POLYMER RHEOLOGY

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Contents

Summary

Liquid polymeric systems have a characteristic rheological behavior. First, the general features are presented for the various types of flow. Linear as well as nonlinear material response is included. Then, the effect of molecular weight and molecular weight distribution on the basic rheological parameters is presented for linear polymers and for the case of long-chain branching. Illustrations are given of how this relationship with structure can be used to deduce molecular parameters from rheological measurements. The discussion of the various molecular mechanisms that contribute to rheological phenomena starts with reviewing the response of isolated molecules. In the subsequent sections, attention is mainly focused on polymer melts. After briefly treating transient network models the reptation approach is introduced. Starting from the basic theory, the various possible molecular mechanisms and their relaxational modes are added, as presented in the various more developed models. Again the emphasis is on linear and long-branched flexible polymers. In a final section one example of a deviating structure is treated, i.e. the case of rigid rod-like molecules. It provides an opportunity to present the rheology of liquid crystalline polymers.

1. Introduction

The properties of polymeric materials, either manmade or in living matter, differ substantially from those of other materials such as metals or ceramics. This is clearly illustrated by their rheological behavior. The viscoelastic phenomena encountered in most polymer liquids are a result of their flexible, chain-like structure. They can include high viscosities, pronounced time effects, strong normal stress differences and strain hardening in extensional flow. The exact nature of their rheological response is very sensitive to the details of their molecular architecture. Molecular models have been developed that provide a physical picture and a quite accurate description of most aspects of polymer rheology. Here, the basic rheological behavior and its links with the molecular structure are reviewed. The focus is on melts of the most representative types of polymers, i.e. linear flexible chains and macromolecules with long branches. The last section discusses some special classes of polymers.

2. Polymer Structure

The molecular characteristic that mainly distinguishes polymers from other materials is their very large molecular weight M. It is typically orders of magnitude larger than in classical low molecular weight materials and it can reach values of the order 10^6 Dalton. A polymer molecule contains one or a few types of building blocks, which are repeated many times in a single molecule. The repeating units can be connected in various ways. The most common architecture is that of a linear chain, the backbone atoms being connected by single bonds. Other structures are possible. They range from linear chains with short side chains, branched structures containing long chains up to interconnected, crosslinked systems. Even within these groups different structures can be distinguished. For instance, asymmetric monomers can be connected head-to-tail or head-to-head. Also, when there are long side chains they can be distributed more or less evenly along the backbone chain, as another extreme several chains can be concentrated at the end of a central chain. These are so-called pom-pom molecules. Different linear chains can also be connected at their end points in a star-like shape. Dendrimers are an extreme case where the molecule grows radially from a central unit in a compact, globular structure. When more than one repeating unit is used, in copolymers, the relative distribution of the different monomers is important. It ranges from statistical or alternating copolymers to block copolymers. The latter can display a rheology that is quite different from that of other polymers.

Chain architecture is an important factor when considering the rheological behavior. The chemical structure, however, does not fully describe the spatial layout of the molecule. The rotational freedom of atoms around single bonds, makes it possible for a linear chain to assume various conformations. Because of their thermal motion the elements of the chain change their relative position continuously in a polymer liquid. Hence the spatial distribution of the elements of a chain, i.e. its conformation, can only be described in statistical terms. In this context a totally stretched chain, respecting locally the bond angles, is very unlikely. The most probable conformation is that of a random coil. The dimensions of the coil depend not only on the molecular weight but also on the flexibility of the chain. The latter is strongly affected by the side groups that are present: bulky side groups are known to strongly reduce chain mobility. Also interactions between chain elements as well as those between chain elements and solvent molecules that might be present play a role. These interactions are governed by the normal intermolecular forces such as van der Waals forces, electrostatic interactions and hydrogen bonding. The degree of flexibility of a polymer is quite variable and is an important parameter that governs transition temperatures and the time scales of molecular relaxation mechanisms. Stiff chains have quite different rheological properties as exemplified by the liquid crystalline polymers.

In the case of dilute polymer solutions the conformation and flexibility of single, isolated macromolecules are the dominant factors. Because of the low concentration interactions between different molecules during flow are unlikely. In this chapter the emphasis is on melts. In melts the domains of the individual molecules then overlap, although their size is still close to that of the unperturbed chain in dilute solutions. The rheology of a melts or concentrated solutions differs nevertheless drastically from that of dilute solutions. Because of the interpenetration of the molecules their mobility is reduced. Macroscopic flow in particular is hindered as it requires whole molecules to move with respect to each other. The mutual hindrance of the individual polymer chains during their relative motion is topological in nature: the normal thermal motion of chain segments is constrained by the presence of the surrounding chain segments. These local constraints are known as *entanglements*.

3. General Rheological Behavior of Polymers

Although there are substantial differences between the rheological behaviors of the various types of polymers, some characteristics apply to most of those that contain flexible chains. Here the properties of linear flexible chains will be used to illustrate these general features. The class of linear chains includes important materials such as high-density polyethylene, polypropylene, polystyrene and the aliphatic polyamides. Steady and transient shear flows are considered as well as uniaxial extensional flow.

3.1. Steady State Flow

During flow a competition arises between the shear stresses, that tend to entrain the chain segments with the convective motion, and the thermal motion that tends to restore the equilibrium structure. The restoring force is entropic in nature and drives the structure to its statistically most probable random configuration. Flow causes a deformation of the molecular coil, more specifically stretching the segments. This can be directly observed with rheo-optical techniques. In concentrated solutions or melts stretching will depend on the connectivity between the chains. With less and/or more mobile entanglements the latter will slip more easily, allowing less stretching of the chain segments. The degree of entanglement can also be changed by flow as the molecules will become less intertwined in strong flows. This causes a change in rheological behavior according to the flow conditions. The results include a nonlinear response at high shear rates, as well as substantial differences between shear and extensional flow.

Plotting the viscosity η of linear and related polymers versus shear rate $(\dot{\gamma})$ produces a characteristic flow curve (Figure 1). At sufficiently low shear rates the behavior is Newtonian. The zero shear viscosity η_0 is much higher than in ordinary low molecular weight fluids. The viscosity remains constant and the thermal motion still dominates the flow-induced motion. At higher shear rates the flow starts to reduce the interpenetration and hence the interaction between molecules, which causes a gradual reduction in viscosity. The decrease can be substantial, i.e. orders of magnitude. In a logarithmic plot the viscosity curves tends to a constant slope, meaning that they can be described by a power law relation:

$$\eta(\dot{\gamma}) = k\dot{\gamma}^{n-1} \qquad (1)$$

in which k and the power law index n are model parameters. This equation is often used to describe stationary flow of polymer melts and solutions, e.g. in tubes. Various equations have been proposed to describe the complete viscosity curve. A common one is the Carreau-Yasuda equation:

$$\eta(\dot{\gamma}) = \eta_0 \left[1 + \lambda\left(\dot{\gamma}\right)^a\right]^{(n-1)/a} \qquad (2)$$

It is a generalization of the Cross equation, to which it reduces when $(n\text{-}1)/a = 1$.

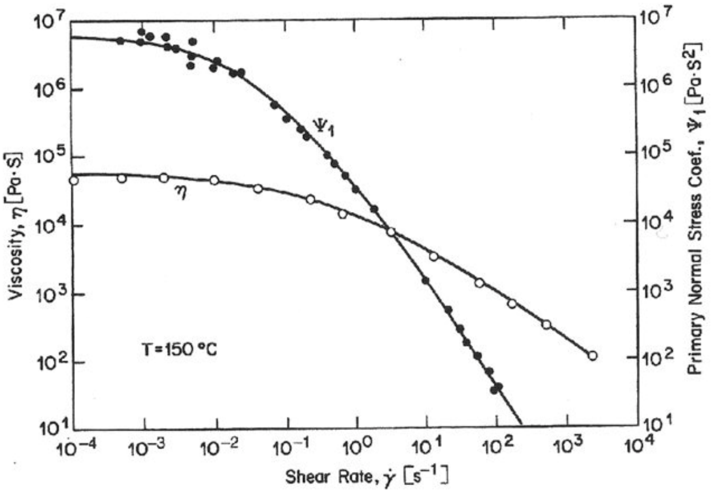

Figure 1. Typical viscosity and first normal stress functions for polymers, data on LDPE (from H.M. Laun, Rheol. Acta 1, 1978, with permission)

In steady state shear flow a polymer fluid is not just described by a viscosity function describing the shear stresses. The stresses normal to a plane are not equal in all directions as in low molecular weight liquids (see section 6), they also depend on shear rate. Hence, the shear rate dependence of the two normal stress difference N_1 and N_2 have to be specified to express the elastic effects. N_2 is very difficult to measure and is rarely reported. For polymers it is negative and its absolute value at zero shear is about 20-30% of that of N_1 and expected to become relatively smaller at higher shear rates. A typical first normal stress difference function $\psi_1(\dot{\gamma})\ (= N_1/\dot{\gamma}^2)$ is also shown in Figure 1. The shape is quite similar to that of the viscosity function, with a zero shear limit $\Psi_{1,0}$ and a power law dependency at high shear rates. Together with the viscosity function, the normal stress functions constitute the so-called *viscometric flow functions.*

3.2. Transient Shear Flow

In the linear region, a viscoelastic fluid can be completely described by a time-dependent *relaxation modulus* $G(t)$. It can, at least in principle, be fully derived from a relaxation experiment (see Figure 3). In such an experiment a constant strain γ is suddenly applied and the resulting decay of the stress $\sigma(t)$ is recorded. The ratio $\sigma(t)/\gamma$, i.e. $G(t)$, is independent of strain for small strains. When higher strains are applied the relaxation modulus $G(t,\gamma)$ gradually decreases with strain (Figure 2). Except for a region at short times the curves of log G versus log t for a given strains are then parallel with the linear curve. Hence they can be superimposed on $G(t)$ by a vertically shift $h(\gamma)$ called the *damping function*.

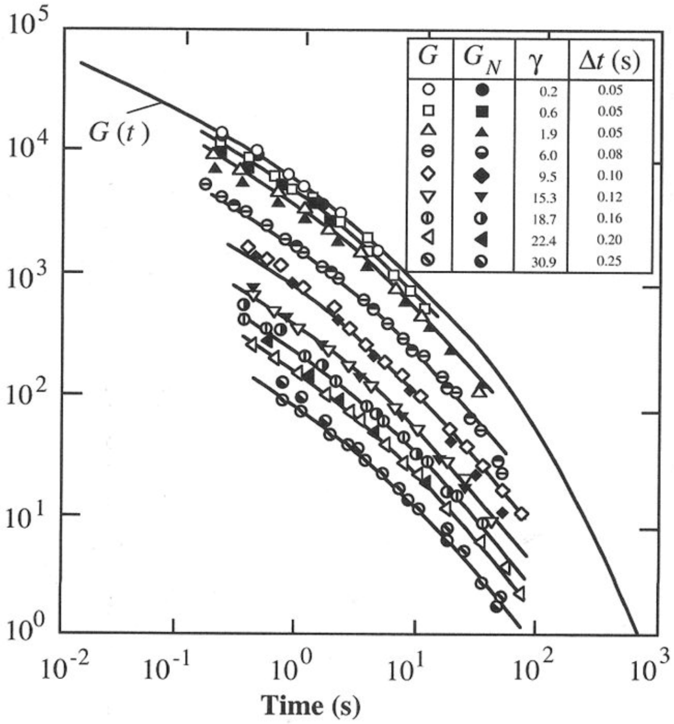

Figure 2. Relaxation moduli at different strains (data on LDPE), curves for large strains are shifted parallel to the linear curve (data from H.M. Laun, Rheol. Acta 1, 1978, Figure from C.W. Macosko, 1994).

The existence of a parallel shift for polymers is important. It means that the nonlinear time-dependent behavior can be expressed by the product of a time function and a strain function:

$$G(t,\gamma) = G(t).h(\gamma) \tag{3}$$

This time-strain separability simplifies considerably the constitutive equations that have to be used to describe the nonlinear viscoelastic behavior of polymers. As is common for general linear models, $G(t)$ is normally expressed as a summation of exponentials. For $h(\gamma)$ several empirical functions have been proposed.

A second type of transient experiment consists in applying suddenly a constant shear rate or constant shear stress. In a start-up flow a constant shear rate is applied. Typical time functions for the transient viscosities $\eta^{+}(\dot{\gamma},t)$ and transient first normal stress coefficient $\psi_1^{+}(\dot{\gamma},t)$ are shown in Figure 3. When plotting these coefficients rather than the stresses themselves, the curves for different shear rates coincide at low shear rates. They reflect linear viscoelastic behavior and can be calculated from $G(t)$. This is also the case for $\psi_1^{+}(\dot{\gamma},t)$ although the normal stress differences are actually nonlinear properties. At higher shear rates the initial parts of the curves remain identical but afterwards the stress transients drop systematically below the low shear limit. At the same time a gradually growing overshoot emerges with increasing shear rate. In not too extreme conditions the peak shear stresses occur at the same strain at all shear rates, the same holds for the normal stresses. The shear stresses reach their peak value at a strain of about 2-2.5, for the first normal stress difference this strain is twice as high. When the shear flow is arrested after the steady state has been reached, the stresses will relax (*relaxation upon cessation of flow*). In the low shear limit the curves for the relaxing viscosity $\eta^{-}(\dot{\gamma},t)$ $\eta^{-}\left(\dot{\gamma},t\right)$ again coincide for different shear rates and can be calculated from $G(t)$ according to the rules of the theory of linear viscoelasticity. At higher shear rates the stresses decay faster. Nonlinear relaxation after cessation of flow is not commonly used to probe nonlinearities.

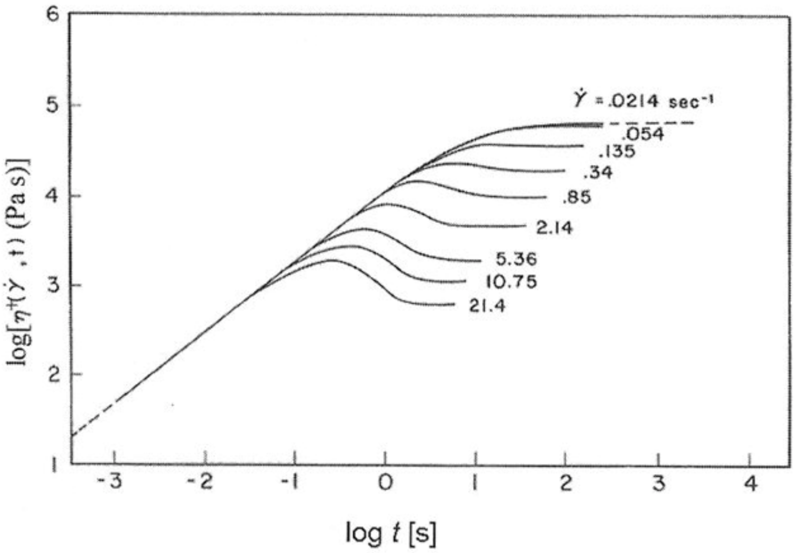

Figure 3. Transient viscosities at different shear rates in the nonlinear region, deviations from linearity and development of a stress overshoot (from Menezes and Graessley, Rheol. Acta 19, 1980, with permission)

In a creep experiment a constant shear stress σ is applied and the ensuing evolution of the strain is measured. To superimpose the data at small shear stresses the compliance $J(\sigma,t)$ i.e. $\gamma(t)/\sigma$ is plotted instead of the strain itself. Again the strain transient or the compliance can be derived from a characteristic function of the linear viscoelasticity such as $G(t)$. After a sufficiently long time the rate of strain becomes constant, corresponding to the steady state viscosity at that stress level. Extrapolating this line back to time zero gives as intercept the steady state shear compliance J_s^0. With increasing shear stress the final rate of strain will gradually increase less than proportional to the shear stress, signaling the onset of the non-Newtonian region. At the end of a creep experiment the stress can be suddenly released. Because of the residual elasticity the sample will recoil back. The final value of the recoil, the *recoverable strain* $\gamma_{\mathrm{r},\infty}$ is a linear function of shear stress at low stresses (Figure 4). It also provides a measure of the steady state compliance and is linked to the low shear characteristics of the polymer:

$$\lim_{\sigma\to 0}\gamma_{\mathrm{r},\infty}(\sigma)=\lim_{\sigma\to\infty}\sigma J_{\mathrm{s}}^{0}=\lim_{\dot{\gamma}\to\infty}\psi_{1.0}\dot{\gamma}/2\eta_{0} \qquad (4)$$

At higher shear rates the recoil increases less than linear with the shear rate and finally levels off at a limiting value, which can be several strain units (Figure 4).

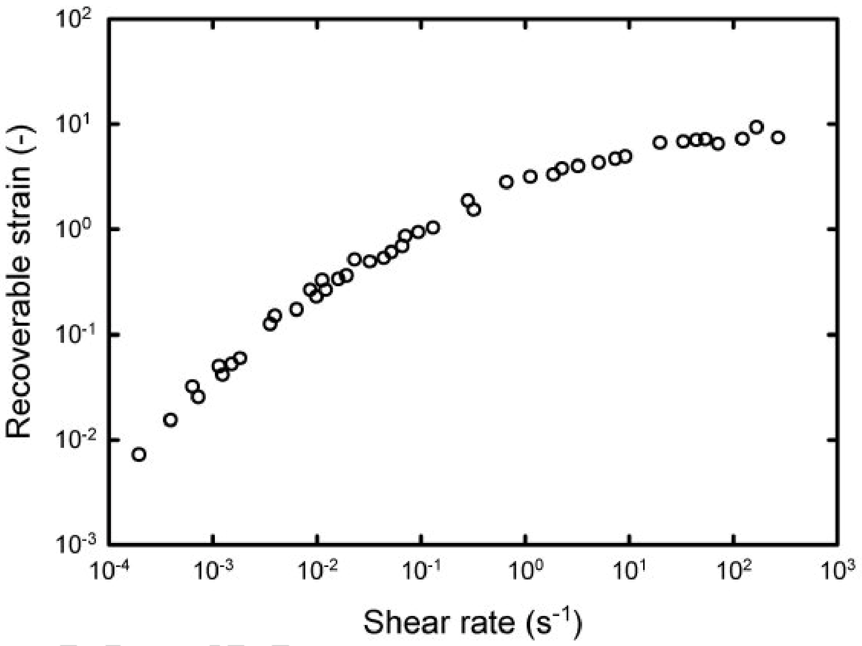

Figure 4: Evolution of the recoverable strain with shear rate for an LDPE (based on data from H.M. Laun, J. Rheol. 30, 484, 1986).

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Biographical Sketches

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.

Jan Mewis was born in Borgerhout (Belgium) on April 22, 1938. He obtained his M.Chem.E. (1961) and Ph.D (1967) from the K.U.Leuven. He worked for I.V.P. (the laboratory of the Belgian Paint and Printing Ink Industry) (1964-1969) before joining the faculty of the Chem.E. Department at K.U.Leuven. There he initiated the Laboratory of Applied Rheology and Polymer Processing. His research activities are in the field of rheology and processing of complex fluids, mainly dealing with colloidal suspensions and complex polymers. He also chaired the Chem. E. department at K.U.Leuven for 9 years, he is professor-emeritus since 2003. He was visiting professor at the University of Delaware (1981, 2004) and at Princeton University (1982). He was chairman of the International Committee on Rheology from 1992 to 1996. In 2005 he received the Gold Medal of the British Society of Rheology and the Bingham medal of The Society of Rheology (US).