RHEO-PHYSICAL AND IMAGING TECHNIQUES

Peter Van Puyvelde, Christian Clasen, Paula Moldenaers, and **Jan Vermant**
K.U. Leuven, Department of Chemical Engineering, W. de Croylaan 46, B-3001 Leuven, Belgium

Keywords: linear dichroism, flow-birefringence, rheo-scattering methods, flow-induced structures, in-situ measurements, direct imaging

Contents

1. Introduction
2. Polarimetry
2.1. Definitions
2.2. Experimental Techniques
2.3. Linear Birefringence Measurements: Case-Studies
2.3.1. The Stress-Optical Relation in Polymers
2.3.2. Separation of the Intrinsic and Form Birefringence
2.4. Linear Conservative Dichroism: Case-studies
2.4.1. Immiscible Polymer Blends
2.4.2. Filled Polymeric Systems
2.5. Conclusion
3. Light scattering
3.1. Theoretical Background
3.2. Experimental Set-ups
3.3. Small Angle Light Scattering: Case-studies
3.3.1. Immiscible Polymer Blends
3.3.2. Filled Polymeric Systems
3.3.3. Flow-induced Crystallization of Polymers
3.4. Conclusion
4. Direct imaging methods
4.1. Optical Microscopy
4.2. Conclusion
5. General conclusion
Acknowledgements
Glossary
Bibliography
Biographical Sketches

Summary

Rheo-optical methods have become an established technique in the study of structured fluids. More than rheology, the techniques provide in-situ information of morphological changes during flow. In this chapter, the emphasis is on indirect optical techniques such as polarimetry and light scattering. The fundamentals of dichroism, birefringence and scattering are briefly reviewed. In order to demonstrate the power of the techniques, several case-studies are provided. They encompass many material classes, ranging from emulsions, suspensions and crystallizing polymeric systems.

1. Introduction

In the classical rheometrical approach, only mechanical measurements are used to determine the constitutive parameters that describe a material (Walters 1975; Macosko 1994). Rheo-optical methods – at least in the narrow sense of the word – were introduced in the rheological community in the 1950's to complement these traditional mechanical measurements. The initial aim of the optical methods was the direct measurement of stresses in the material (Lodge 1955; Philipoff 1956; Janeschitz-Kriegl 1983). Compared to the mechanical approach, the rheo-optical measurements have much shorter response times and higher sensitivities than the mechanical counterparts. In addition, they allow us to obtain the spatial distribution of the stresses, rather than the bulk response as measured by the mechanical approach. In the last two decades, the applicability of the rheo-optical methodology has broadened its horizon. It is now regarded as an approach that is used to understand the often complex rheological behaviour of a material based on its microstructural evolution (Fuller 1995; Sondergaard and Lyngaae-Jörgensen 1995; Wagner 1998). Examples of such complex materials – in which structures on the microscopic scale are used to improve their functionality – are ample in modern day life. They encompass a multitude of products such as for instance emulsions, particle filled materials, polymers with finely tuned molecular architectures, polymer blends, and many more (Larson 1999). For these materials, a mere mechanical characterization is not sufficient to clarify the complex relation between the rheological behavior and flow-induced changes of the microstructure. In order to optimize the formulation – and hence the performance – of such multiphase materials, techniques are required that are able to follow the morphology development during the processing step. The latter is not straightforward since it requires a high time resolution in order to obtain an in-situ analysis of the structure rather than a post-mortem picture of the morphology as for instance obtained by classical bright field microscopy or electron microscopy methods. In addition, time-resolved measurements of the structure are needed in order to capture the often anisotropic structural evolution. Although these requirements are not easy to achieve, various experimental techniques have already been coupled with flow geometries. As such combinations of flow (rheo-) with microscopy (Alderman and Mackley 1985; Larson and Mead 1992; Vermant, Moldenaers et al. 1994; Guido, Greco et al. 1999), with scattering at various length scales (light, X-ray, neutrons) (Koga, Hashimoto et al. 2008), with polarimetry, with NMR (Callaghan 2006), with dielectric measurements (Boersma and Van Turnhout 1999), ... are nowadays known as established experimental techniques.

In this overview, we will concentrate on techniques that use visible light to investigate structural changes during flow. These methods are based either on changes in the properties of the transmitted light (polarimetry) or on the spatial dependence of the scattered light (light scattering). Both techniques are remarkably complementary as will be explained further in this text. Polarimetry measures properties of the transmitted light that is affected by phenomena that occur at all length scales present in the material. On the contrary, light scattering at small angles is limited to structural phenomena at well-defined length scales, typically of the order of magnitude of the wavelength of the used light. In this chapter, the basic principles of the methods will be explained. In addition, some case studies will be presented to highlight the ability of these methods. Finally, the

advantages of the presented rheo-optical approach will be compared with direct structure visualization methods.

2. Polarimetry

2.1. Definitions

Polarimetry refers to the measurement of linear birefringence and linear dichroism, based on the interaction of polarized light with matter (Azzam and Bashara). Light is an example of electromagnetic radiation. Here we will only consider the electric field to describe its interaction with matter. The electrical field of a plane wave that propagates parallel to a vector $\vec{k}$ can be described by:

$$\vec{E} = \vec{E}\,\exp i\left[\frac{2\pi}{\lambda} n\vec{u}.\vec{x} - \omega t\right] \qquad (1)$$

in which $\vec{E}$ is the complex amplitude, n the refractive index of the material, and λ and ω respectively the wavelength and frequency of the light. The wavevector $\vec{k}$ is defined as:

$$\vec{k} = \frac{2\pi}{\lambda} n\vec{u} \qquad (2)$$

When such an electrical field propagates through matter, it interacts with its electrons. This can lead for instance to a decrease in propagation speed as compared to the speed in vacuum, and is determined by the real part of the refractive index n' (see also Figure 1). Likewise, the amplitude of the electrical field might be attenuated, which can be described by the imaginary or dissipative part of the refractive index n''.

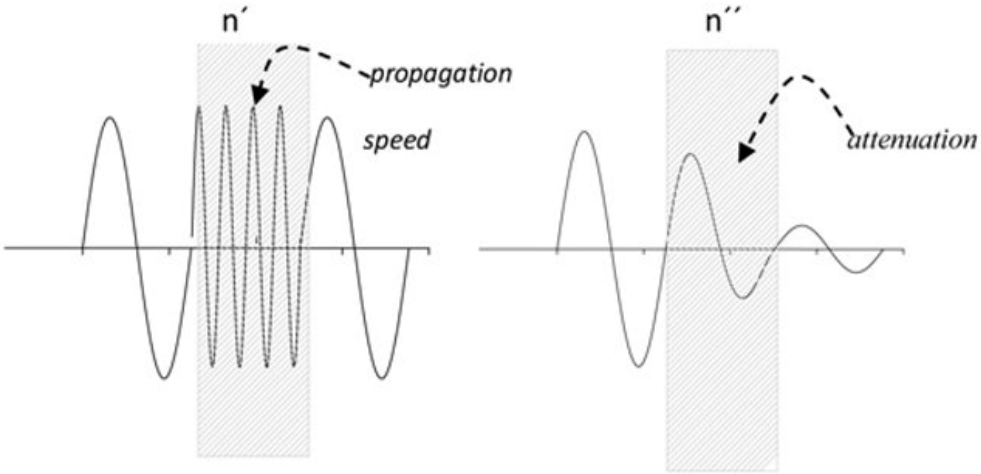

Figure 1. Interaction of polarized light with matter: effect of the real and imaginary part of the refractive index.

When a material is deformed by a shear flow or an extensional flow field, the refractive index of the material will not necessarily be described anymore by a scalar quantity. When the optical properties become anisotropic, which means that they become different along the different principal axes of the material, a refractive index tensor $\bar{n} = \bar{n}' + i\bar{n}''$ will become necessary to describe the optical response. When the material becomes anisotropic, the principal values of the real part of this tensor (n_1', n_2', n_3') (and the complex part (n_1'', n_2'', n_3'') can be different). Using these notations, the linear birefringence $\Delta n'$ is defined as the difference between the real parts of the refractive indices along the principal axes. Likewise, for the dissipative part, linear dichroism $\Delta n''$ is defined as the difference between the imaginary parts of the refractive indices. For instance, when considering the principal directions 1 and 3, the linear birefringence $\Delta n'$ and linear dichroism $\Delta n''$ are defined as:

$$\Delta n' = n_1' - n_3' \tag{3}$$

$$\Delta n'' = n_1'' - n_3'' \tag{4}$$

From a physical point of view, there are two fundamental contributions to both the birefringence and the dichroism: an intrinsic and a form contribution (Peterlin 1976; Onuki and Doi 1986; Fuller 1990). In the case of polymeric systems, the intrinsic birefringence is directly related to the orientation of macromolecules and its value depends on the anisotropy of the polarizabilities along the principal axis of the molecules. The form contribution, however, appears when a large difference in polarizabilities is present between oriented objects and the surrounding matrix materials such as the matrix fluid in immiscible blends, or the solvent in the case of solutions. In contrast to the intrinsic contribution to the birefringence, this form contribution is related to the shape of objects during flow and hence gives complementary information to the intrinsic birefringence. Unfortunately, it is not always easy to deconvolute both effects which makes the use of birefringence to determine form effects rather difficult (see also section Section 2.3.2 in which a case-study is presented where such a separation is possible).

Along the same line of thoughts, the form contribution of the dichroism – called the conservative dichroism – is also related to the global shape of objects (Meeten 1981). This is due to the fact that this conservative dichroism is determined by the anisotropic light scattering of the objects under investigation. The intrinsic contribution to the dichroism originates from the spectroscopic absorption of the light by specific chemical bonds within the sample. Because this contribution depends on the wavelength of the light – the form contribution is less sensitive to that – a proper selection of the wavelength allows for the separation of both effects. Hence, the linear conservative dichroism becomes an interesting tool to investigate effects on the form and organization of flow-induced structures.

2.2. Experimental Techniques

Linear birefringence is caused by a difference in propagation speed when the electrical field is directed along different principal axes of the material. In purely birefrigent

materials, this results in an optical retardation that emerges as a phase difference between two optical paths. This retardation induces a modification from a linearly polarized state to an elliptical polarization. Likewise, in purely dichroic materials, the two components of the polarized light are still in phase but one of the components is attenuated more than the other. When a material is both birefringent as well as dichroic, the optical analysis becomes more complex.

The techniques to measure birefringence and dichroism are based on the characterization of the polarization state of light. From a mathematical point of view, the Jones and Muller calculus provides a simple matrix-based approach as explained for instance by Azzam and Bashara or in the monologue by Fuller.

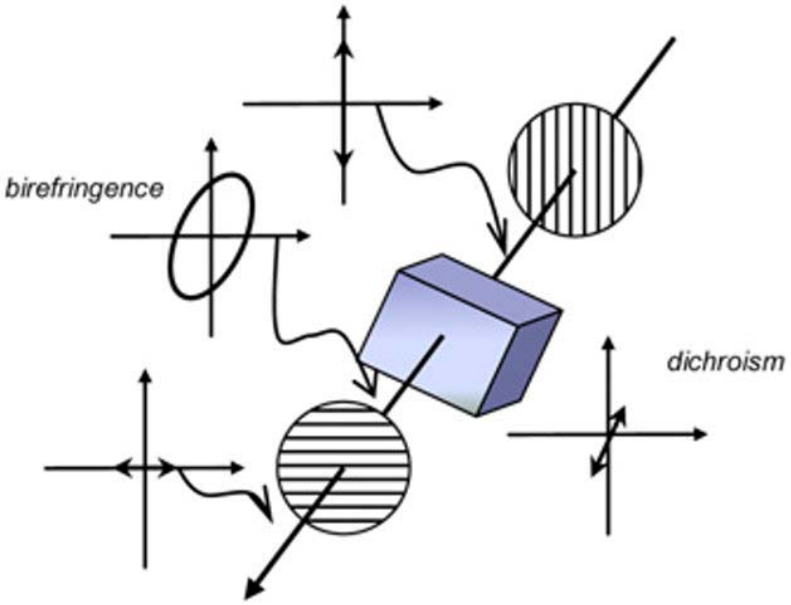

Figure 2. Simple experimental method to measure birefringence and dichroism. Light is sent through a polarizer oriented at zero degrees with respect of the reference laboratory frame. Next, the light passes through the sample oriented at a certain angle with respect to the reference frame. The birefringence of the sample changes the polarization state of the light from a planar to an elliptical state.The dichroism induces a polarization dependent attenuation of the light. Finally, a second polarizer (analyzer) oriented at 90° is used.

Several designs of optical arrangements are possible to measure optical anisotropies. The simplest arrangement is shown in Figure 2. In this example, a coaxially birefringent and dichroic sample (oriented at an angle θ) is inserted between crossed polarizers. Based on the Jones and Muller calculus, the transmitted intensity from this optical train is calculated to be:

$$I = \frac{I}{4}\sin\left(2\theta\right)\left(\cosh\delta'' - \cos\delta'\right) \qquad (5)$$

Here I is the intensity of the incident beam, and δ' and δ'' are the optical retardation and the extinction that can be converted to the birefringence and the dichroism as defined by:

$$\Delta n' = \frac{\delta' \lambda}{2\pi d} \tag{6}$$

$$\Delta n'' = \frac{\delta'' \lambda}{2\pi d} \tag{7}$$

with d the thickness of the sample. Such a crossed polarizer set-up has been used extensively for birefringence measurements. However, as Eq. (5) indicates, a number of shortcomings can be observed in this simple method. First of all, the measured intensity is affected by both the birefringence and the dichroism and a proper birefringence measurement will only be possible if the dichroism can be neglected. In addition, if both the birefringence and orientation angle θ are unknown, this single measurement is clearly not sufficient to determine them simultaneously.

An additional drawback of the method proposed above comes into play when one wants to observe the birefringence and dichroism in transient flow fields due to the lack of time resolution. In order to solve this problem, faster polarization modulation methods can be used where a regular time-dependent variation of the properties of the incident light is induced. Such a modulation can be performed either by the rotation of an optical element with fixed optical properties, or by the modulation of the optical properties of an element with fixed orientation. A typical experimental setup is shown in Figure 3.

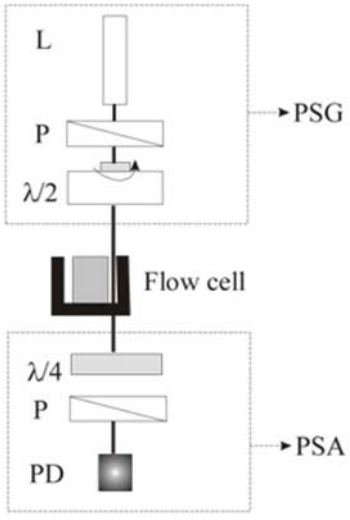

Figure 3. Example of an optical set-up to measure birefringence. A polarization state generator (PSG) is used after which the light is sent through the sample. A polarization state analyzer (PSA) is used to analyze the transmitted light. A photodiode (PD) is used to capture the intensity of the light.

Light emitted by a laser source (which is typically a helium-neon laser with a wavelength of 632.8 nm) is polarised by a Polarization State Generator (PSG), passes through the sample and is analyzed by a Polarization Stage Analyzer (PSA) that contains a photodiode (PD) to measure the transmitted intensity. It is essential in these polarimetric methods to choose the proper optical components in order to highlight the desired information present in the sample.

A possible set-up to measure birefringence and/or dichroism consists for instance of a polarizer (P) oriented at 0° (with respect to the laboratory reference frame), followed by a rotating half-wave plate that rotates at a frequency ω. Based on the Jones and Muller calculus, one can calculate that the light that emerges from this PSG will be polarized at a frequency of 4ω. This high modulation frequency (~1-10 kHz depending on the PSG, with the highest modulation frequencies attained by a photo-elastic modulation) allows us to follow fast transient structural rearrangements as they may occur in a flowing system.

In the case of birefringence measurements, the PSA consists of a quarter wave plate and a polarizer oriented at 90° with respect to the reference plane. In the case of small anisotropies, the transmitted intensity is calculated to be (see the monograph by Fuller for a detailed coverage of these calculations):

$$I = \frac{I}{4}\left[1 - \left(\cos 2\theta \sin \delta'\right)\sin 4\omega t + \left(\sin 2\theta \sin \delta'\right)\cos 4\omega t\right] \tag{8}$$

As can be seen from this equation, the harmonic content of the signal allows to retrieve the desired birefringence via the retardation δ' and corresponding orientation angle θ. This can be done, for instance, by a digital analysis of the intensity by means of a fast Fourier transformation or by using lock-in amplifiers that are set at the modulation frequency. By using the latter approach, the amplitudes of $\sin R$ and $\cos R$ contributions of Eq. (8) can be isolated:

$$R = -\left(\cos 2\theta \sin \delta'\right) \tag{9}$$

$$R = \sin 2\theta \sin \delta' \tag{10}$$

Based on these amplitudes, the values of the birefringence and the orientation angle can then be calculated as:

$$\Delta n' = \frac{\lambda}{2\pi d}\left[\arcsin\sqrt{R + R}\right] \tag{11}$$

$$\theta = \frac{1}{2}\arctan\left(\frac{R}{R}\right) \tag{12}$$

In the case of dichroism measurements, the PSA consists of only a photodiode without any additional optics. The analysis to retrieve the dichroism is similar and can be found in the monograph by Fuller.

Under flow conditions, the orientation angle θ is defined relative to the principal directions of the flow. In the case of simple shear flow (see Figure 4), two approaches are possible. When the light is sent parallel to the velocity gradient direction (which is typical when using a parallel plate setup), only a projection of the structures under investigation is observed. However, in order to obtain the orientation angle in the flow field, one needs to send the incident light along the vorticity axis. In this case, a Couette (concentric cylinder) geometry as depicted in Figure 3 is appropriate.

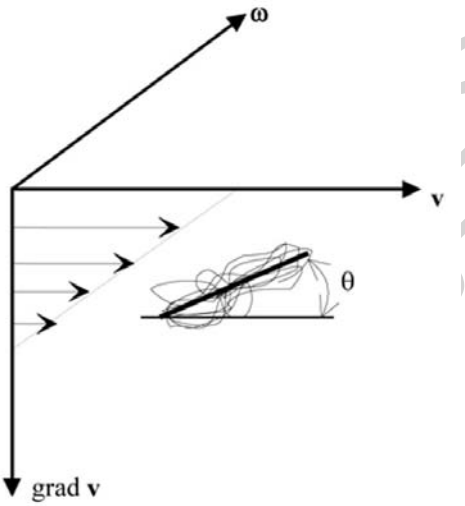

Figure 4. Orientation of a polymeric chain during simple shear flow. ***v*** corresponds to the flow direction, ω is the vorticity direction.

-
-
-

Bibliography

Alderman, N. J. and M. R. Mackley (1985). Optical Textures Observed During the Shearing of Thermotropic Liquid-Crystal Polymers. Faraday Discussions, 149-165. [Combination of flow and microscopy in the study of the texture of liquid crystalline polymers.]

Azzam, R. M. A. and N. M. Bashara (1999). Ellipsometry and Polarized Light, Elsevier. [The basic book for polarimetry.]

Baaijens, F. P. T., S. H. A. Selen, et al. (1997). Viscoelastic flow past a confined cylinder of a low density

polyethylene melt. Journal of Non-Newtonian Fluid Mechanics 68(2-3), 173-203. [In this paper, birefringence measurements are used to spatially measure stresses in polymeric fluids.]

Baaijens, H. P. W., G. W. M. Peters, et al. (1995). Viscoelastic Flow Past a Confined Cylinder of a Polyisobutylene Solution. Journal of Rheology 39(6), 1243-1277. [In this paper, birefringence measurements are used to spatially measure stresses in polymeric fluids.]

Baert, J. and P. Van Puyvelde (2008). Density fluctuations during the early stages of polymer crystallization: An overview. Macromolecular Materials and Engineering 293(4), 255-273. [Review article on the use of small angle light scattering in the study of flow-induced crystallization.]

Baert, J., P. Van Puyvelde, et al. (2006). Flow-induced crystallization of PB-1: From the low shear rate region up to processing rates. Macromolecules 39(26), 9215-9222. [Paper that describes the use of birefringence to determine the kinetics of flow-induced crystallization at processing speeds.]

Boersma, A. and J. van Turnhout (1999). Dielectric on-line spectroscopy during extrusion of polymer blends. Polymer 40(18), 5023-5033. [An example of the use of the combination of flow and dielectrical measurements.]

Brown, E. F., W. R. Burghardt, et al. (1995). Comparison of Optical and Mechanical Measurements of 2nd Normal Stress Difference Relaxation Following Step Strain. Rheologica Acta 34(3), 221-234.

Callaghan, P. T. (2006). Rheo-NMR and velocity imaging. Current Opinion in Colloid & Interface Science 11(1), 13-18. [Review of the combination of NMR with flow.]

Clasen, C. (2001). Neue Charakterisierungsmöglichkeiten von supramolkularen Strukturen in Biopolymerlösungen mit rheo-optischen Methoden. Aachen, Shaker Verlag. Rheo-optic

Clasen, C. and W. M. Kulicke (2001). A convenient way of interpreting steady shear rheo-optical data of semi-dilute polymer solutions. Rheologica Acta 40(1), 74-85. Rheo-optic

Clasen, C. and W. M. Kulicke (2001). Determination of viscoelastic and rheo-optical material functions of water-soluble cellulose derivatives. Progress in Polymer Science 26(9), 1839-1919. Rheo-optic

Clasen, C. and W. M. Kulicke (2003). The gelation of (1 -> 3)(1 -> 4)-beta-D-glucans. Monatsschrift Fur Brauwissenschaft 56(9-10), 161-171. Clasen

Clasen, C. and W. M. Kulicke (2003). Rheo-optical studies of barley (1 -> 3)(1 -> 4)-beta-glucan solution: Detection of the flow behavior of aggregates in the sol state. Journal of Rheology 47(2), 321-335. Rheo-optic

Crocker, J. C. and D. G. Grier (1996). Methods of digital video microscopy for colloidal studies. Journal of Colloid and Interface Science 179(1), 298-310. [A nice example of image processing algorithms for extracting quantitative data from digitized video microscope images of colloidal suspensions.]

Degroot, J. V., C. W. Macosko, et al. (1994). Flow-Induced Anisotropic Sals in Silica-Filled Pdms Liquids. Journal of Colloid and Interface Science 166(2), 404-413. [In this paper, small angle light scattering is used to visualize aggregated structures in suspensions.]

Doi, M. and S. F. Edwards (1986). The theory of polymer dynamics, Oxford University Press. [Classical book in the description of polymer dynamics and its relation to constitutive relations.]

Frattini, P. L. and G. G. Fuller (1987). Conservative Dichroism of a Sheared Suspension in the Rayleigh-Gans Light-Scattering Approximation. Journal of Colloid and Interface Science 119(2), 335-351. [Comparison of theory and experiments in the case of particles aligning in a flow field.]

Fuller, G. G. (1990). Optical Rheometry. Annual Review of Fluid Mechanics 22, 387-417. [Review article on the use of polarimetry in the investigation of flow-induced structures.]

Fuller, G. G. (1995). Optical Rheometry of Complex Fluids. New York, Oxford University Press. [In this monologue, the state-of-the-art of optical measurements is explained from the theoretical point of view]

Fuller, G. G. and P. L. Frattini (1984). Flow-Induced Dichroism and Average Angle of Orientation of Colloidal Suspensions in Transient Shear-Flow. Journal of Rheology 28(4), 497-497. [Use of dichroism measurements to determine the transient orientation of particles during flow.]

Gortemaker, F. H., M. G. Hansen, et al. (1976). Flow Birefringence of Polymer Melts - Application to

Investigation of Time-Dependent Rheological Properties. Rheologica Acta 15(5), 256-267. [Use of birefringence to rapidly determine stresses.]

Guido, S., F. Greco, et al. (1999). Experimental determination of drop shape in slow steady shear flow. Journal of Colloid and Interface Science 219(2), 298-309. [An example of the combined use of rheology and microscopy.]

Hashimoto, T., T. Takebe, et al. (1988). Ordered Structure and Critical Phenomena of a Semidilute Solution of Polymer Mixtures under Shear-Flow. Journal of Chemical Physics 88(9), 5874-5881.

Hobbie, E. K., H. Wang, et al. (2003). Optical measurements of structure and orientation in sheared carbon-nanotube suspensions. Review of Scientific Instruments 74(3), 1244-1250.

Hobbie, E. K., H. Wang, et al. (2003). Orientation of carbon nanotubes in a sheared polymer melt. Physics of Fluids 15(5), 1196-1202.

Janeschitz-Kriegl, H. (1983). Polymer Melt Rheology and Flow-Birefringence. Berlin, Springer-Verlag. [Classical book on the use of experimental rheo-optical methods.]

Johnson, S. J. and G. G. Fuller (1987). The Dynamics of Colloidal Particles Suspended in a 2nd-Order Fluid. Faraday Discussions, 271-+.

Johnson, S. J., A. J. Salem, et al. (1990). Dynamics of Colloidal Particles in Sheared, Non-Newtonian Fluids. Journal of Non-Newtonian Fluid Mechanics 34(1), 89-121. [In this article, the dynamics of particles in viscoelastic media is presented.]

Kalogrianitis, S. G. and J. W. vanEgmond (1997). Full tensor optical rheometry of polymer fluids. Journal of Rheology 41(2), 343-364.

Koga, T., T. Hashimoto, et al. (2008). New insight into hierarchical structures of carbon black dispersed in polymer matrices: A combined small-angle scattering study. Macromolecules 41(2), 453-464. [In this article, the combination of flow with X-ray and neutron scattering methods is demonstrated.]

Kornfield, J. A., G. Kumaraswamy, et al. (2002). Recent advances in understanding flow effects on polymer crystallization. Industrial & Engineering Chemistry Research 41(25), 6383-6392. [Review article on flow-induced crystallization.]

Kumaraswamy, G. (2005). Crystallization of polymers from stressed melts. Journal of Macromolecular Science-Polymer Reviews C45(4), 375-397. [Review article on flow-induced crystallization.]

Larson, R. G. (1999). The structure and rheology of complex fluids (Topics in Chemical Engineering). Oxford, Oxford University Press. [In this book, an overview of various complex fluids is given.]

Larson, R. G. and D. W. Mead (1992). Development of Orientation and Texture During Shearing of Liquid-Crystalline Polymers. Liquid Crystals 12(5), 751-768.

Lauger, J., R. Lay, et al. (1995). Structure Development of a Polybutadiene/Polyisoprene Blend During Spinodal Decomposition - Comparison between Light-Scattering and Optical Microscopy. Macromolecules 28(20), 7010-7015. [A nice demonstration of the combined use of various optical techniques in structural investigations.]

Lodge, A. S. (1955). Variation of Flow Birefringence with Stress. Nature 176(4487), 838-839. [Classical book on the use of birefringence in the measurement of stresses.]

Lyon, M. K., D. W. Mead, et al. (2001). Structure formation in moderately concentrated viscoelastic suspensions in simple shear flow. Journal of Rheology 45(4), 881-890. [Experimental results on the evolution of the particle microstructure for noncolloidal particles that are suspended in a viscoelastic medium are reported.]

Macosko, C. W. (1994). Rheology: Principles, Measurements and Appliciations, VCH Publishers. [This is one of the standard reference books on rheology and rheometry]

Magda, J. J., J. Lou, et al. (1991). 2nd Normal Stress Difference of a Boger Fluid. Polymer 32(11), 2000-2009. [In this paper, birefringence is used to measure the second normal stress difference.]

Meeten, G. H. (1981). Conservative Dichroism in the Rayleigh-Gans-Debye Approximation. Journal of Colloid and Interface Science 84(1), 235-239. [A theoretical paper on the calculation of form or linear

conservative dichroism.]

Mewis, J., H. Yang, et al. (1998). Small-angle light scattering study of droplet break-up in emulsions and polymer blends. Chemical Engineering Science 53(12), 2231-2239. [In this paper, a theoretical description of small angle light scattering patterns of breaking fibrils is provided.]

Michele, J., R. Patzold, et al. (1977). Alignment and Aggregation Effects in Suspensions of Spheres in Non-Newtonian Media. Rheologica Acta 16(3), 317-321. [In this paper, the apparition of strings of particles in elastic media is demonstrated.]

Onuki, A. and M. Doi (1986). Flow Birefringence and Dichroism of Polymers .1. General-Theory and Application to the Dilute Case. Journal of Chemical Physics 85(2), 1190-1197. [Theoretical description of the relation between linear conservative dichroism and anistropy calculated from a light scattering pattern.]

Pearson, D. S., A. D. Kiss, et al. (1989). Flow-Induced Birefringence of Concentrated Polyisoprene Solutions. Journal of Rheology 33(3), 517-535. [The paper demonstrates the use of birefringece for a fast measurement of the stress.]

Peterlin, A. (1976). Optical Effects in Flow. Annual Review of Fluid Mechanics 8, 35-55. [A review paper on the effects of flow on optical properties of fluids.]

Philippoff, W. (1956). Flow-Birefringence and Stress. Nature 178(4537), 811-812. [A key book on the relationship between stress and birefringence.]

Philippoff, W. (1956). Flow Birefringence and Stress. Journal of Applied Physics 27(9), 984-989. [A key paper in the description of the stress-optical relationship in polymeric fluids.]

Priore, B. E. and L. M. Walker (2001). Coalescence analysis through small-angle light scattering. Aiche Journal 47(12), 2644-2652. [Small angle light scattering is used to determine the morphology evolution in immiscible polymer blends in complex flows.]

Priore, B. E. and L. M. Walker (2001). Small angle light scattering analysis of morphology development of a model immiscible polymer blend in transient slit-contraction flows. Journal of Rheology 45(2), 383-402. [Small angle light scattering is used to determine the morphology evolution in immiscible polymer blends in complex flows.]

Rothstein, J. P. and G. H. McKinley (2002). A comparison of the stress and birefringence growth of dilute, semi-dilute and concentrated polymer solutions in uniaxial extensional flows. Journal of Non-Newtonian Fluid Mechanics 108(1-3), 275-290. [An example of the breakdown of the stress-optical relation in strong flows.]

Scirocco, R., J. Vermant, et al. (2004). Effect of the viscoelasticity of the suspending fluid on structure formation in suspensions. Journal of Non-Newtonian Fluid Mechanics 117(2-3), 183-192. [In this paper, the effect of matrix rheology on particle alignment is discussed.]

Sondergaard, K. and J. Lyngaae-Jörgensen (1995). Rheo-Physics of multiphase polymer systems: characterization by rheo-optical techniques, Technomic Publishing Company. [Textbooks giving background on rheo-optical techniques with some case-studies.]

Sridhar, T., D. A. Nguyen, et al. (2000). Birefringence and stress growth in uniaxial extension of polymer solutions. Journal of Non-Newtonian Fluid Mechanics 90(2-3), 299-315. [In this paper, the breakdown of the stress-optical relationship in strong flows is discussed.]

Stein, R. S. and P. R. Wilson (1962). Scattering of Light by Polymer Films Possessing Correlated Orientation Fluctuations. Journal of Applied Physics 33(6), 1914-&. [A pioneering article in the use of small angle light scattering for studying crystallizing polymers.]

Takahashi, T. and G. Fuller (1996). Stress tensor measurement using birefringence in oblique transmission. Rheologica Acta 35(4), 297-302. [In this paper, full tensor optical rheometry is demonstrated.]

Tucker, C. L. and P. Moldenaers (2002). Microstructural evolution in polymer blends. Annual Review of Fluid Mechanics 34, 177-210. [Review article on flow induced structure evolution in immiscible polymer blends.]

Van de Hulst, H. C. (1982). Light scattering by small particles, Dover Publcations. [A standard reference book on small angle light scattering.]

Van Hemelrijck, E., P. Van Puyvelde, et al. (2004). Direct evidence for breakup of liquid fibrils via Rayleigh instabilities in model polymer blends in step-up experiments. Langmuir 20(9), 3498-3500. [In this paper, it is demonstrated using small angle light scattering experiments, that fibril break during flow by means of Rayleigh instabilities.]

Van Puyvelde, P., H. Yang, et al. (1998). Rheo-optical probing of relaxational phenomena in immiscible polymer blends. Journal of Colloid and Interface Science 200(1), 86-94. [This article shows the use of linear conservative dichroism and small angle light scattering on the flow-induced structures in immiscible blends.]

Van Puyvelde, P., H. Yang, et al. (2000). Breakup of filaments in blends during simple shear flow. Journal of Rheology 44(6), 1401-1415. [This article provides, based on rheo-optical experiments, a scaling relation to determine the breakup time of droplets during flow.]

Vananroye, A., P. Van Puyvelde, et al. (2007). Effect of confinement on the steady-state behavior of single droplets during shear flow. Journal of Rheology 51(1), 139-153. [In this paper, a combination of a counterrotating flow cell and a microscope is used to determine droplet deformation and breakup in confined conditions.]

Venerus, D. C., S. H. Zhu, et al. (1999). Stress and birefringence measurements during the uniaxial elongation of polystyrene melts. Journal of Rheology 43(3), 795-813. [In this article, the breaking down of the stress-optical relationship in strong flows is discussed.]

Vermant, J. (2001). Large-scale structures in sheared colloidal dispersions. Current Opinion in Colloid & Interface Science 6(5-6), 489-495. [Review articel on flow-induced structural phenomena in colloidal systems.]

Vermant, J., P. Moldenaers, et al. (1994). A Comparison between Texture and Rheological Behavior of Lyotropic Liquid-Crystalline Polymers During Flow. Journal of Non-Newtonian Fluid Mechanics 53, 1-23.

Vermant, J. and M. J. Solomon (2005). Flow-induced structure in colloidal suspensions. Journal of Physics-Condensed Matter 17(4), R187-R216. [A review articel on structure development in colloidal suspensions.]

Vermant, J., P. Van Puyvelde, et al. (1998). Anisotropy and orientation of the microstructure in viscous emulsions during shear flow. Langmuir 14(7), 1612-1617. [This paper shows the combined approach of small angle light scattering and linear conservative dichroism to determine the structural evolution in immiscible blends.

Vermant, J., H. Yang, et al. (2001). Rheooptical determination of aspect ratio and polydispersity of nonspherical particles. Aiche Journal 47(4), 790-798. [This paper discusses the use of linear conservative dichroism to rapidly determine the aspect ratio and polydispersity of nonspherical particles.

Wagner, N. J. (1998). Rheo-optics. Current Opinion in Colloid & Interface Science 3(4), 391-400. [A review article on the use of rheo-optical methods in structured fluids.]

Wagner, N. J. and B. J. Ackerson (1992). Analysis of Nonequilibrium Structures of Shearing Colloidal Suspensions. Journal of Chemical Physics 97(2), 1473-1483. [This paper shows the expansion of the structure factor determined by light scattering in spherical harmonics in order to deduce small anisotropies in the scattering.]

Walters, K. (1975). Rheometry. London, Chapman and Hall - Wiley. [This is one of the first text books on rheology]

Yang, H., H. J. Zhang, et al. (1998). Rheo-optical investigation of immiscible polymer blends. Polymer 39(23), 5731-5737. [In this paper, linear conservative dichroism measurements are shown to be very sensitive to structural changes in immiscible polymer blends.]

Zebrowski, B. E. and G. G. Fuller (1985). Rheo-Optical Studies of Concentrated Polystyrene Solutions Subjected to Transient Simple Shear-Flow. Journal of Polymer Science Part B-Polymer Physics 23(3), 575-589. [This paper shows the fast time response of birefringence methods to measure stresses in a

fluid.]

Biographical Sketches

Peter Van Puyvelde is professor in the group of Applied Rheology and Polymer Processing of the Chemical Engineering Department of the K.U. Leuven. He obtained his PhD from the same institute, working on the use of rheo-optical methods in the study of morphology development in immiscible polymer blends. In 2002, he was a post-doc in the Materials Technology group of the T.U. Eindhoven, headed by Prof. H.E.H. Meijer. His current research focuses on structure development in solidifying (polymeric) systems and on the development of new biobased materials.

Christian Clasen is Associate Professor in the Department of Chemical Engineering at the K.U.Leuven. He was born on February 23rd in Hamburg (Germany). He obtained his Diploma in Chemistry from Hamburg University in 1999 and conducted there his doctoral studies at the Institute of Technical and Macromolecular Chemistry under the supervision of Prof. W.-M. Kulicke. He held a postdoctoral position at the Department of Mechanical Engineering of the Massachusetts Institute of Technology (MIT) from 2001 to 2002, to return then to Hamburg where he obtained his Habilitation in Technical Chemistry in 2008. He joined the Chemical Engineering Department of K.U.Leuven in October 2006 where he took up the position for Chemical Product Design within the Group of Applied Polymer Processing and Rheology. His research focuses on the investigation of the flow and deformation properties of complex fluids and soft solids in microdimensions and free surface flows. Honours and awards include a RheoFuture Young Scientist Award, the Publication Award of the Society of Rheology in 2007, and 2008 an ERC Starting Grant awarded by the European Research Council.

Jan Vermant is a Full Professor of Chemical Engineering at K.U. Leuven. He was born on august 20th 1968. He studied Chemical Engineering at K.U. Leuven and obtained his PhD in 1996 under the supervision of Prof. Jan Mewis and Paula Moldenaers. After a period of postdoctoral research at Stanford, Ecole des Mines and the CNRS and K.U. Leuven, he joined the faculty at K.U. Leuven in 1999. He has held visiting appointments at the University of Delaware, Stanford University and Princeton University. His research focuses on the relation between structure and rheology in complex fluids, both in bulk and at interfaces. Honors and awards include a Dupont Young Faculty Award and the 2007 Exxon-Mobil Chemical Science and Engineering Award Europe.

Paula Moldenaers was born in Leuven (Belgium) on May 2, 1957. She obtained a Master in Chemical Engineering from the K.U. Leuven (Belgium) in 1980 and a Ph. D. in 1987 under the supervision of Prof. Jan Mewis.

She is a Full Professor at the Department of Chemical Engineering of the Katholieke Universiteit in Leuven and is head of the Laboratory of Applied Rheology and Polymer Processing. Her research is situated in the area of rheology and morphology of complex fluids such as immiscible blends, liquid crystals, filled systems and gels. She published over 120 international journal papers. She received the Annual Award of the British Society of Rheology in 1991 and the Publication Award of the Society of Rheology in 1997 (with I. Vinckier and J. Mewis). She is a member of the Royal Flemish Academy of Belgium for Arts and Sciences.