH ALEXANDER HANDGE¹, JELENA LILLEPÄRG¹, SOFIA RANGOU¹, and VOLKER ABETZ^{1,2} — ¹Institute of Polymer Research, Helmholtz-Zentrum Geesthacht, Max-Planck-Straße 1, 21502 Geesthacht, Germany — ²Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, 20146 Hamburg, Germany

Because of the high demand of polymer foams for application in the fields of lightweight construction, membrane technology, thermal and acoustic isolation the characterization of thermal and rheological properties of polymers for foam extrusion processes is of high relevance. In this study, we discuss the thermal and rheological properties of polystyrene-b-poly(4-vinyl pyridine) diblock copolymers and processing of these diblock copolymers via batch foaming. Carbon dioxide is used as blowing agent. High pressure differential calorimetry measurements reveal that the solution of carbon dioxide in these diblock copolymers leads to a decrease of the glass transition temperature of the polystyrene and the poly(4-vinyl pyridine) blocks. Furthermore rheological experiments in the oscillatory mode were carried out in order to elucidate the influence of composition and molecular weight on the flow properties. Stress-growth experiments reveal that the steady-state viscosity is characterized by a pronounced structure viscous behavior. Batch foaming experiments show that a larger molecular weight yields a lower foam density.

CPP 64.8 Thu 11:30 C 264

Combined rheology and structure analysis techniques — •JÖRG LÄUGER — Anton Paar Germany, Ostfildern, Germany

The simultaneous use of rheological and structural analysis techniques is helpful to gain a better understanding of the dependencies between the microstructure and the mechanical properties of complex fluids. Optical techniques like Small-Angle-Light-Scattering (SALS) or microscopy measurements have been used in combination with rheology. Other techniques are Small-Angle-X-ray (SAXS) and Neutron (SANS) Scattering. The decision on which technique to choose is based on the size and type of the structure as well as on the general sample properties to be investigated. Density and orientation fluctuations within a sample, averaged over the whole scattering volume, can be well monitored by SALS. The advantage that individual structure elements are seen in microscopy can be turned into a disadvantage when combined with a rheometer. At larger shear rates or deformations the specific structure element easily moves out of the field of view and can't be followed during an experiment. A way to overcome this issue is the use of a rheometer employing two motors operating in a counter rotation or counter oscillation fashion. The aim of this paper is to give an overview over the various techniques used for structural investigations simultaneous to rheological measurements and to introduce some new techniques and methods.

CPP 64.9 Thu 11:45 C 264

Combined rheo-optics and rheo-scattering study of structure evolution in biobased liquid-crystalline polymers — •DIETMAR AUHL¹, CAROLUS WILSENS¹, ERIC STELLAMANN², and SANJAY RASTOGI¹ — ¹Maastricht University, Maastricht, The Netherlands — ²Photon Science DESY, Hamburg, Germany

Thermotropic liquid-crystalline polymers (TLCP) are often used in high-performance applications, for which the chemical composition and flow effects on the micro- and mesoscale orientation need to be well designed. Recently developed TLCP based on p-hydroxybenzoic acid, suberic acid, and vanillic acid are partially aliphatic in contrast to commercial TLCP such as "Vectra", and they exhibit stable nematic melt morphologies up to 300°C [1,2]. In this study, we investigate the effects of temperature, shear deformation and rate on the molecular orientation and relaxation by rheo-optics as well as rheo-scattering with x-ray and small-angle light-scattering. The results show that the threaded morphology on a mesoscale breaks and orients along the flow direction under continuous flow, while also the molecules orient on a microscopic scale. The study provides detailed insights into the structure evolution of TLCP and a unique toolbox to correlate molecular parameters to properties and performance. [1] Wilsens, C., Noordover, B., Rastogi, S. Polym. (2014) 2432; [2] Wilsens, C., Verhoeven, J., Noordover, B., Hansen, M., Auhl, D., Rastogi, S. (2014) 3306