VISCOELASTIC PROPERTIES AND ORIENTATION OF POLYMERS IN SOLUTION

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ABSTRACT

Using rheological shear and oscillation measurements, it is possible to determine the viscoelastic properties of a system quantitatively, as a function of the many influential parameters. The aim here was to establish structure-property relationships for a polymer in a solvent system from the viscoelastic material functions correlated with data from polymer analysis These structure-property relationships make it possible to quantitatively predict the viscoelastic properties as a function of the molecular parameters.

In addition to these rheo-mechanical measurements, recent years have also seen the parallel determination of rheo-optical material functions, such as flow birefringence and flow dichroism, used in order to investigate macroscopic viscoelastic flow behaviour at a molecular level. Apart from determining these moduli, which are proportional to rheo-mechanical parameters, it was also possible to determine the orientation of polymer segments and aggregated structures. In particular, it became possible to explain aggregation behaviour during the sol-gel transition and during temperature-induced phase separation on a molecular level. The overriding aim of these investigations was to establish new structure-property relationships by correlating the rheo-mechanical and the rheo-optical material functions.

KEYWORDS: RHEOLOGY, RHEO-OPTIC, ORIENTATION, AGGREGATES, ASSOCIATES, STRUCTURE-PROPERTY-RELATIONSHIP

INTRODUCTION

Polymers in solution are used in a wide variety of industrial applications and products to adjust the viscosity, the elasticity, the surface tension or in general the flow behaviour. The addition of a polymer to a solution to acquire a desired properties profile results in an increase of the variable parameters as now – in addition to the usual influential factor of concentration – the molar mass, the molar mass distribution, the substitution pattern and resulting conformation in the selected solvent also have to be taken into account. This is made more difficult by the fact that a lot of the polymers employed in solution tend to form aggregates, which, while being desirable in special applications, does, however, cause problems in establishing a selected properties profile. To date great effort has often been expended on empirically determining the amount of substance that needs to be added, and for mixtures of polymer additives this quantity has often been heavily dependent upon chance.

By using rheological shear and oscillation measurements, it is possible to determine the viscoelastic properties of a system quantitatively, as a function of the many influential parameters (Fig 1). The overriding aim here was to establish structure-property relationships for a polymer in a solvent system from the viscoelastic material functions correlated with data from polymer analysis [1]. These structure-property relationships make it possible to quantitatively predict the viscoelastic properties as a function of the molecular parameters [2], [3], [4], [5], [6].
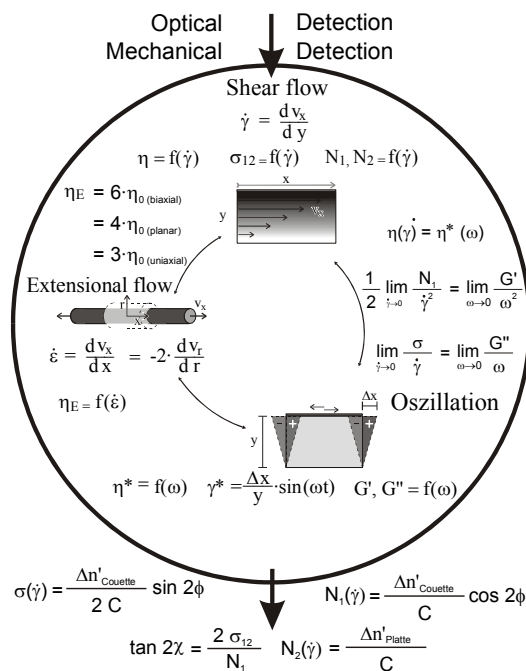

Fig. 1   Rheological circle. Materialfunctions for rheo-mechanical and rheo-optical measurements

The determination of rheo-optical material functions, such as flow birefringence and flow dichroism, can be used in order to investigate the macroscopic viscoelastic flow behaviour at a molecular level. In homogeneous solutions these moduli are proportional to rheo-mechanical parameters. They can also be used to determine the orientation of polymer segments and aggregated structures. In particular, it became possible to explain aggregation behaviour during the sol-gel transition and during temperature-induced phase separation on a molecular level.

EXPERIMENTAL

The rheo-mechanical measurements were performed on commercially available rheometers of the following types: RFS-8500 and ARES (Rheometrics, Inc., Piscataway, NJ, USA), UDS 200 (Paar/Physica Messtechnik GmbH, Stuttgart, Germany) and CS 50 (Bohlin Reologi AB, Lund, Sweden).

Rheo-optical stationary shear measurements were performed on a measuring apparatus of our own construction with a Couette geometry. An optical measuring path integrated into a commercial rheometer was used for dynamic measurements. A detailed description of this method is given in references [7], [8].
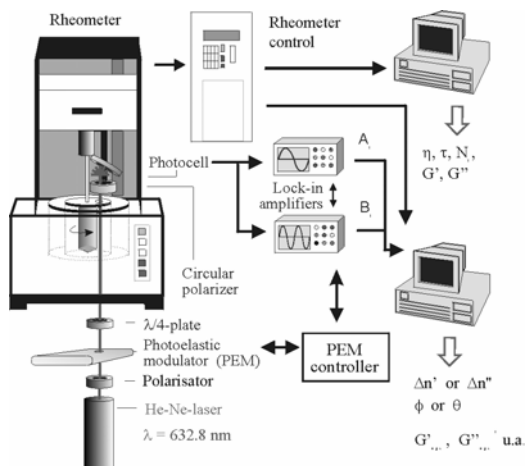

Fig. 2: Combined rheo-mechanical and rheo-optical apparatus, using a commercial rheometer and a self-build optical unit.

RESULTS AND DISCUSSION

The description of rheo-mechanical material functions by means of empirical structure-property relationships is illustrated in detail by the ideal, coiled system of polystyrene/toluene [9]. For polysaccharides, too, the following structure-property relationships were established (Table 1).

In the case of systems that form aggregates it is often not possible to indicate the exact molar mass, and this is substituted by the Staudinger index, [η].

For solutions with mixtures of substances, these material functions cannot be obtained additively from the structure-property relationships of the individual components. Intermolecular interactions result in a change in the solution structure, which leads to drastic changes in the macroscopic flow behaviour. It is also difficult to obtain these structure-property relationships for systems that contain shear instabil aggregates and associated structures.

Table 1 Structure-property relationships for aqueous polysaccharide solutions

CMC:
$$\eta_0[\text{Pa}\cdot\text{s}] = 8.91\cdot10^{-4} + 1.30\cdot10^{-5}\cdot c\cdot M_w^{0.9} +$$
$$5.33\cdot10^{-8}\cdot c^2\cdot M_w^{1.8} + 4.60\cdot10^{-15}\cdot c^{4.34}\cdot M_w^{3.91}$$

HPC:
$$\eta_0[\text{Pa}\cdot\text{s}] = 8.91\cdot10^{-4} + 8.91\cdot10^{-4}\cdot c\cdot[\eta] +$$
$$6.1123\cdot10^{-4}\cdot(c\cdot[\eta])^2 + 1.28\cdot10^{-4}\cdot(c\cdot[\eta])^{4.24}$$

Schizophyllan:
$$\eta_0[\text{Pa}\cdot\text{s}] = 8.91\cdot10^{-4} + 8.91\cdot10^{-4}\cdot c\cdot[\eta] +$$
$$3.74\cdot10^{-4}\cdot(c\cdot[\eta])^2 + 3.65\cdot10^{-7}\cdot(c\cdot[\eta])^{5.03}$$

Xanthan:
$$\eta_0[\text{Pa}\cdot\text{s}] = 8.91\cdot10^{-4} + 8.91\cdot10^{-4}\cdot c\cdot[\eta] +$$
$$5.08\cdot10^{-4}\cdot(c\cdot[\eta])^2 + 1.34\cdot10^{-4}\cdot(c\cdot[\eta])^{3.50}$$

(1,3)(1,4)-β-glucan:
$$\eta_0[\text{Pa}\cdot\text{s}] = 8.91\cdot10^{-4} + 5.38\cdot10^{-5}\cdot c\cdot M_w^{0.71} +$$
$$2.28\cdot10^{-6}\cdot c^2\cdot M_w^{1.42} + 2.41\cdot10^{-15}\cdot c^{5.18}\cdot M_w^{3.68}$$

In these cases rheo-optical measurements yield more information on the structure, deformability, and orientation of the polymersegments and aggregates on a molecular level.

The mean orientation of polymer segments in the shear flow has been investigated for polymer standards (fig. 3) and homogeneous solutions over the whole range of solution states.
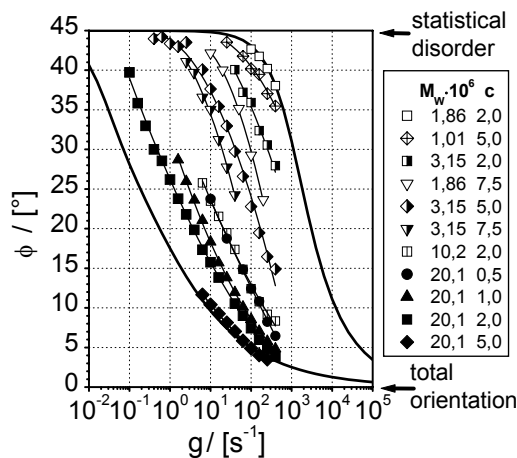

Fig. 3 Orientation φ of the flowbirefringence for narrowly distributed polystyrene standards in toluene in semi-dilute solutions (T =25°C)

Apart from the behaviour of polymersegments in a homogenous it is also possible to investigate the orientation and deformation behaviour of associated structures. It is in particular possible to investigate the stability of these structures by measuring the formbirefringence (fig. 4) and the flowdichroism
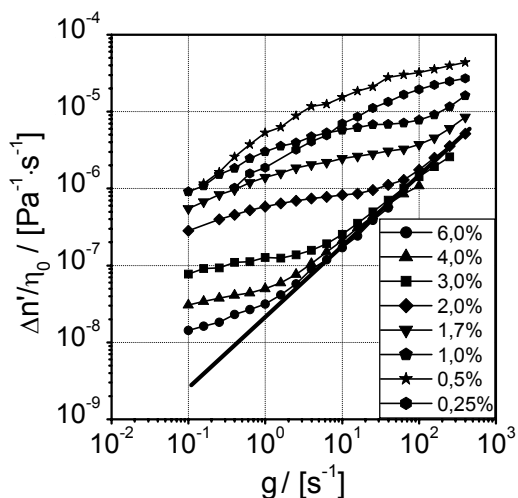
Fig 5   Reduced flowbirefringene for barley (1,3)(1,4)-β-
glucan in aqueous solution (T =25° C).
Formbirefringence superimposed on the intrinsic
birefringence

The flowdichroism gives information on the deformability and orientation of aggregated structures. It can also be used to detect changes in the solution structure and to investigate the intermolecular interactions of polymersolution mixtures (fig. 5).
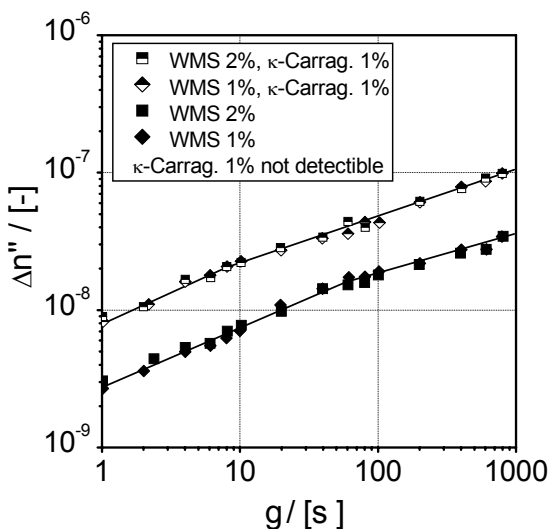

Fig. 5   Flow dichroism, Δn'', of the mixed system of
waxy maize starch (WMS) and κ-Carrageenan versus
shear rate (T = 298 K)

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