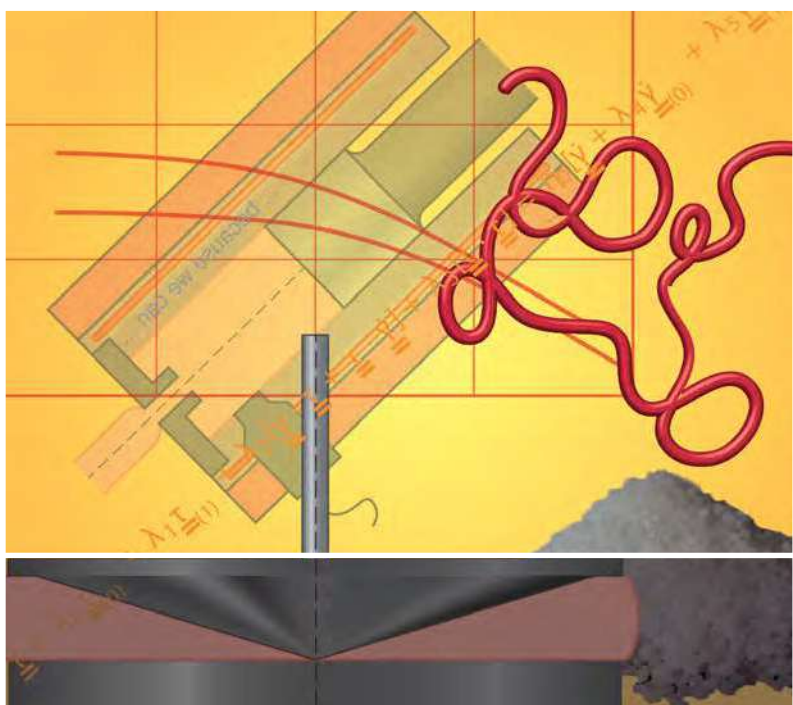


Tim A. Osswald
Natalie Rudolph

Polymer Rheology

Fundamentals and Applications



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Dedication

We dedicate this book to our friend, colleague, and mentor Professor Dr.-Ing. Dr. h.c. Gottfried W. Ehrenstein. His lifelong commitment to learning, teaching, and research has inspired more than a generation of students and engineers, and has resulted in a continuous flow of ideas and innovation in plastics technology.

Preface

Designed to provide a polymer rheology background to both engineering students and practicing engineers, this book is written at an intermediate level with the technical information and practical examples required to enable the reader to understand the complex rheological behavior of polymers and its far-reaching consequences. It also provides the necessary decision-making tools for the appropriate choice of rheological testing methods, and the means to troubleshoot rheology related problems encountered in polymer processing. The organization of Polymer Rheology – Fundamentals and Applications and the practical examples throughout the book make it an ideal textbook and reference book, and the information provided is particularly valuable to processors and raw materials suppliers.

The authors would like to acknowledge the invaluable help of many during the preparation of this manuscript: our colleagues at the Polymer Engineering Center at the University of Wisconsin-Madison and at the Institute for Polymer Technology at the Friedrich-Alexander-University in Erlangen, Germany. In particular we would like to thank Dr. Andrew Schmalzer for serving as a sounding board and for his input, John Puentes for helping with the example problems in Chapter 4, Chuanchom Aumnate for the measurements used in the examples in Chapters 2 and 5, and Camilo Perez for reviewing Chapter 3. We are grateful to Tobias Mattner for his outstanding job in not only drawing the figures, but also making excellent suggestions on how to more clearly present the information. Thanks are due to Dr. Christine Strohm for her valuable expertise in editing this book. Dr. Nadine Warkotsch, Dr. Mark Smith and Jörg Strohbach of Carl Hanser Verlag in Munich are thanked for their support throughout this project. Above all, the authors would like to thank their families for their continued support of their work and their input throughout the writing of this book.

Summer 2014

Tim Osswald and Natalie Rudolph
Madison, Wisconsin, USA

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1

Introduction to Rheology

On December 9th of 1929, a little over a month after the Wall Street crash, and seven years after he published his book *Fluidity and Plasticity* [1], Eugene Bingham (Fig. 1.1), a chemistry professor at Lafayette College in Easton, Pennsylvania, and a group of chemists, engineers, and physicists met for the first time in Washington D.C.; they called themselves the *Society of Rheology*. Hence, for the first time the word rheology, coined by Markus Reiner and Eugene Bingham in 1920, was officially used¹.



Figure 1.1

Professor Eugene Bingham, in 1945 shortly before his death (Courtesy of Special Collections & College Archives, Skillman Library, Lafayette College)

¹ The roots of the word rheology are the Greek “reo” (flow) and “logos” (study).

However, the history of the field of rheology goes back centuries prior to Bingham and Reiner. A historical review is not complete until the more important events and discoveries through time, and the people who made those events and discoveries possible, have been identified. In Table 1.1 we list these events, discoveries, and important publications. If we inadvertently left out some, we apologize.

Table 1.1 Historical overview of the field of rheology

When	Who	What	Ref
1663	B. Pascal	Published works on inviscid fluids	[2]
1678	R. Hooke	Published work on elastic springs	[3]
1687	I. S. Newton	Published work on viscous fluids	[4]
1705	Bernoulli brothers	Publish the Bernoulli equation	[5]
1807	T. Young	Proposes the elastic (Young's) modulus	[6]
1820	C. Navier	Describes behavior of Newtonian fluids which eventually becomes the Navier-Stokes equation	[7]
1822	A. Cauchy	Describes stress and strain and formulates the Cauchy deformation tensor	[7]
1829	S. Poisson	Describes Poisson's ratio, ν	[8]
1839	G. Hagen	Builds the first capillary viscometer	[9]
1840	J. L. M. Poiseuille	Studies the rheology of blood and builds a capillary viscometer	[10]
1845	G. G. Stokes	Formulates a three dimensional Newtonian fluid model	[11]
1849	G. G. Stokes	Studies the parabolic velocity distribution in a capillary	[5]
1851	G. G. Stokes	Sphere fall experiments	[12]
1859	A. V. Lourenço	Observes viscosity increase with an increase in molecular weight	[13]
1861	A. Lipowitz	Builds a penetrometer to measure the hardness of a gel with a sinking weight	[14]
1861	T. Graham	Coins the word "Colloid"	[15]
1867	J. C. Maxwell	Formulates the viscoelastic Maxwell model	[16]
1873	J. D. Van der Waals	Publishes work on intramolecular forces	[17]
1874	L. Boltzmann	Publishes the superposition principle	[18]
1876	L. Boltzmann	Publishes work on the memory function	[19]
1881	M. Margules	Derives equations that describe the viscosity in the shear flow between two concentric cylinders	[20]
1886	M. M. Couette	Derives equations that describe the viscosity in the shear flow between two concentric cylinders	[21]
1888	M. M. Couette	Builds the first concentric cylinder system to measure viscosity; the drag flow viscometer or the Couette device	[22]
1890	W. Thomson-Kelvin	Describes a "solid viscosity", meaning a viscoelastic solid, known today as the Kelvin model	[5]
1890	W. Voigt	Publishes experiments on viscoelastic solids	[23]
1891	W. Ostwald	Builds a capillary viscometer, Ostwald viscosimeter	[14]

Table 1.1 (*continued*) Historical overview of the field of rheology

When	Who	What	Ref
1894	J. Finger	Formulates the Finger-Strain Tensor for shear and elongational deformation test specimens	[24]
1905	F. T. Trouton	Derives the equation $\mu_E = 3\mu_S$, which describes the relation between elongational and shear viscosities, known today as the Trouton viscosity	[25]
1906	A. Einstein	Derives the equation $\mu = \mu_0(1 + 2.5\phi)$, which defines the viscosity of a suspension as a function of the volume fraction of solid particles	[26]
1916	E. Bingham	Describes fluids with a yield stress; the Bingham fluid	[27]
1920	H. Staudinger	Describes polymers as rigid rods that he calls macromolecules	[28]
1922	E. Bingham	Publishes his book “Fluidity and Plasticity”	[29]
1923	A. de Waele	Derives a power relation between viscosity and rate of deformation; the power-law model.	[30]
1925	W. Ostwald	Two years after de Waele, derives the power relation between viscosity and rate of deformation; the power-law model or the Ostwald-de Waele model	[31]
1927	S. B. Ellis	Publishes work on flow behavior	[5]
1928	E. Hatschek	Publishes his book “The Viscosity of Liquids”	[32]
1929	E. Bingham	Founds the Society of Rheology	[33]
1929	R. Eisenschitz, B. Rabinowitsch and K. Weissenberg	Propose the rheological energy triangle	[34]
1929	B. Rabinowitsch	Derives a correction factor for the shear rate of non-Newtonian fluids in capillary viscometers	[35]
1929	H. Jeffreys	Publishes his book “The Earth”, in which he describes “elastoviscous” (viscoelastic fluids) materials	[36]
1930	C. W. Brabender	Builds a dough kneader; Farinograph or Extensograph	[14]
1931	A. Nadai	Publishes his book “Plasticity”	[37]
1934	M. Mooney	Proposes a “shearing disc viscometer” or parallel disc viscometer	[38]
1934	M. Mooney and R. H. Ewart	For the first time use a cone-and-plate rheometer	[39]
1935	H. Freundlich	Coins the word “Thixotropy” to describe changes in fluid behavior caused by movement	[40]
1935	J. M. Burgers	Develops a viscoelastic model by combining the Maxwell and the Kelvin-Voigt models	[41]
1936	E. Guth and R. Simha	Modify Einstein’s 1906 equation to $\mu = \mu_0(1 + 2.5\phi + 14.1\phi^2)$ for the viscosity of a suspension	[42]
1938	G. W. S. Blair	Publishes his book “An Introduction to Industrial Rheology”, for the first time using the word “rheology” in the title of a book	[43]
1940	M. Mooney	Publishes work on rubber elasticity	[44]
1945	M. Reiner	Proposes that the theories of fluid viscosity also apply to polymer melts	[45]

Table 1.1 (*continued*) Historical overview of the field of rheology

When	Who	What	Ref
1945	Brookfield Company	First Brookfield rotational viscometer is marketed in Stoughton, Massachusetts	[46]
1946	M. S. Green and A. V. Tobolsky	Propose the Transient Network Model for uncross-linked polymers	[47]
1946	R. J. Russell	Measures normal stresses using parallel disc and cone-and-plate rheometers	[48]
1947	K. Weissenberg	Discovers the rod climbing effect, today known as the Weissenberg Effect	[49]
1948	R. S. Rivlin	Applies theories of fluid viscosity to polymer melts	[50]
1948	G. W. S. Blair	First International Congress on Rheology	[51]
1953	P. E. J. Rouse	Proposes a bead-spring model for cross-linked polymers; known as the Rouse model	[52]
1955	M. L. Williams, R. F. Landel and J. D. Ferry	Propose the time-temperature superposition principle	[53]
1955	Haake Company	Rotational viscometer is marketed in Berlin and Karlsruhe, Germany	[46]
1956	B. H. Zimm	Includes hydrodynamic interactions in the Rouse model for dilute polymeric suspensions: Rouse-Zimm model.	[54]
1956	A. Lodge	Expands the Transient Network Model by Green and Tobolsky	[55]
1956	F. R. Eyrich	Publishes his book “Rheology – Theory and Applications”	[56]
1957	E. B. Bagley	Derives the entrance pressure corrections for capillary viscometers, known today as Bagley end correction factor	[57]
1958	W. P. Cox and E. H. Merz	Propose a relation between frequency in the oscillatory test and rate of deformation in the rotational viscometer (Cox-Mertz relation)	[58]
1960	R. B. Bird, W. E. Stewart and E. Lightfoot	Publish their book “Transport Phenomena”, nicknamed “BSL”	[59]
1960	A. S. Lodge	Publishes his book “Elastic Liquids”	[60]
1960	M. Reiner	Publishes his book “Deformation, Strain and Flow”	[61]
1962	A. Kaye	Develops the integral viscoelastic model that later became known as the K-BKZ model	[62]
1963	B. Bernstein, E. Kearsley and L. Zapas	Develop the integral viscoelastic model that Kaye published 2 years earlier. The model became known as the K-BKZ model	[63]
1965	M. M. Cross	Proposes the Cross model for shear-thinning fluids with a small shear rate Newtonian plateau	[64]
1966	H. Giesekus	Develops the differential viscoelastic model that became known as the Giesekus model	[65]
1967	S. F. Edwards	Proposes Entanglement Theory for polymers	[66]
1968	P. J. Carreau	Proposes a viscosity model with a small and large shear rate Newtonian plateau; Bird-Carreau Model	[67]

Table 1.1 (*continued*) Historical overview of the field of rheology

When	Who	What	Ref
1969	J. Meissner	Designs the uniaxial elongational rheometer	[68]
1971	P. G. DeGennes	Proposes the Reptation Model for polymer molecules	[69]
1977	R. B. Bird, R. C. Armstrong and O. Hassager	Publish their book “Dynamics of Polymeric Liquids”	[70]
1977	R. B. Bird, O. Hassager, R. C. Armstrong and C. F. Curtis	Publish their book “Kinetic Theory”	[71]
1982	J. M. Dealy	Publishes his book “Rheometers for Molten Plastics”	[72]
1985	R. B. Bird and H. Giesekus	Develop model for non-linear deformation behavior	[46]
1986	M. Doi and S. F. Edwards	Further develop the Reptation model	[73]
1990	J. M. Dealy and K. F. Wissbrun	Publish their book “Melt Rheology and Its Role in Plastics Processing”	[74]
1994	C. W. Macosko	Publishes his book “Rheology: Principles, Measurements and Applications”	[75]
1997	P. J. Carreau, D. C. R. DeKee and R. P. Chhabra	Publish their book “Rheology of Polymeric Systems – Principles and Applications”	[76]

■ 1.1 The Field of Rheology

While the motto of the Society of Rheology has always been the quote by Simplicius and Heraclitus “Πάντα ῥεῖ” (Panta rei) [77–81] or “everything flows,” the field of rheology covers the behavior of perfectly viscous liquid (Newtonian fluid) materials and perfectly elastic solid (Hookean solid) materials, as depicted in the diagram in Fig. 1.2. From the outside, rheology is framed by the rigid solid, or Euclidean solid, and the ideal inviscid fluid, or Pascalian fluid. The Euclidean solid and Pascalian fluid are both mathematical idealizations. In the case of the Euclidean solid we assume that the body does not deform, and when it moves, it does so by pure translation and rotation. On the other hand, the assumption for the Pascalian fluid is that the stresses acting on the fluid are only a result of pressure, or hydrostatic stresses, and not the result of deformation during flow. From a material behavior point of view, a Euclidean solid has an infinite modulus, while a Pascalian fluid exhibits zero viscosity, two unrealistic extremes.

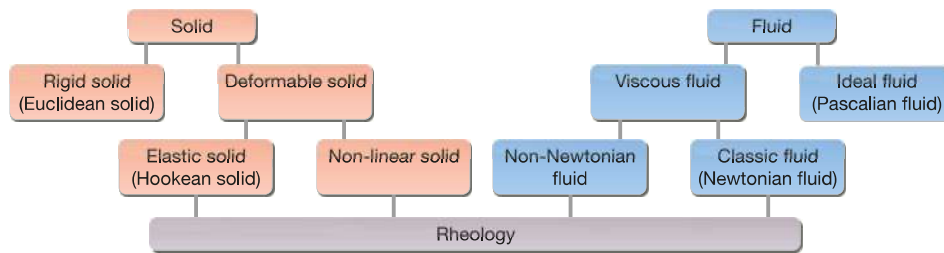


Figure 1.2 The field of rheology in perspective

While the field of rheology encompasses materials with a finite modulus and a measurable viscosity, most materials are neither perfectly viscous liquids nor perfectly elastic solids, but viscoelastic materials that can be described from a fluids or a solids point of view by a rheologist or a solid mechanician, respectively. Either way, when deforming complex materials such as polymers, there will always be a viscous and an elastic force component. To simplify our lives and make calculations and predictions possible, particularly when the flow geometry is complex, such as plastic flow during injection molding, we often drop the elastic response of plastics during flow.

In 1929, Eisenschitz, Rabinowitsch, and Weissenberg [7] proposed a triangular coordinate system (Fig. 1.3) to clarify the boundaries of the field of rheology. It represents the work or energy in all rheological phenomena in the form of kinetic energy, elastic or stored energy, and dissipated or lost energy. It is a simple and descriptive way to illustrate the interconnection between these energies or work. In most cases, the state of a body or system is represented by a point in the interior of the triangle, where the distance a is the fraction of the total energy represented by kinetic energy, b is the fraction representing elastic or stored energy, and c is the fraction representing dissipated or lost energy, such that

$$a + b + c = 1 \quad (1.1)$$

Eisenschitz, Rabinowitsch and Weissenberg called the line AB “Elasticity,” which represents a Hookean solid or perfectly elastic solid. Vertex A represents a pure Euclidean solid (or Pascalian liquid when on line AC) where all the external work is converted to kinetic energy, as would be the case for an infinitely stiff body. Furthermore, they called line AC “Viscosity,” which represents a Newtonian fluid or perfectly viscous liquid where all external work is dissipated or lost. On that line, vertex A represents an infinite Reynolds number in fluid mechanics. Line BC , which they called “Relaxation,” represents creeping viscoelastic flows, and is the domain where we typically see the field of rheology of highly viscous materials such as polymers. Vertex C represents a creeping flow or Stokes flow where the Reynolds number is very low. In such flows inertial effects are negligible when compared to the forces caused by viscous friction.

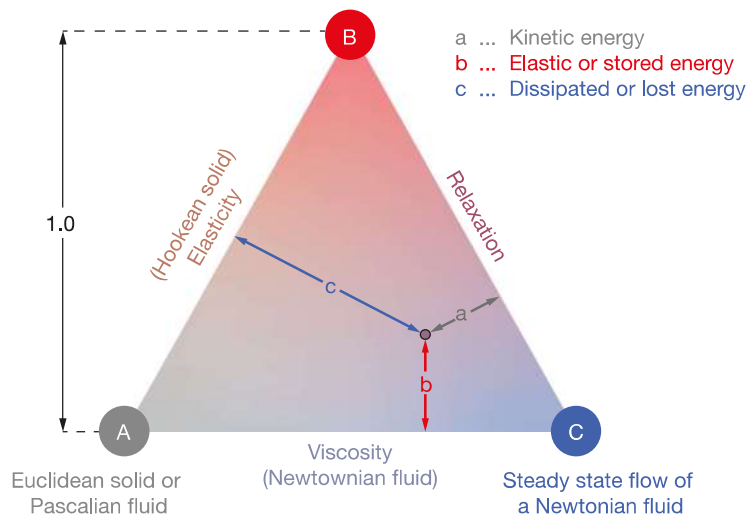


Figure 1.3 Rheological energy in triangular coordinates

1.2 Viscous Liquids or the Newtonian Fluid

Sir Isaac Newton (Fig. 1.4) was the first person to formulate a hypothesis that described the resistance to motion experienced by deforming fluids. In 1686 he published this work in *Philosophiæ Naturalis Principia Mathematica* [4] in a chapter titled “On the Circular Motion of Liquids”. His hypothesis clearly states what we know today as a characteristic of a Newtonian fluid²:

That the resistance which arises from the lack of slipperiness of the parts of the fluid, other things being equal, is proportional to the velocity with which the parts of the liquid are separated from one another.

The phenomenon, described by Newton as “*defectu lubricitatis*,” or “lack of slipperiness” between two fluid particles, was attributed to “*attritus*,” meaning internal friction, or viscous friction. Since that time, the term “internal friction” and “viscous friction” have been used interchangeably. Although Newton’s original work contains a mistake, corrected by Sir George Stokes [3] 150 years later, his main conclusion is still correct; it basically states that the force F required to maintain the motion between two fluid planes located at two arbitrary positions, say C and D in Newton’s diagram (Fig. 1.5), is proportional to the difference between the velocity, u , of the

² The authors are using Emil Hatschek’s translation from the Latin [2].

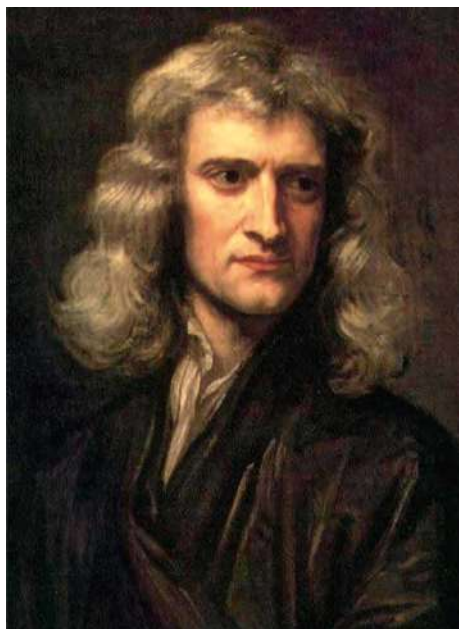


Figure 1.4
Sir Isaac Newton (1643–1727),
painted in 1689 by Sir Godfrey Kneller

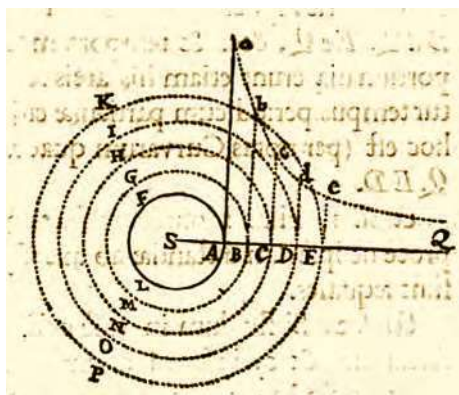


Figure 1.5
Diagram from Newton's 1686 publication [2]

two planes, and inversely proportional to the distance, r , between those two surfaces, the viscosity, η , and the area of the surfaces that separates them, A ,³

$$F = A\eta \frac{u_d - u_c}{r_d - r_c} \quad (1.2)$$

³ Newton used upper case A, B, C, D, etc. to describe the position of the surfaces, and lower case a, b, c, d, etc. to describe the velocity of those surfaces.

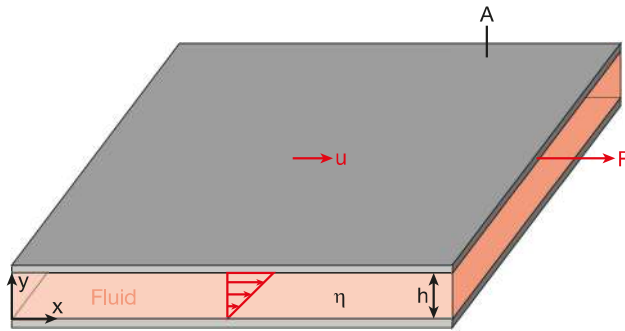


Figure 1.6 Simple shear flow with Cartesian coordinates

As shown in Newton's diagram, his analysis pertained to a rotating cylinder immersed in an infinitely large fluid body. For a more simplified system, such as the simple shear flow generated between two parallel plates presented in Fig. 1.6, Equation 1.2 can be expressed in terms of shear stress, and written as

$$F/A = \eta \frac{u}{h} \quad (1.3)$$

or

$$\tau_{xy} = \eta \dot{\gamma}_{xy} \quad (1.4)$$

where τ_{xy} is the shear stress in the x direction on a plane with its normal direction pointing in the y direction, and $\dot{\gamma}_{xy}$ is the corresponding rate of shear, or rate of deformation. The stress (here τ_{xy}) that leads to the deformation of the fluid contained within the system is also often referred to as the deviatoric stress⁴.

The Newtonian model, or the viscous component of a material, is often also represented using a dashpot, shown in Fig. 1.7.

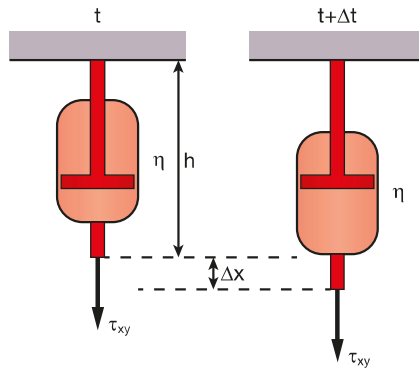


Figure 1.7 The dashpot – a schematic representation of a Newtonian fluid

⁴ As will be shown in Chapter 2, which covers flow, the total stress, σ , is divided into the deviatoric stress component, τ , which causes deformation, and the hydrostatic stress component, which results from pressure, p .

While the schematic representation in Fig. 1.7 reflects an elongational deformation along the x -axis, the dashpot can also be used for shear deformation, which is written as

$$\gamma_{xy} = \frac{\Delta x}{h} \quad (1.5)$$

Figure 1.7 also shows that the deformation is time dependent and, in the case of a Newtonian fluid, the dependence between deformation and time is linear. In terms of shear strain rate, we can write

$$\gamma_{xy} = \dot{\gamma}_{xy} \Delta t \quad (1.6)$$

In Fig. 1.8, the strain within a Newtonian fluid, labeled as viscous strain, is presented for the case where a constant stress is applied during a time period from 0 to Δt . Once the load is released at time Δt , the material element remains deformed. This reflects point “C” in the Eissenschitz, Rabinowitsch and Weissenberg triangle, at which all energy is dissipated or lost and the deformation can no longer be recovered.

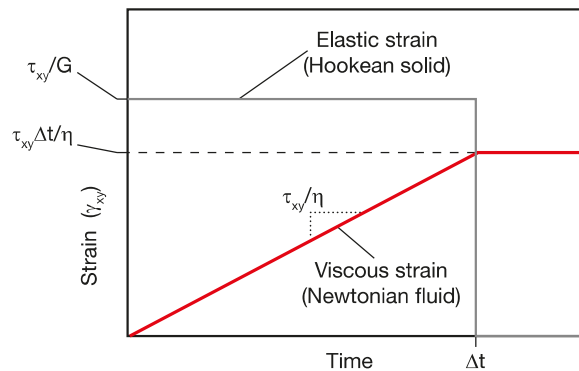


Figure 1.8 Strain response of a Newtonian fluid and a Hookean solid

■ 1.3 Linear Elasticity or the Hookean Spring

Robert Hooke is a relatively unknown English scientist and engineer of the 17th century, who was completely overshadowed by his contemporary, Isaac Newton. In fact, an animosity between the two existed after Hooke claimed that Newton's work on gravitation was based on work he had done. As a result, Newton's obsession was to make sure that Hooke be forgotten; something he almost accomplished. Two years after Hooke's death in 1703, Newton became president of the Royal Society, and in that function made sure that every memory of Hooke was erased from the society, including his portrait and laboratory equipment, which mysteriously disappeared when the Royal Society moved to a new location after 1705.

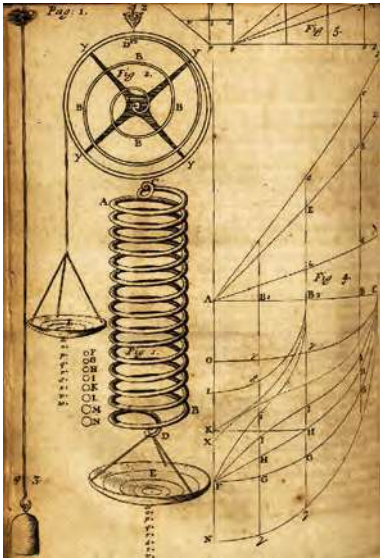


Figure 1.9 Diagram from Hooke's 1678 paper

However, while Hooke is certainly not part of popular culture in the way Newton has become, today his name remains well known among engineers who deal with solid mechanics, thanks to his theory of linear elasticity. Robert Hooke was the first person to find a relation between force and deflection in linear elastic solids, and published that work in his 1678's "*Lectures de Potentia Restitutiva*," or, "Of Spring". The basic theory behind what we today refer to as the Hookean spring (Fig. 1.9) is summarized in Latin by Hooke's words "*Ut tensio sic vis*" or "*As the extension, so the force*." More simply stated, we can say that the force, F , is directly proportional to the deflection, Δx . This can be written using

$$F = k \Delta x \quad (1.7)$$

where k is the constant of proportionality or the spring constant, also called the stiffness. Hooke's concept was modified in 1727 by Leonhard Euler, who represented the force in terms of stress, F/A , and the displacement in terms of strain, $\Delta x/h$, where h represents the original length. The units in the constant of proportionality can be adjusted by using a modulus of elasticity or stiffness, E , or for a system that is deformed in shear, such as the one depicted in Fig. 1.10, a modulus of rigidity, G ,

$$F/A = G (\Delta x/h) \quad (1.8)$$

In terms of stress and strain the above equation can be written as

$$\tau_{xy} = G \gamma_{xy} \quad (1.9)$$

where τ_{xy} is the shear stress and γ_{xy} the corresponding shear strain.

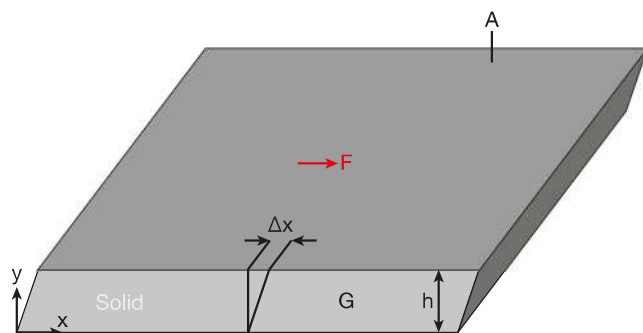


Figure 1.10 Perfectly Hookean solid deformed in shear

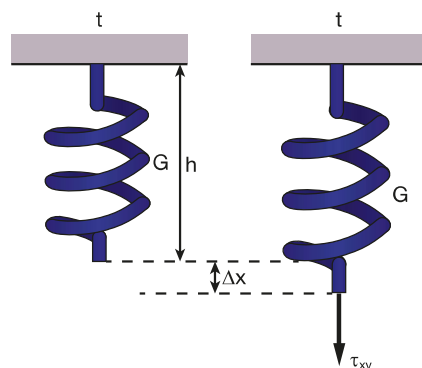


Figure 1.11 The spring – a schematic representation of a Hookean solid

Just like Hooke's approach in 1678, today the elastic component of a material is often represented using a spring, as shown in Fig. 1.11. The spring reflects a stretching body; however, it can also be used to represent shear. In Fig. 1.11 we can see how the spring deforms as soon as the load is applied and remains constant as long as the load remains the same. Once the load is released at time Δt , the material element will almost instantly return to its initial shape. This reflects point "B" in the Eissenschitz, Rabinowitsch and Weissenberg triangle, where the energy is stored and fully recovered.

In his publication, Robert Hooke boldly concluded that the elastic behavior is not only observed in springs, "but in all other springy bodies whatsoever, whether Metal, Wood, Stones, baked Earths, Hair, Horns, Silk, Bones, Sinews, Glass, and the like." His statement may be true for metal, stone, baked earths, and perhaps glass; however, all the other materials have a viscous force component, introducing time dependency when they are deformed, and should therefore be considered as viscoelastic materials.

1.4 Viscoelasticity and the Maxwell Model

After Newton and Hooke proposed their fluid and solid models, the world would have to wait almost two centuries before someone would attempt to model the behavior of a body that has both a viscous and an elastic force component during deformation. In 1867, James Clerk Maxwell (Fig. 1.12) published his paper “On the Dynamical Theory of Gases” [16], in which he presented a model for a system that combines elastic and viscous effects. His model and the resulting linear differential equations that relate stress and strain represent today’s Maxwell model, which is graphically depicted by an instantaneous change of the spring and a time-dependent reaction, $t + \Delta t$, of the dash-pot in series, as depicted in Fig. 1.13.

In principle, the model is based on the fact that when a stress τ_{xy} is applied to the system, this stress is the same in both fluid and solid elements, and the total strain is the sum of the elastic strain, γ_{xy}^G , and the viscous strain, γ_{xy}^η , such that

$$\tau_{xy} = \tau_{xy}^\eta = \tau_{xy}^G \quad (1.10)$$

and

$$\gamma_{xy} = \gamma_{xy}^G + \gamma_{xy}^\eta \quad (1.11)$$

which can also be differentiated in time to give a function for total rate of deformation, or rate of strain

$$\dot{\gamma}_{xy} = \dot{\gamma}_{xy}^G + \dot{\gamma}_{xy}^\eta \quad (1.12)$$



Figure 1.12
James Clerk Maxwell

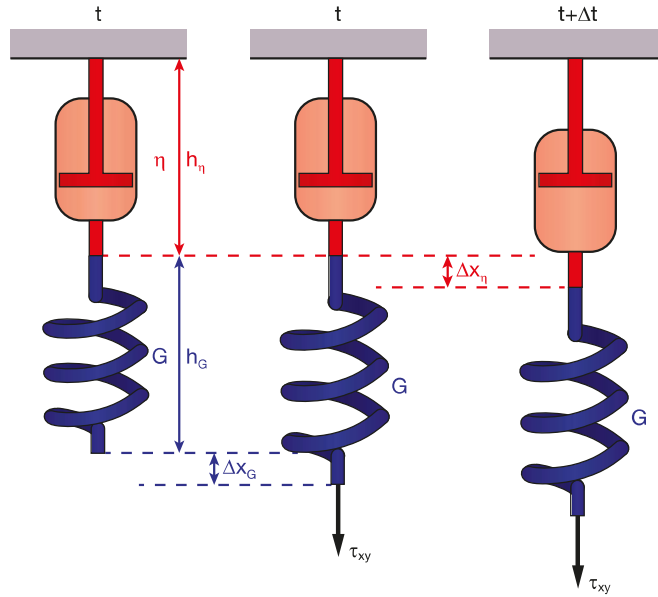


Figure 1.13 Schematic representation of the viscoelastic Maxwell model

Combining Eqs. 1.10–1.12 with the constitutive laws for the dash-pot (Eq. 1.4) and the spring (Eq. 1.9), results in Maxwell’s linear differential equation given by

$$\frac{d\tau_{xy}}{dt} = G \frac{d\gamma_{xy}}{dt} - \frac{\tau_{xy}}{\lambda} \quad (1.13)$$

where $\lambda = G/\eta$, which Maxwell called “time of relaxation”, and which is now commonly referred to as relaxation time.

In the case of constant stress, Maxwell’s linear differential equation is solved for strain

$$\gamma_{xy} = \frac{\tau_{xy}}{\eta} t + \frac{\tau_{xy}}{G} \quad (1.14)$$

which is schematically shown in Fig. 1.14 for the case where the constant stress τ_{xy} is applied from $t = 0$ to $t = \Delta t$. The figure shows how the material element experiences an instant deflection, caused by its elastic component, and continues to deform at a constant rate, caused by its viscous component. The continuous flow experienced by the material under constant load is commonly referred to as creep or retardation. Once the load is released, the stored elastic deformation is recovered, and the viscous deformation remains.

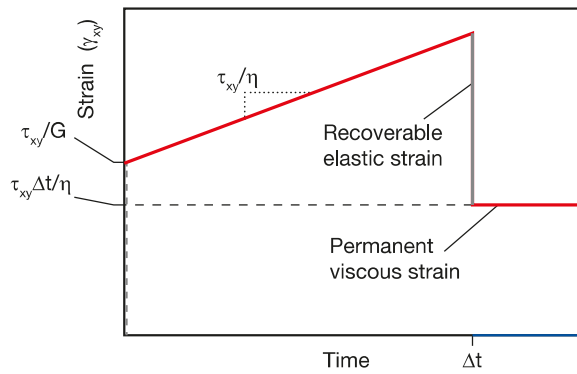


Figure 1.14 Creep in a Maxwell model

In the case of constant strain applied to the Maxwell material model, the linear differential equation is solved for stress

$$\tau_{xy} = G \gamma_{xy} e^{-\frac{t}{\lambda}} \quad (1.15)$$

which is schematically depicted in Fig. 1.15 for a case where $G = 100 \text{ MPa}$, $\lambda = 1 \text{ s}$ and the imposed strain $\gamma_{xy} = 1$. Here, we see a gradual reduction in stress, a phenomenon commonly referred to as stress relaxation, which is represented by the line BC on the Eisenschitz, Rabinowitsch and Weissenberg triangle (see Fig. 1.3). At point B in their triangle, the relaxation time λ is infinite, reflecting a Hookean solid, while at position C it is zero, which reflects a Newtonian fluid.

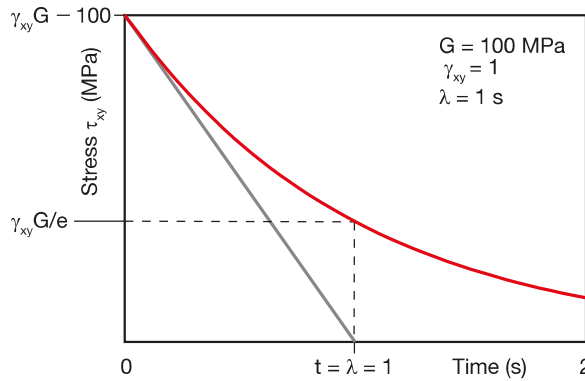


Figure 1.15 Stress relaxation in a Maxwell model

1.5 Time Scale and the Deborah Number

As Maxwell's model easily demonstrates, relaxation time is a property characteristic of a specific material, and the relaxation time limits of zero and infinite frame the field of rheology, ranging from a solid to a liquid. However, when studying a material we need to consider not only its relaxation time, but also the time scale of the process to which the material is subjected under specific circumstances. For example, how fast or how slowly is the material being deformed, or the length of the residence time of a polymer inside an extrusion die.

Returning to Maxwell's model, we can also deform the system at a constant rate of deformation $\dot{\gamma}_{xy}$. For this specific case, Maxwell's model can be solved for stress

$$\tau_{xy} = G \dot{\gamma}_{xy} \left(1 - e^{-\frac{t}{\lambda}} \right) \quad (1.16)$$

Figure 1.16 presents the stress as a function of strain for three different rates of deformation, with $G = 100$ MPa and $\lambda = 1$ s. Each curve is associated with its own time scale. For example, for $\dot{\gamma}_{xy} = 10 \text{ s}^{-1}$, it takes 0.1 s to reach $\gamma_{xy} = 1.0$, therefore having a time scale $t_p = 0.1$ s. For such a small time scale, the material behaves almost like a solid, because there is not sufficient time for the material to relax the stress that built up during deformation. On the other hand, for the material deforming at a much slower rate of 0.1 s^{-1} , the time scale is $t_p = 10$ s, and there is sufficient time for the stress to relax so that the material behaves more like a fluid. Therefore, while the

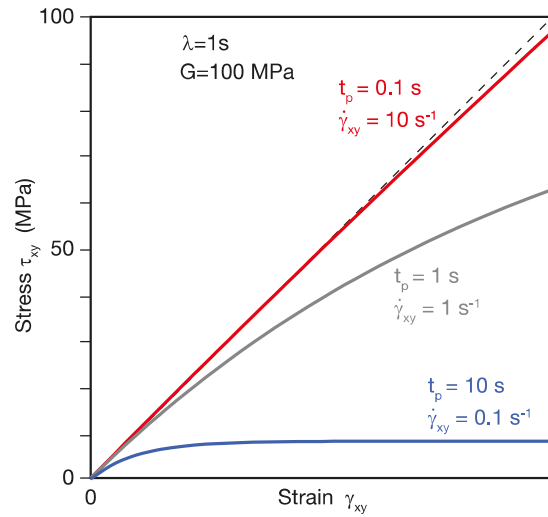


Figure 1.16 Stress as a function of strain for a Maxwell model at various rates of deformation

spring-dashpot system represented in Fig. 1.13, and its response shown in Fig. 1.16, have a fixed relaxation time of 1 s and clearly represent a viscoelastic material, the material's behavior is bound between an elastic solid (straight diagonal line in the diagram), when the process time is zero, and a viscous liquid (horizontal line that represents the strain axis), when the process time is infinite.

While Maxwell explained the viscoelastic behavior of materials using conceptual spring and dashpot elements, it wasn't until polymers became of age for further understanding of viscoelastic behavior of materials to become of extreme importance. Of course, today it is well known that because of their molecular structure, polymers represent the quintessential viscoelastic material. However, it took until 1955 for the concept of stress relaxation and relaxation time, and their relation to molecular structure, to be explained by John Ferry and his coworkers Malcolm Williams and Robert Landel. Williams, Landel, and Ferry directly related stress relaxation time of polymers to the materials' temperature. In their classic paper "The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids" [53], Ferry and his coworkers explained how, in order to relax stresses, polymer molecules slide past each other when subjected to a stress. In addition, they demonstrated how a temperature increase accelerates stress relaxation. This effect can be explained by the increase in free volume between the molecules, allowing these molecules to move with more ease, and consequently reducing the relaxation time. Hence, Ferry presented a basic relation between relaxation time and temperature, which today is referred to as time-temperature superposition principle, or often abbreviated as the WLF equation. We shall take a look at Ferry's work in more detail in Chapter 2 of this book.

But lets go back again to the question of whether a material, and particularly a polymeric material, should be considered a solid, a liquid, or a viscoelastic material. Here, we must consider the material's behavior in the context of its specific situation or process. This dilemma was solved in 1964 by Marcus Reiner, of the Technion in Haifa, who introduced the Deborah number (De), a dimensionless number that best captures the effect of process time scale on a material's deformational behavior [5]. He chose the name after the Song of Deborah, Judges 5:5, which states "*The mountains flowed before the Lord.*" (Fig. 1.17), which he interpreted to mean that even mountains can appear to flow given a sufficiently large time scale.

The Deborah number is defined by

$$De = \frac{\lambda}{t_p} \quad (1.17)$$

A Deborah number of zero represents a viscous fluid and a Deborah number of ∞ an elastic solid. For the cases presented in Fig. 1.16, the Deborah number varies between 0.1, for the low rate of deformation, and 10, for the high deformation rate.



Figure 1.17 “The mountains flowed before the Lord.” Coyote Buttes North 1 Second Wave, Arizona. Courtesy of Wolfgang Cohnen (© 1998)

■ 1.6 Deformation, Rate of Deformation, and the Deviatoric Stress Tensors

Rheology is concerned with the behavior of fluids undergoing deformation. This deformation can be shear, elongation, or a combination of deformations such as those occurring in the complex flow field within a mixer. If the upper plate in the simple shear flow experiment shown in Fig. 1.6 had a constant speed u_0 , it would move a distance D_x in a small time interval Δt . Hence, the shear deformation, which in the xy -plane is defined by

$$\gamma_{xy} = \frac{\partial D_x}{\partial y} + \frac{\partial D_y}{\partial x} \quad (1.18)$$

becomes $\gamma_{xy} = D_x/h$ or $\gamma_{xy} = u_0 \Delta t/h$.

In the stretching process depicted in Fig. 1.18, assuming a linear increase in velocity from $u_x = u_0$ at $x = 0$, to $u_x = D_R u_0$ at $x = L$, the deformation the material undergoes between those two points is $\gamma_{xx} = (D_R u_0 - u_0) \Delta t/L$, where D_R is referred to as the draw-down ratio. In addition, the material is also deforming in the y -direction by the amount $\gamma_{yy} = -\gamma_{xx}$. Similar to the flow depicted in Fig. 1.18, in polymer processing and rheometry the deformation is a combination of shear and stretching similar to that at the entrance of the capillary in a capillary rheometer. Thus, a more general representation of the deformation is given in tensor form, written as

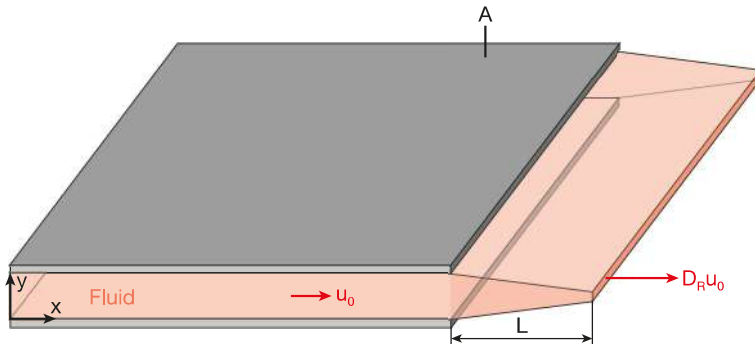


Figure 1.18 Schematic of stretching flow

$$\underline{\underline{\gamma}} = \gamma_{ij} = \begin{bmatrix} \gamma_{xx} & \gamma_{xy} & \gamma_{xz} \\ \gamma_{yx} & \gamma_{yy} & \gamma_{yz} \\ \gamma_{zx} & \gamma_{zy} & \gamma_{zz} \end{bmatrix} \quad (1.19)$$

The rate of deformation tensor can be computed by taking the time derivative of the deformation tensor as

$$\frac{\partial \underline{\underline{\gamma}}}{\partial t} = \dot{\underline{\underline{\gamma}}} = \begin{bmatrix} \dot{\gamma}_{xx} & \dot{\gamma}_{xy} & \dot{\gamma}_{xz} \\ \dot{\gamma}_{yx} & \dot{\gamma}_{yy} & \dot{\gamma}_{yz} \\ \dot{\gamma}_{zx} & \dot{\gamma}_{zy} & \dot{\gamma}_{zz} \end{bmatrix} \quad (1.20)$$

which can also be written as

$$\dot{\underline{\underline{\gamma}}} = \nabla \underline{u} + \nabla \underline{u}^T \quad (1.21)$$

where the velocity gradient $\nabla \underline{u}$ is represented by

$$\nabla \underline{u} = \begin{bmatrix} \frac{\partial u_x}{\partial x} & \frac{\partial u_x}{\partial y} & \frac{\partial u_x}{\partial z} \\ \frac{\partial u_y}{\partial x} & \frac{\partial u_y}{\partial y} & \frac{\partial u_y}{\partial z} \\ \frac{\partial u_z}{\partial x} & \frac{\partial u_z}{\partial y} & \frac{\partial u_z}{\partial z} \end{bmatrix} \quad (1.22)$$

Similar to the definition of the deviatoric shear stress component of Eq. 1.4, we can define the deviatoric stress tensor using

$$\underline{\underline{\tau}} = \eta \dot{\underline{\underline{\gamma}}} \quad (1.23)$$

where $\underline{\underline{\tau}}$ is written as

$$\underline{\underline{\tau}} = \tau_{ij} = \begin{bmatrix} \tau_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \tau_{yy} & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \tau_{zz} \end{bmatrix} \quad (1.24)$$

■ 1.7 Guide to the Book

The content of this book can be fitted into an Eizenschitz, Rabinowitsch and Weissenberg triangle. Because plastics are extremely viscous, with a viscosity one million times higher than that of water, the first simplification we can make is to eliminate the effects of inertia. That leaves us with only the behavior represented by line BC in Fig. 1.19. While the fundamentals of polymer flow during processing (Chapter 2), their modeling (Chapter 4), and their measurement (Chapter 6) are more related to the molten, liquid-like behavior around vertex C, the behavior of the material during rapid deformation and solidification (Chapter 5) is related to its structure (Chapter 2) and will therefore be discussed in terms of viscoelasticity.

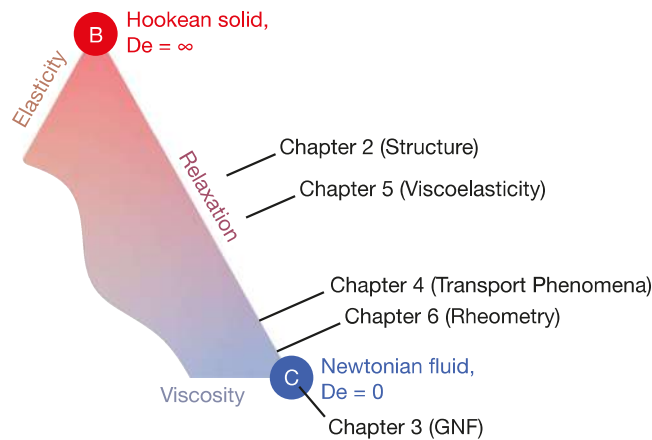


Figure 1.19 The Eizenschitz, Rabinowitsch and Weissenberg triangle and its significance for this book

■ Problems

- 1.1 Please retrieve Rabinowitsch's 1929 paper on the capillary viscometer correction factor and write a short essay and presentation summarizing the paper.
- 1.2 Please retrieve the Bernstein, Kearsley and Zapas paper on the non-linear integral viscoelastic model and write a short essay and presentation summarizing the paper.
- 1.3 Compare the Cross and Carreau models from their 1965 and 1968 publications.
- 1.4 Compare the 1923 de Waele model to Ostwald's 1925 model.
- 1.5 Please retrieve Einstein's 1905 paper on filled fluids and compare the model with Guth and Simha's model from their 1936 paper.
- 1.6 Please retrieve Williams, Landel and Ferry's 1955 paper on the time-temperature superposition principle and write a short essay and presentation summarizing the paper.
- 1.7 Choose a paper from the references and write a short essay and presentation summarizing the paper.

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2

Structure and Properties of Deforming Polymers

Because of their molecular structure, polymers are by far the most complex fluids engineers will encounter. Therefore, what seems trivial when dealing with Newtonian fluids, is a complex experimental and mathematical exercise for a rheologist dealing with polymeric melts. An important aspect of any rheologist's work is to find relations between deformation and stresses for various well defined conditions, such as transient shear flows, step strain, creep, and oscillatory shear flow, to name a few. These relations, also called material functions, are determined using different types of rheometric techniques. This chapter will introduce the reader to the causes of the various phenomena only observed with plastics and the relation of these effects to the molecular architecture of polymer melts.

■ 2.1 Molecular Structure of Polymers

Polymers are macromolecular structures that are typically generated synthetically but sometimes also through natural processes. These macromolecules start as monomers, such as ethylene, schematically represented in Fig. 2.1. Once these mono-

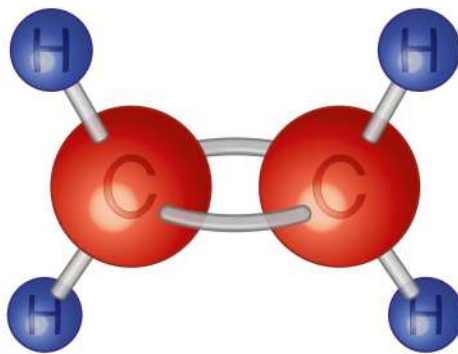


Figure 2.1 Schematic representation of an ethylene monomer

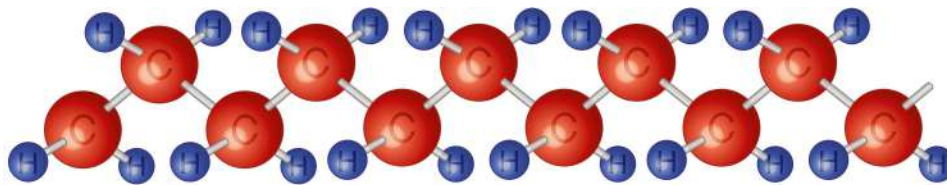


Figure 2.2 Schematic representation of a polyethylene molecule

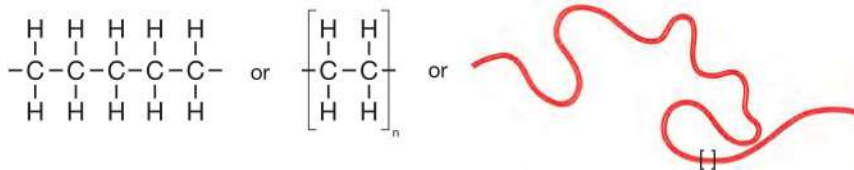


Figure 2.3 Symbolic representation and cartoon of a polyethylene molecule

mers are polymerized, they take the form of long polymer chains with thousands of repeating units. The ethylene of Fig. 2.1 becomes polyethylene, as schematically depicted in Fig. 2.2. Polymer molecules may also be represented symbolically or by using a cartoon as depicted in Fig. 2.3.

Several forces hold a polymeric material together on the molecular level. The most basic acting forces are covalent bonds that hold together the backbone of a polymer molecule, such as the C–C bond. The energy holding together two carbon atoms amounts to approx. 350 kJ/mol, which is equivalent to a polymer component strength between 14 and 19 GPa and a stiffness of up to 300 GPa. However, because the long polymer chains are typically not aligned, the strength of polymers ranges only between 10 and 100 MPa and their stiffness is approx. 1 GPa.

The comparatively low strength found in polymer components indicates that the forces holding a polymer component together do not originate from the C–C bonds but are intermolecular forces, or so-called Van-der-Waals forces. The energy that generates the intermolecular attraction between two polymeric molecules increases with decreasing distance of the molecules as described by Eq. 2.1

$$\varepsilon \sim \frac{1}{r^6} \quad (2.1)$$

where $\varepsilon < 10$ kJ/mol and r is the distance between the molecules. Thus, it becomes clear that as a polymer sample is heated, and the distance between the molecules increases with increasing vibration amplitude of the molecules, the intramolecular forces diminish. This increase in free volume allows the molecules to move more freely, enabling the material to flow at the macroscopic level. An increase in free

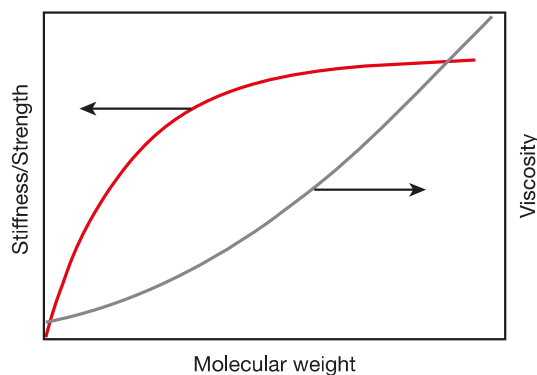


Figure 2.4 Influence of molecular weight on rheological and mechanical properties

volume, and consequently more ease of movement, can also be achieved by introducing solvents or plasticizers between the molecules. As these low molecular weight plasticizers wedge themselves between the molecules, they generate free volume, just as an increase in temperature would.

The properties of polymeric materials are strongly linked to the number of repeat units, n , in the molecular chain, or the molecular weight of the polymer, as shown schematically in Fig. 2.4. A polymer, such as polystyrene, is stiff and brittle at room temperature with a degree of polymerization of 1000, or $n = 1000$. At a degree of polymerization of 10, polystyrene is sticky and soft at room temperature. While the stiffness properties reach an asymptotic maximum, the viscosity increases steadily with molecular weight.

Some thermoplastics, such as some polyamide 11 resins, increase in molecular weight during processing. This leads to a rise in viscosity and may reduce sag once the polymer emerges from the extrusion die. The same is true for thermosets as they cure, or cross-link, during processing. As the curing progresses, the molecular weight increases, causing the viscosity to increase until the gel point is reached, at which point the material is considered a solid. The field studying these effects is referred to as chemorheology, and is covered in more detail in Chapter 3.

Figure 2.5 shows the relationships between molecular weight, temperature, and properties of a typical polymeric material. The glass transition temperature region increases with molecular weight. Therefore, the temperature range at which the polymer can flow (processing temperature), which for most polymers is 45 to 100 K above the glass transition, also increases with molecular weight. On the other hand, the degradation temperature steadily decreases with increasing molecular weight. Hence, it is necessary to find the molecular weight that renders ideal material properties for the finished polymer product, while providing flow properties that make it easy to shape the material during the manufacturing process. It is important to note

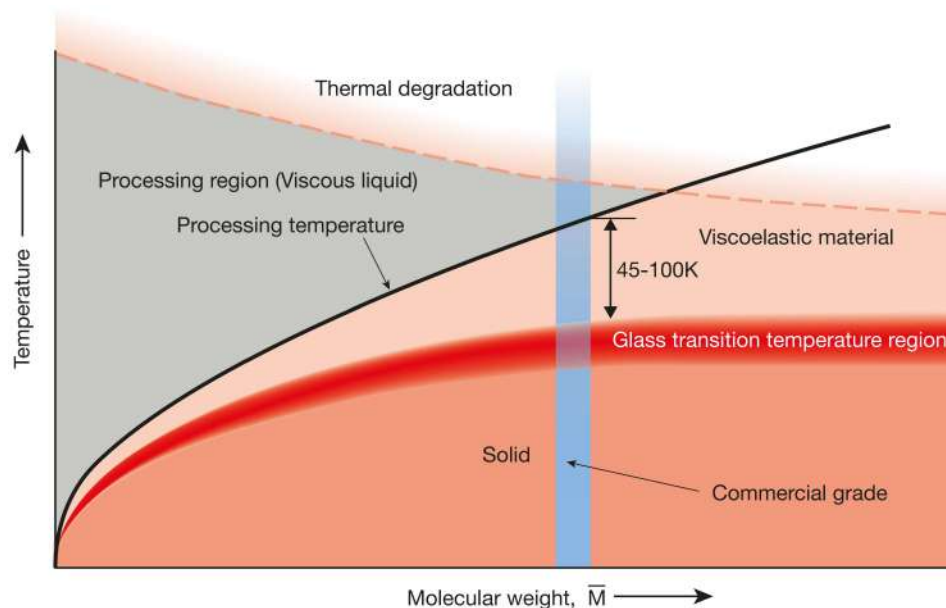


Figure 2.5 Diagram representing the relation between molecular weight, temperature, and properties of a typical thermoplastic

that the temperature scale in Fig. 2.5 corresponds to a specific time scale, e.g., time required for a polymer molecule to flow through an extrusion die. If the time scale is reduced (e.g., by increasing the extruder throughput), the molecules do not have enough time to relax, or get used to the shape of the die. Now a somewhat higher temperature is required to assure flow. In fact, at a specific temperature, a polymer melt may behave like a solid when the time scale is reduced sufficiently. Hence, for this new time scale the stiffness properties and flow temperature curves must be shifted upward on the temperature scale. A limiting factor is the fact that the thermal degradation curve remains fixed, forcing processing conditions to remain above certain time scales.

With the exception of some naturally occurring polymers, most polymers exhibit a molecular weight distribution, in other words, they are composed of molecules of different length, as shown in Fig. 2.6. There are various ways to compute an average molecular weight for such a molecular weight distribution. The number average, $\bar{M}_n$, simply adds all the molecular weights of all the molecules and divides it by the total number of molecules. This is written as

$$\bar{M}_n = \frac{\sum m_i}{\sum n_i} = \frac{\sum n_i M_i}{\sum n_i} \quad (2.2)$$

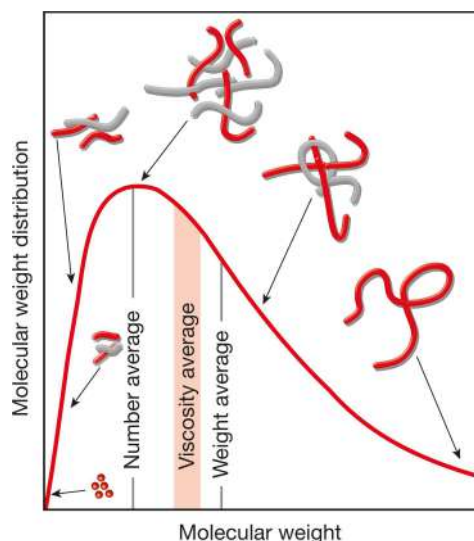


Figure 2.6 Molecular weight distribution of a typical thermoplastic

where m_i is the weight, M_i the molecular weight, and n_i the number of molecules with i repeat units. This gives the short chains, that contribute little to the total performance and weight of the material, equal importance as the long chains. To avoid this, one can take a weighted average, where before adding up all the molecules, the number of molecules with a specific molecular weight is multiplied by the molecular weight of those chains, and instead of dividing this sum by the total number of chains, the total molecular weight of the sample is used. This is represented as

$$\bar{M}_w = \frac{\sum m_i M_i}{\sum m_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i} \quad (2.3)$$

Another form of molecular weight average is the viscosity average, M_v , which is calculated using

$$[\eta] = k \bar{M}_v^\alpha \quad (2.4)$$

where $[\eta]$ is the intrinsic viscosity and, α and k are material-dependent parameters. This relation is sometimes referred to as the Mark-Houwink relation. Figure 2.7 [1] schematically presents the viscosity of a typical polymer as a function of molecular weight. The figure shows how the viscosity changes from a linear ($\alpha = 1$) to a power dependence ($\alpha = 3.4$) at some critical molecular weight. The linear relationship is sometimes referred to as Staudinger's rule [2] and applies to a perfectly monodispersed polymer of relatively low molecular weight¹. This linear relationship is a

¹ A monodispersed polymer is composed of a single molecular weight species.

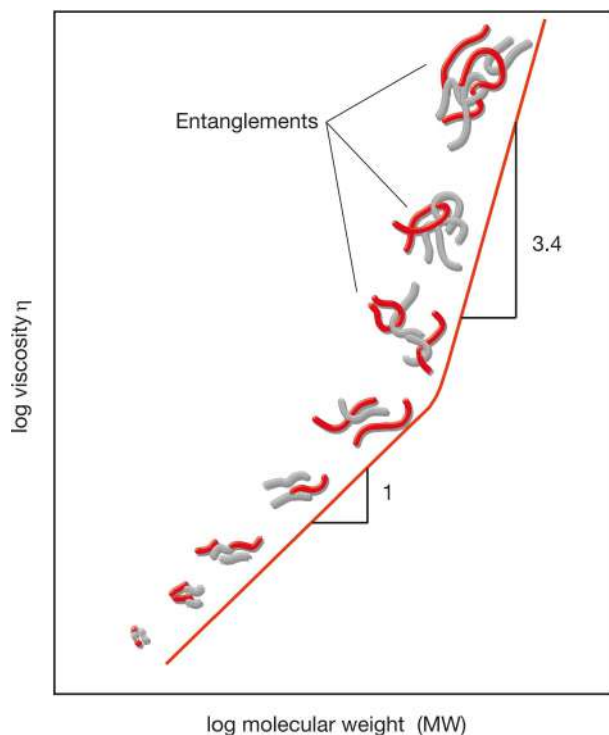


Figure 2.7 Schematic of zero shear rate viscosity for polymers as a function of weight average molecular weight

result of the intramolecular friction, which increases proportionally to the length of the molecules. As the molecular weight increases with increasing length of the molecules, the molecules tend to entangle, causing a power relation between molecular weight and viscosity, or $\alpha = 3.4$.

The broadness of a molecular weight distribution is related to the polydispersity of the molecular chains. A monodispersed polymer is described by

$$\bar{M}_w = \bar{M}_n = \bar{M}_v \quad (2.5)$$

while in a polydispersed polymer

$$\bar{M}_w > \bar{M}_v > \bar{M}_n \quad (2.6)$$

Hence, a measure of the broadness of a polymer's molecular weight distribution is the polydispersity index defined by

$$PI = \frac{\bar{M}_w}{\bar{M}_n} \quad (2.7)$$

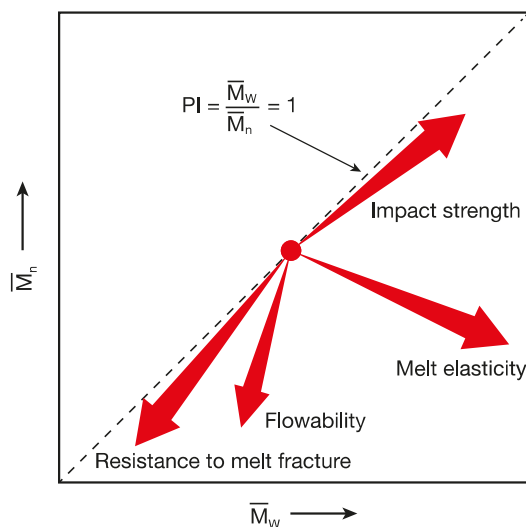


Figure 2.8 Influence of molecular weight number average and weight average on properties of thermoplastic polymers

Here, $PI = 1$ represents a polymer, in which all molecules have the same chain length. However, PI varies with the type of polymerization and the polymer itself. For step growth polymerized plastics, such as polyamides, polycarbonates and epoxies, to name a few, the polydispersity index $PI \approx 2$. For chain polymerized plastics, such as polyolefines, polystyrenes, polyacetal, etc., $PI = 1.01 \dots 50$, where branched polymers exhibit a polydispersity index ranging between 20 and 50.

Figure 2.8 is a graphical representation of the relationship between number average and weight average and its influence on the properties of polymers. The arrows in the diagram indicate an increase in a specific property.

Branching of the polymer chains also influences the final structure, crystallinity, and properties of the polymeric material. Figure 2.9 shows the molecular architecture of high density (PE-HD), low density (PE-LD), and linear low density polyethylenes (PE-LLD).

The PE-HD has between 5 and 10 short branches for every 1000 carbon atoms. The PE-LD has the same number of branches as PE-LD; however, they are much longer and are themselves usually branched. The PE-LLD has between 10 and 35 short chains for every 1000 carbon atoms. Polymer chains with fewer and shorter branches can crystallize with more ease, resulting in higher density.

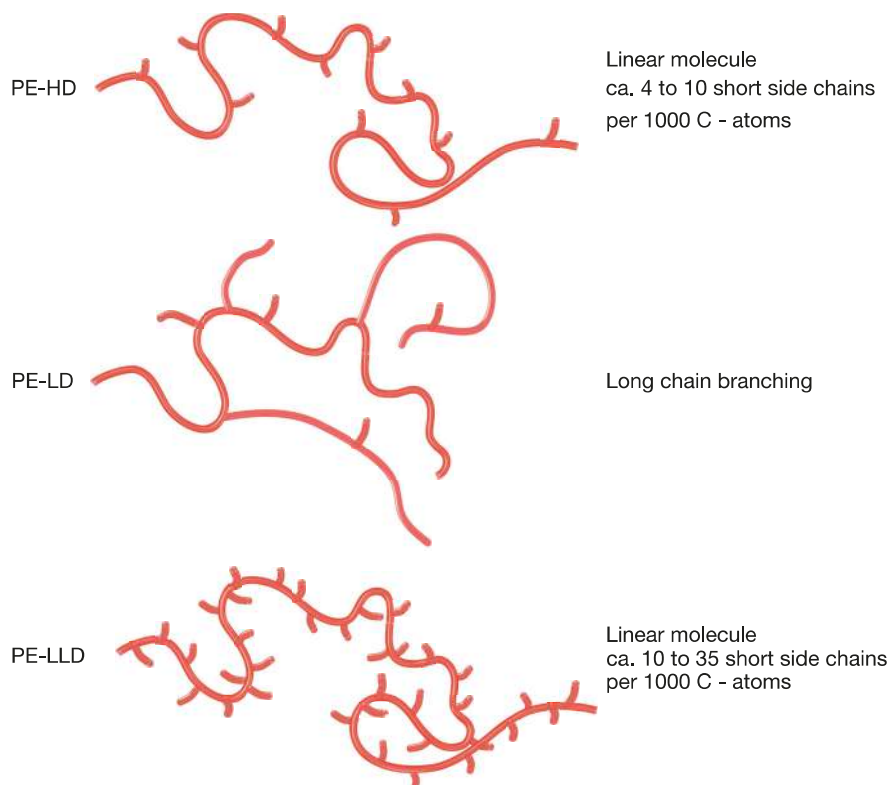


Figure 2.9 Schematic of the molecular structure of different polyethylenes

■ 2.2 Stress Relaxation Behavior

The most basic phenomenon in polymer melts and solids is stress relaxation. Because polymers are composed of macromolecules, and these large molecules have the ability to slide past each other, hindered only by intramolecular forces and molecular entanglements, they tend to relax stresses that arise when subjected to a deformation. Hence, as a mass of polymer is subjected to a stress, the molecules tend to move in an effort to relax those stresses. If these stresses are caused by a constant strain, the initial stress caused by this deformation relaxes in a given time interval, sometimes referred to as relaxation time, λ .

In a stress relaxation test, a polymer test specimen undergoes a fixed deformation, ϵ_0 , and the stress required to hold this amount of deformation is recorded over time. This test is very cumbersome to perform, so design engineers and material scientists tend to ignore it. In fact, the standard relaxation test ASTM D2991 was dropped from

the standards in 1990. However, rheologists have been consistently using the stress relaxation test to interpret the viscoelastic behavior of polymers.

Figure 2.10 [3] presents the stress relaxation modulus of polyisobutylene² measured at various temperatures. Here, the stress relaxation modulus is defined by

$$E_r(t) = \frac{\sigma(t)}{\varepsilon_0} \quad (2.8)$$

where ε_0 is the applied strain and $\sigma(t)$ is the stress being measured. From the test results it is clear that stress relaxation is time and temperature dependent, especially around the glass transition temperature, where the slope of the curve reaches a maximum. In the case of the polyisobutylene shown in Fig. 2.10, the glass transition temperature is about -70°C . The measurements were completed in an experimental time window between a few seconds and one day. The tests performed at lower temperatures were used to record the initial relaxation, while the tests performed at higher temperatures only captured the end of relaxation of the rapidly decaying stresses.

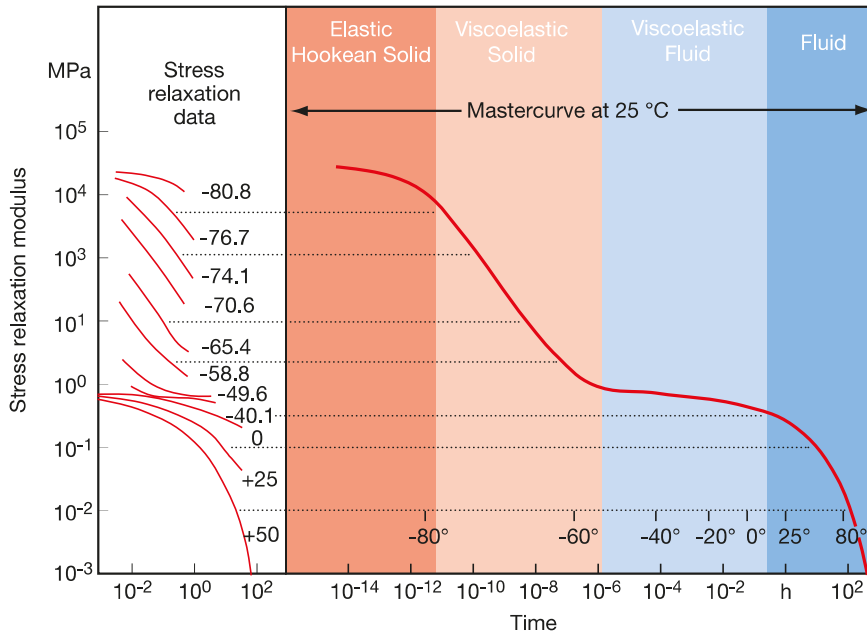


Figure 2.10 Relaxation modulus curves for polyisobutylene at various temperatures and corresponding master curve at 25°C

² Better known as chewing gum.

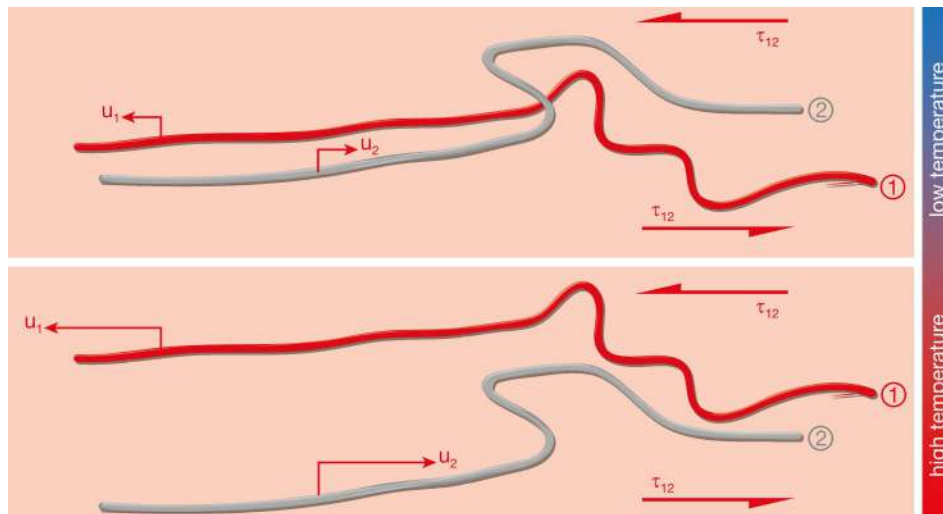


Figure 2.11 Schematic of stress relaxation on a molecular level at low (top) and high (bottom) temperatures

It is well known that high temperatures lead to short molecular relaxation times³ and low temperatures lead to long relaxation times. This is caused by the fact that at low temperatures the free volume between the molecules is small, restricting or slowing down their movement, as schematically shown in Fig. 2.11. At high temperatures, the free volume is larger and the molecules can move with more ease. When changing temperature, the shape of creep⁴ or relaxation test results remains the same, except that they are horizontally shifted to the left or right, which represents lower or higher response times, respectively.

The same behavior observed for varying temperatures can be seen when the pressure is varied. As the pressure is increased, the free volume between the molecules is reduced, slowing down molecular movement. Here, an increase in pressure is equivalent to a decrease in temperature. Hence, it is clear that in the melt state, the viscosity of a polymer increases with pressure. Figure 2.12 [4] illustrates the effect of pressure on stress relaxation.

The time-temperature equivalence seen in stress relaxation test results can be used to reduce data at various temperatures to one general master curve for a reference temperature, T_0 . To generate a master curve at the reference temperature, the curves shown on the left of Fig. 2.10 must be shifted horizontally, maintaining the reference curve stationary. Density changes are usually small and can be neglected, eliminating the need to perform tedious corrections. The master curve for the data in Fig. 2.10 is shown on the right side of the figure. Each curve was shifted horizontally until

³ Relaxation time usually refers to the time it takes for applied stresses to relax within a material.

⁴ In a creep test the polymer specimen is loaded to a constant stress, and the strain response is recorded in time.

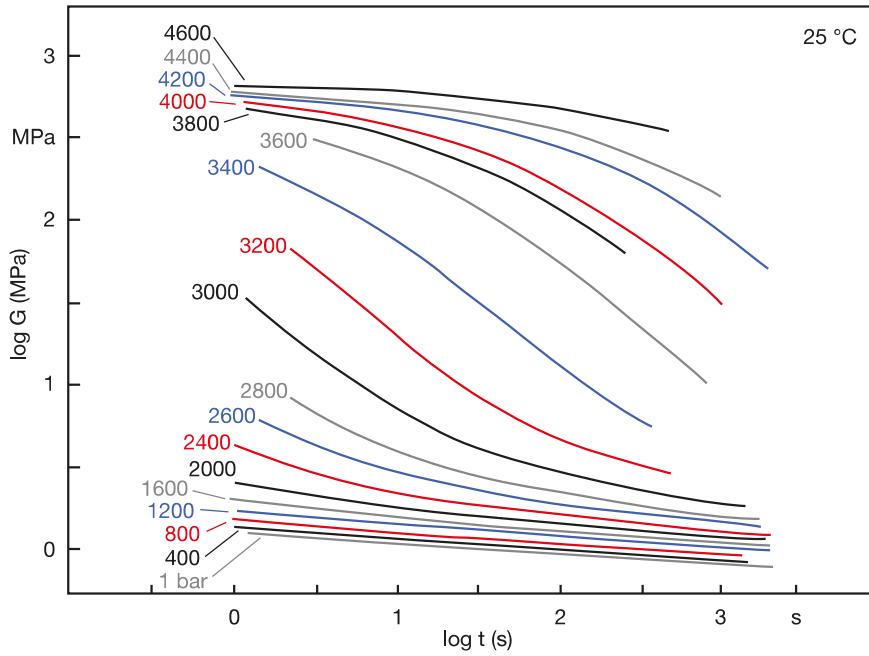


Figure 2.12 Shear relaxation modulus for a chlorosulfonated polyethylene at various pressures

the ends of all the curves became superimposed. The amount by which each curve was shifted can be plotted with respect to the temperature difference taken from the reference temperature, T_0 . For the data in Fig. 2.10 the shift factor is shown in the plot in Fig. 2.13. The amounts by which the curves were shifted, $\log a_T$, are represented by

$$\log T - \log T_0 = \log \left(\frac{T}{T_0} \right) = \log a_T \quad (2.9)$$

where T is the temperature of the measurement and T_0 the reference temperature. This shift will be explained in more detail in Chapter 3.

Although the results in Figure 2.13 were shifted to a reference temperature of 298 K (25 °C), Williams, Landel and Ferry (WLF) [5] chose $T_0 = 243$ K, or 45 K above the glass transition temperature. This temperature is often chosen because for most amorphous polymers it coincides with a typical processing temperature, where the measureable elastic effects are smaller than the viscous effects during deformation. The shift, or time-temperature superposition, is given in general form by

$$\log a_T = -\frac{C_1(T - T_0)}{C_2 + (T - T_0)} \quad (2.10)$$

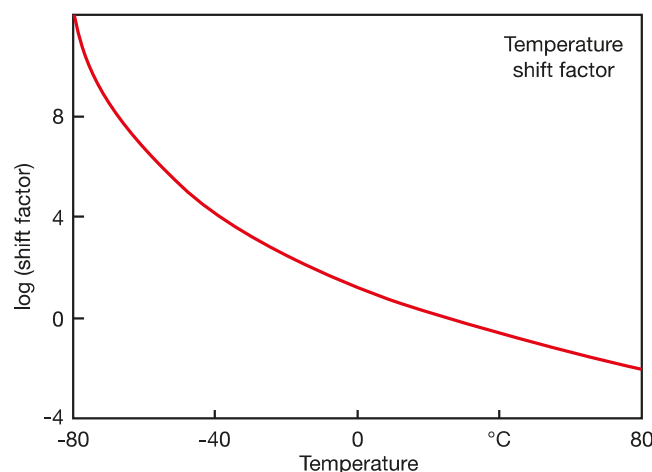


Figure 2.13 Plot of the shift factor as a function of temperature used to generate the master curve plotted in Figure 2.10

where C_1 and C_2 are material dependent constants. Equation 2.10 is often referred to as WLF-equation. Master curves of stress relaxation tests are important because the polymer's behavior can be traced over much longer periods of time than can be determined experimentally. The WLF equation and its use is covered in detail in Chapter 3.

Example 2.1 Relaxation Time Measurement

Using a blow molding grade high density polyethylene, determine the relaxation time for standard processing temperatures.

A sliding plate rheometer can be used to measure relaxation time. In a sliding plate rheometer, two parallel plates separated by a small gap move parallel to one another. The advantage of using a sliding plate rheometer is that a constant stress and strain field is generated between the gap, as the material deforms in simple shear⁵. For a relaxation time measurement, a step strain is imposed by rapidly moving one of the plates a certain distance. This causes the shear to rapidly increase to its maximum value $\tau_{\max}$. Because the system remains stationary after applying the step strain, the stress decreases over time. Typically, the relaxation time, λ , is the time it takes for the maximum stress to decrease to 1% of its initial value. Figure 2.14 presents the stress as a function of time for a blow molding grade PE-HD⁶ (MFI = 1.2 g/10 min) tested at 190 °C. The imposed strain was $\gamma = 20$, applied to a 2 mm thick sample using rate of shear of 2 s^{-1} . The instant the plates stopped moving, the shear stress reached 90 kPa. The plot presented in Figure 2.14 shows that it took about 1.2 s for this stress to relax to 1% of its initial value.

⁵ The sliding plate rheometer is discussed in detail in Chapter 6.

⁶ NOVA Chemicals Sclair® 19G Homopolymer HDPE Film Resin.

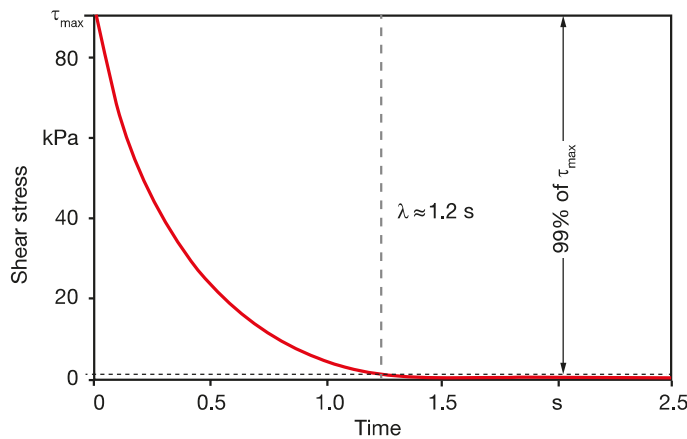


Figure 2.14 Stress as a function of time after imposing a step strain, measured using a sliding plate rheometer and a blow molding grade PE-HD.

2.3 Shear Thinning Behavior

To illustrate shear thinning behavior, picture the randomly oriented entangled macromolecules depicted in Fig. 2.15. At low rates of deformation, the entangled molecules have a hard time sliding past each other, resulting in a relatively high viscosity. Polymer melts exhibit this behavior over a range of small rates of deformation. This constant high viscosity is referred to as a Newtonian plateau, depicted in Fig. 2.16. However, as the rate of deformation increases, the corresponding increased shear stress is sufficiently high to disentangle and unravel the molecules. The disentangled molecules can slide past their neighbors with more ease, resulting in an overall lower melt viscosity. This phenomenon is referred to as shear thinning behavior, pseudoplasticity, or structural viscosity. Eventually, the molecules can no longer stretch out any further. This point is seen in a second Newtonian plateau at higher rates of deformation, reflecting the lowest possible viscosity.

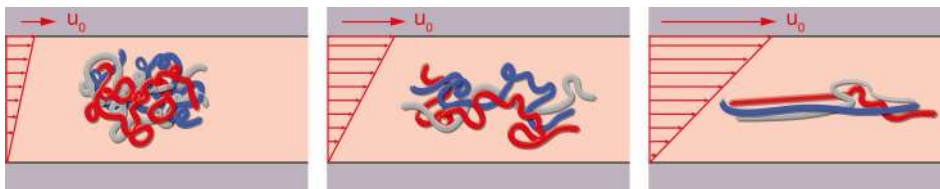


Figure 2.15 Molecular structure with increasing shear

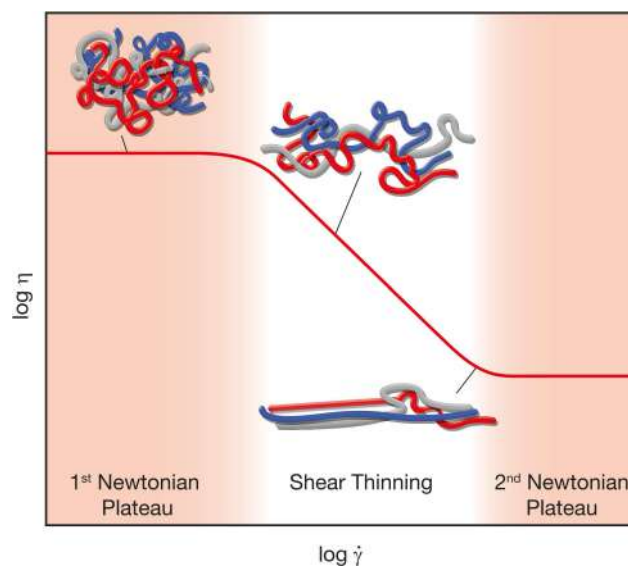


Figure 2.16 Shear thinning behavior or pseudoplasticity

The same effect depicted for shear in Fig. 2.15 occurs in elongation flows as well as in combined deformation flows of various levels of shear and elongation. Therefore, the viscosity of a polymer is a function of the magnitude of the rate of deformation tensor

$$\tau_{xy} = \eta(\dot{\gamma}, T) \dot{\gamma}_{xy} \quad (2.11)$$

Because the free volume between the molecules increases with temperature, the intra-molecular friction decreases, resulting in an overall lower viscosity as shown in Fig. 2.16 for various polymers. Figure 2.17 also presents the range of rate of deformation experienced by polymer melts when using various processing techniques.

Figure 2.18 shows the effect of molecular weight variations on the shear thinning behavior of thermoplastics. The shear rate independent plateau is shifted to higher viscosity values with increasing molecular weight as the friction between chains increases. Side branching leads to lower viscosity (shear thinning) caused by the lubrication effect of the side group chains. With increasing width of the molecular weight distribution, shear thinning sets in at higher shear rates, which can be attributed to the smaller shear thinning effect of short chains.

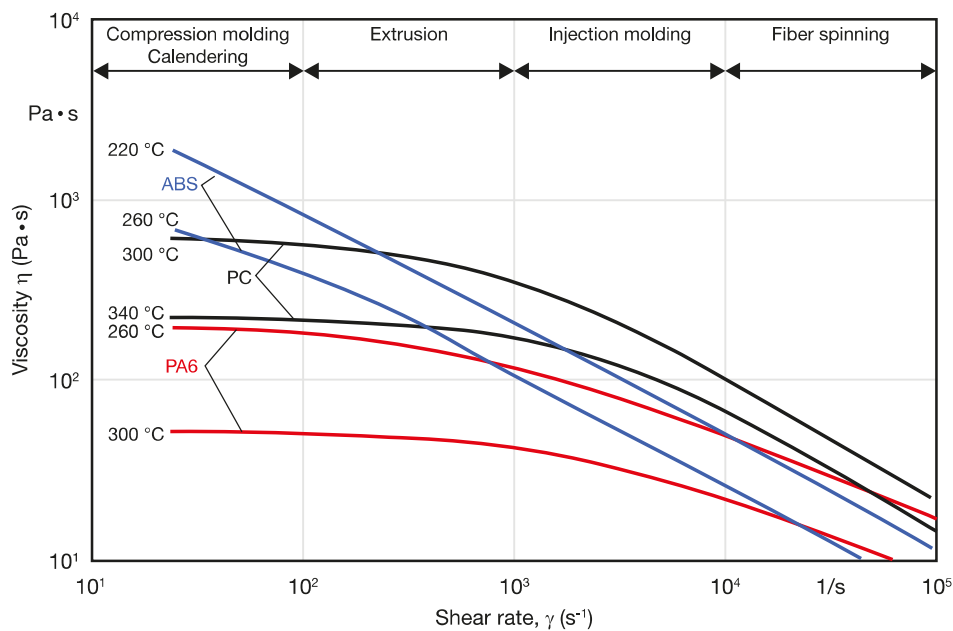


Figure 2.17 Viscosity curves for various polymers at different temperatures

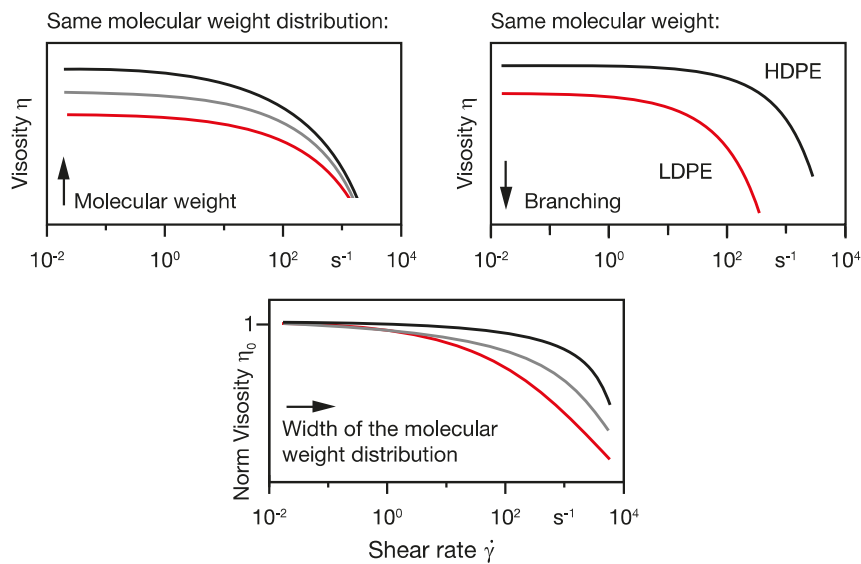


Figure 2.18 Schematic representation of the influence of molecular weight, branching, and molecular weight distribution on the shear rate dependent viscosity of polyolefins [6]

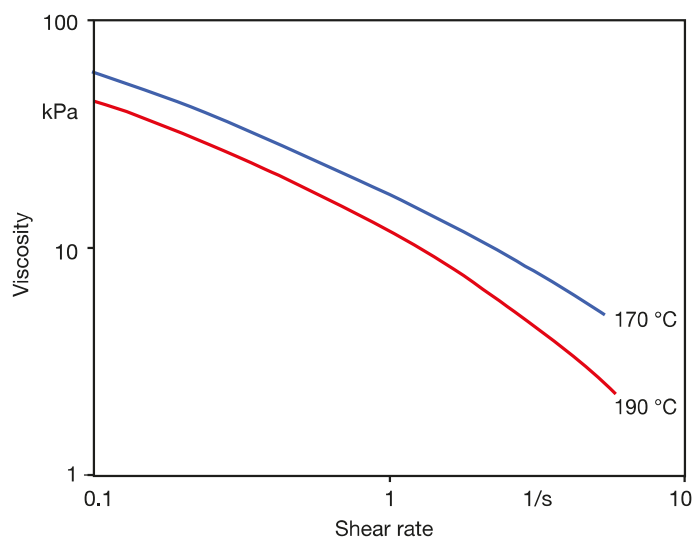


Figure 2.19 Viscosity as a function of rate of deformation for two different temperatures, measured using a sliding plate rheometer and a blow molding grade PE-HD.

Example 2.2 Shear Thinning Behavior Measurement

Using the same extrusion blow molding grade high density polyethylene as in Example 2.1, measure the viscosity as function of rate of deformation for two processing temperatures.

The same sliding plate rheometer used in the stress relaxation experiment of Example 2.1 was used to measure the viscosity of the molding grade polyethylene for rates of deformation between 0.1 and 10 s^{-1} . The measurements were done for test temperatures of 170 °C and 190 °C. Figure 2.19 presents the results. The figure clearly reveals fairly high viscosities at relatively low rates of deformation. From the results it is obvious that this material is not appropriate for injection molding applications. Furthermore, because during the test high shear stresses are generated, tests at higher rates of deformation resulted in surface slip conditions between resin and rheometer surface.

2.4 Normal Stresses in Shear Flow

The tendency of polymer molecules to “curl-up” while they are being stretched in shear flow results in normal stresses in the fluid. For example, in a shear flow that exhibits a deviatoric stress defined by Eq. 1.4 or 2.11, a measurable reaction from the molecular structure is perceived in the form of normal stresses and defined as

normal stress differences, $N_1 = \tau_{xx} - \tau_{yy}$ and $N_2 = \tau_{yy} - \tau_{zz}$. This effect is schematically depicted in Fig. 2.20, where stress differences, referred to as the first and second normal stress differences, are shown. An experimental set-up illustrating normal stress difference effects is the so-called rod-climbing experiment, or the Weissenberg effect, shown in Fig. 2.21. In this experiment, a rotating shaft causes the polymeric solution to move towards the shaft and not away from it as seen with Newtonian fluids. As a result, the polymer starts to move up the rotating shaft. Figure 2.22 is a schematic explanation of this effect. As the polymer molecules are stretched by the Couette devices's shear stresses, normal stresses arise. Because the stretched molecules are aligned along the curvilinear streamline, they tend to migrate toward the rotating shaft, leading to the rod-climbing phenomenon.

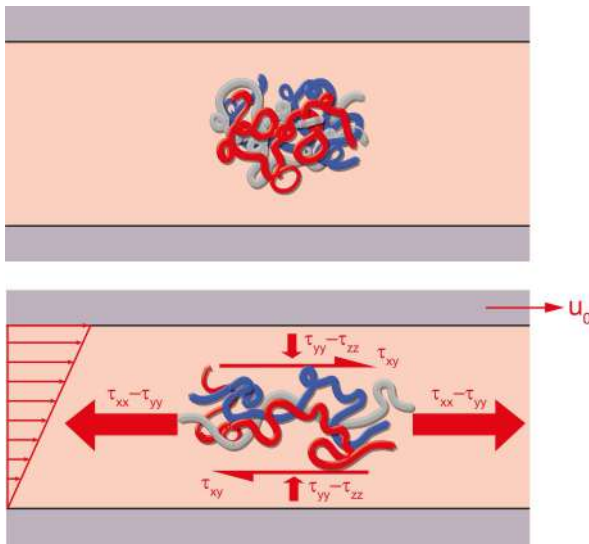


Figure 2.20 Schematic diagram of melt at rest and normal stress reactions during shear flow

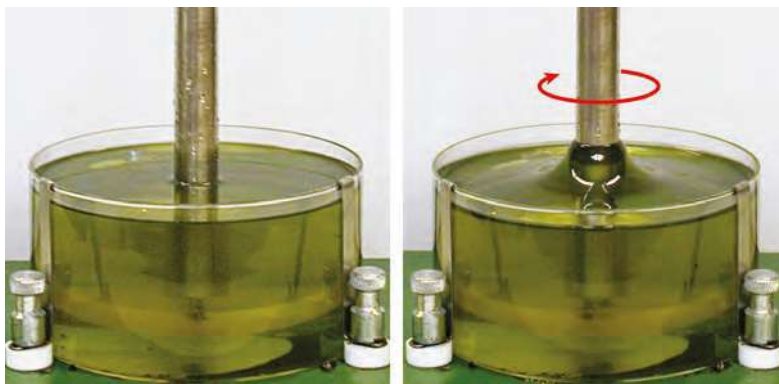


Figure 2.21 The rod-climbing or Weissenberg effect

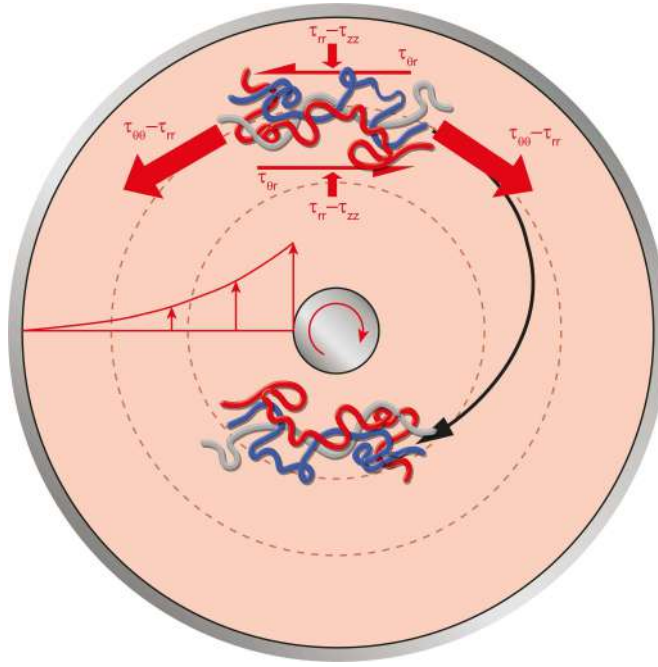


Figure 2.22 Schematic representation of normal stresses in a Couette flow

Just like viscosity, the first and second normal stress differences are material dependent and are defined by

$$N_1 = \tau_{xx} - \tau_{yy} = \psi_1(\dot{\gamma}, T) \dot{\gamma}_{xy}^2 \quad (2.12)$$

$$N_2 = \tau_{yy} - \tau_{zz} = \psi_2(\dot{\gamma}, T) \dot{\gamma}_{xy}^2 \quad (2.13)$$

where ψ_1 and ψ_2 are material functions called the primary and secondary normal stress coefficients. These material properties are also functions of the strain rate tensor magnitude and the temperature. Also, similar to viscosity, the first and second normal stress differences do not change in sign when the direction of the strain rate changes, clearly reflected in Eqs. 2.12 and 2.13. Figure 2.23 [7] presents the first normal stress difference coefficient for the low density polyethylene melt shown in Fig. 3.2 in Chapter 3 at a reference temperature of 150 °C. Second normal stress differences are more difficult to measure and therefore the data are often approximated by

$$\psi_2(\dot{\gamma}) \approx -0.1 \psi_1(\dot{\gamma}) \quad (2.14)$$

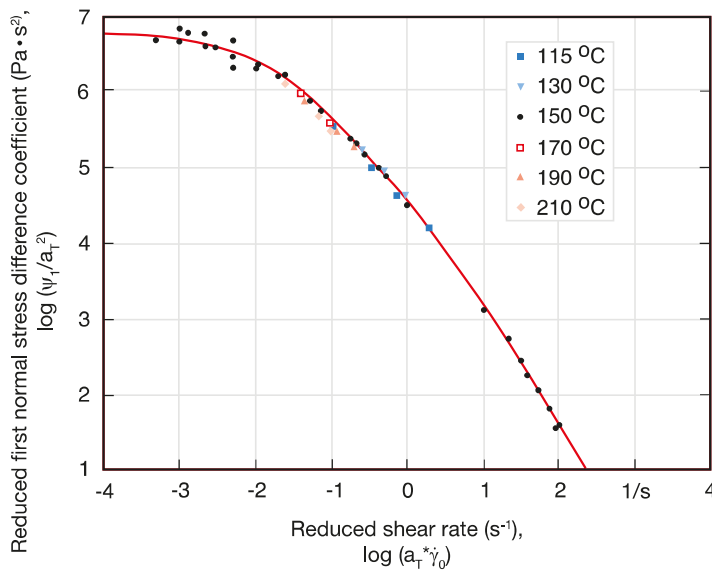


Figure 2.23 Reduced first normal stress difference coefficient for a low density polyethylene melt at a reference temperature of 150 °C

Example 2.3 Normal Stress Measurements

Using the same extrusion blow molding grade high density polyethylene as in Example 2.1, measure the first normal stress difference coefficient as a function of rate of deformation for two processing temperatures.

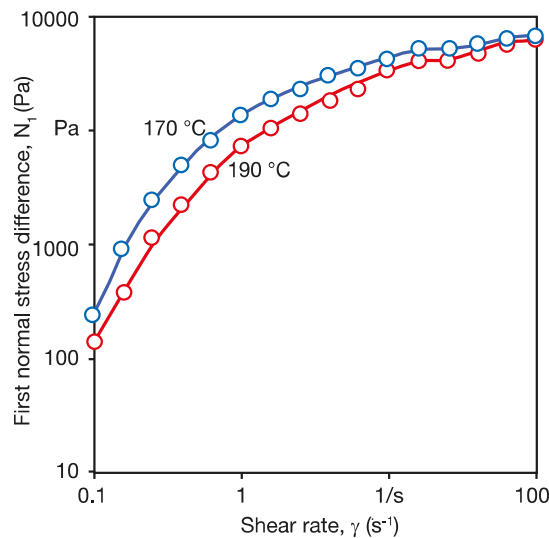


Figure 2.24 First normal stress difference of blow molding grade PE-HD as a function of shear rate and temperature

The first normal stress difference, N_1 , was measured for test temperatures of 170 °C and 190 °C, using the same sliding plate rheometer employed in Examples 2.1 and 2.2. As expected, a clear increase in normal stress but a reduction in growth was observed with increased rate of deformation (Fig. 2.24). Furthermore, a reduction in normal stress difference was seen with increase in temperature.

■ 2.5 Stress Overshoot during Start-up Flow

When a polymer sample that is initially at rest is suddenly subjected to a deformation rate, its stress response presents a slight stress overshoot, to a maximum value of $\tau_{\max}$, before decreasing and reaching a steady state value. Figure 2.25 schematically depicts this phenomenon. It has been suggested by many researchers [8] that the cause for this stress overshoot is the polymer melt's initial higher resistance to deformation resulting from molecular entanglements. Once the polymer deformation exceeds a certain value, the molecules begin to disentangle, reducing the resistance to deformation, causing the stresses to relax to a steady state value in a time typically shorter than the relaxation time of the melt.

When the flow is restarted after a short rest time, the maximum overshoot stress will be lower than the one experienced during the first start-up. However, if the rest time is sufficiently long, the maximum stress reached during overshoot will approach the value reached during the first start-up, $\tau_{\max}$. The rest time that the polymer needs to recover to its original state is based on the time it takes for molecular reentanglement. This time is longer than the characteristic stress relaxation time, λ .

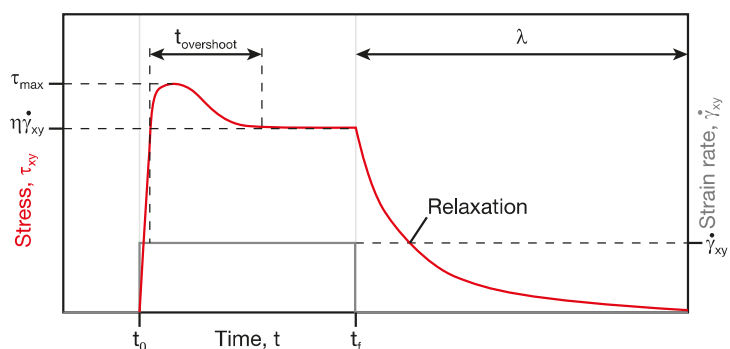


Figure 2.25 Schematic of stress overshoot during start-up flow

Example 2.4 Stress Overshoot Measurement

Using the same extrusion blow molding grade high density polyethylene as in Example 2.1, introduce a constant shear and assess the stress overshoot effect.

To capture the stress overshoot using the same sliding plate rheometer and blow molding grade PE-HD used in the previous three examples, a 2 mm sample was subjected to a constant shear rate of 2 s^{-1} . As can be seen, the shear stress first jumped to a value above 80 kPa, and eventually settled at a stress about half that value (Fig. 2.26). The material was tested at 190°C .

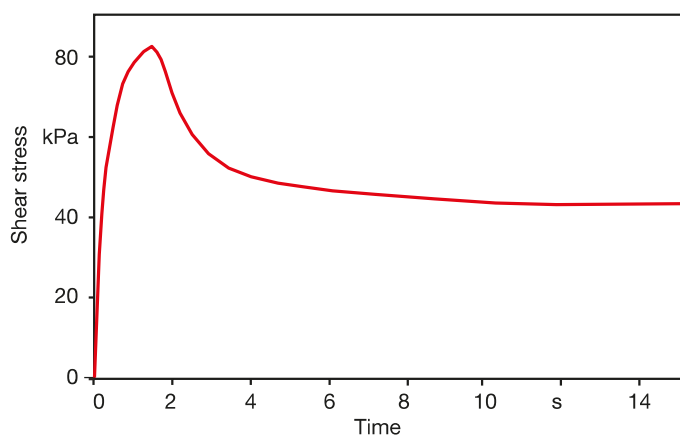


Figure 2.26 Measured stress overshoot at a constant shear rate of 2 s^{-1}

■ 2.6 Melt Strength or Melt Fracture

When a polymer is forced to deform and move at speeds that result in processing times shorter than the relaxation time of the polymer, the stresses will build up until they exceed the melt strength, leading to so called melt fracture. Depending on the process, this phenomenon will present itself in different forms. For example, waves in the extrudate may appear as a result of high speeds during extrusion, where the polymer is not allowed to relax within the extrusion die. This phenomenon is generally referred to as shark skin shown in Fig. 2.27 a [9] for a high density polyethylene.

It is possible to extrude at such high speeds that an intermittent separation of melt and inner die walls is caused, as shown in Fig. 2.27 b.

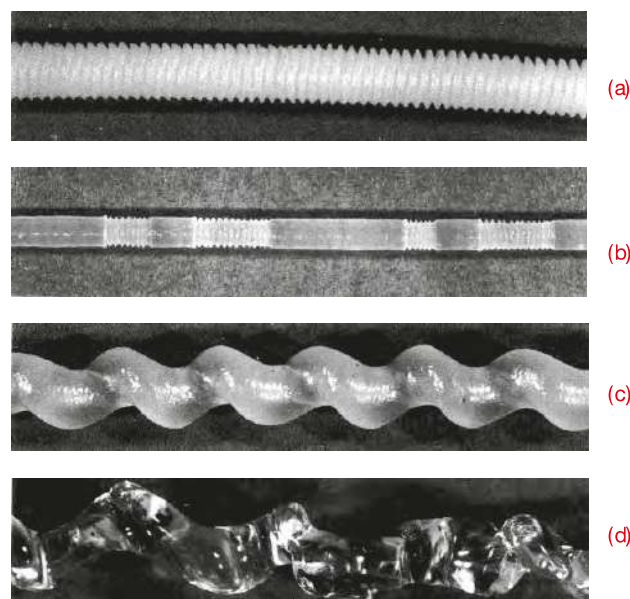


Figure 2.27 Melt fracture during extrusion of a polymer strand

This phenomenon is often referred to as the stick-slip effect or spurt flow and is attributed to high shear stresses between the polymer and the die wall. It occurs when the shear stress is near a critical value of 0.1 MPa [10–12]. However, it is influenced by the molecular weight of the polymer, as schematically shown in Figure 2.28. As the figure shows, a high molecular weight polymer molecule has more contact points with the surface of the mold or the rheometer. Hence, a higher molecular weight polymer exhibits better resistance to melt fracture than a lower molecular weight polymer. It was reported that the critical shear stress of 0.1 MPa is inversely proportional to the weight average molecular weight [11, 13]. However, Vinogradov et al. [10] presented results indicating that the critical stress was independent of molecular weight, except for low molecular weights. The interested reader is referred to the extensive overview of Koopmans et al. [14].

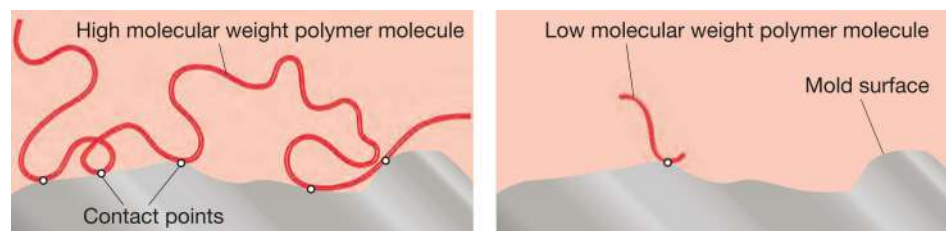


Figure 2.28 Influence of molecular weight on the slip between polymer and tool surface

If the speed is further increased, a helical geometry is extruded, as shown for a polypropylene extrudate in Fig. 2.27 c. Eventually, the speeds are so high that a chaotic pattern develops, such as the one shown in Fig. 2.27 d. This well known phenomenon is called melt fracture. The shark skin effect is frequently absent and spurt flow seems to occur only with linear polymers.

Another form of melt fracture may occur during elongational deformation, for example during fiber spinning. Here, when the drawing speed is too high, the stresses build up before having a chance to relax, until the thread rips, or fractures. We can observe the same effect when stretching silly putty at high speeds.

Although the molecular weight is lower in injection molding grades, these flow instabilities can also occur during mold filling, e.g., with polyacetal or high density polyethylene. These instabilities result in surface defects on the finished part that may take the form of matte surfaces, regular helices, or irregularly spaced ripples.

Production guidelines often recommend a reduction of injection velocity or extrusion speed, an increase of mold and melt temperature, or an increase of the gate diameter to eliminate melt fracture.

■ 2.7 Dynamic Response

In an oscillatory test, a sample is excited with a low frequency stress or strain input which is recorded along with the strain or stress response. Figure 2.29 presents schematic diagrams of a shear strain input, γ_{xy} , and shear stress response, τ_{xy} , for a perfectly elastic solid, an ideal viscous fluid, and a viscoelastic fluid with a linear viscoelastic response.

If the sample in an oscillatory test is perfectly elastic, or a Hookean solid, the strain input and stress response can be described as follows:

$$\gamma_{xy}(t) = \gamma_0 \sin \omega t \quad (2.15)$$

$$\tau_{xy}(t) = \tau_0 \sin \omega t \quad (2.16)$$

where t is time and $\omega = 2\pi f$ with f being the frequency of strain oscillation. As expected, the stress response is in phase with the strain input. Hence, when computing the shear modulus, the transient effects cancel out, and an elastic modulus, G , results as

$$G = \frac{\tau_0 \sin \omega t}{\gamma_0 \sin \omega t} = \frac{\tau_0}{\gamma_0} \quad (2.17)$$

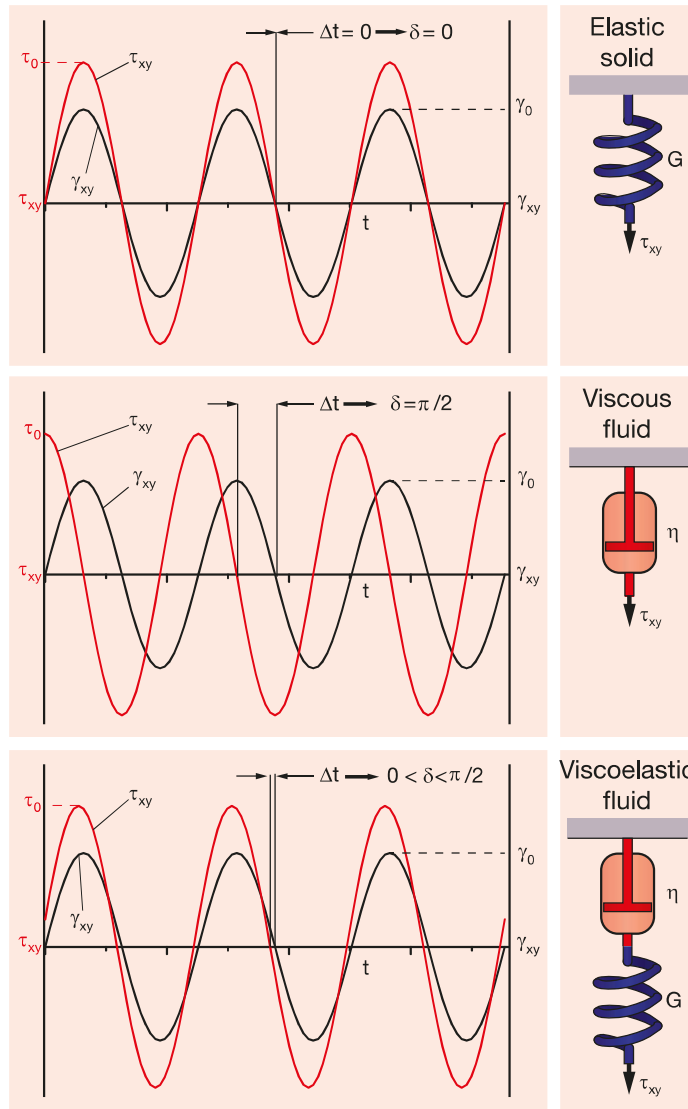


Figure 2.29 Oscillatory shear experiments for an elastic solid, a viscous fluid, and a viscoelastic fluid

On the other hand, if an ideal viscous fluid is subjected to an oscillatory strain, the stress response is proportional to the strain rate, $\gamma_0 \omega \cos \omega t$, which can also be interpreted as a lag of $\pi/2$ radians behind the strain input:

$$\gamma_{xy}(t) = \gamma_0 \sin \omega t \quad (2.18)$$

$$\dot{\gamma}_{xy}(t) = \dot{\gamma}_0 \cos \omega t \quad (2.19)$$

$$\tau_{xy}(t) = \tau_0 \cos \omega t = \tau_0 \sin \left(\omega t - \frac{\pi}{2} \right) \quad (2.20)$$

where $\dot{\gamma}_0 = \gamma_0 \omega$. Using the above equations we can compute the viscosity using the definition of a Newtonian fluid as

$$\eta = \frac{\tau_0 \cos \omega t}{\dot{\gamma}_0 \cos \omega t} = \frac{\tau_0}{\dot{\gamma}_0} \quad (2.21)$$

We can see that here, too, the transient effects cancel each other out, resulting in a constant viscosity.

However, viscoelastic materials, such as polymers, behave somewhere in between the perfectly elastic and the perfectly viscous materials, depending on the time scale. Their response can be described by

$$\gamma_{xy}(t) = \gamma_0 \sin \omega t \quad \text{and} \quad (2.22)$$

$$\tau_{xy}(t) = \tau_0 \sin(\omega t - \delta) \quad (2.23)$$

showing that the stress response lags δ radians behind the strain input, see Fig. 2.29. The shear modulus, computed using the ratio of stress to strain, takes a complex form with real and imaginary terms

$$G^* = \frac{\tau_{xy}(t)}{\gamma_{xy}(t)} = \frac{\tau_0 e^{i\delta}}{\gamma_0} = \frac{\tau_0}{\gamma_0} (\cos \delta + i \sin \delta) = G' + iG'' \quad (2.24)$$

which is graphically represented in Fig. 2.30, and referred to as complex modulus. The length of each vector represents the absolute value of the parameter. Therefore, G^* is the resulting vectorial sum. G' is usually referred to as storage modulus and is represented by

$$G' = \frac{\tau_0}{\gamma_0} \cos \delta \quad (2.25)$$

It is a measure for the stored energy, e.g., during a shearing process. Upon release this energy can be used completely for the recovery of the deformation, which makes it reversible. G'' is referred to as loss modulus and can be computed using

$$G'' = \frac{\tau_0}{\gamma_0} \sin \delta \quad (2.26)$$

It is a measure for the lost energy dissipated, e.g., as heat or used for structural changes of the material. Thus, ideal viscous materials are changed by deformation, which makes the process irreversible. The ratio of loss modulus to storage modulus is referred to as loss factor or loss tangent:

$$\tan \delta = \frac{G''}{G'} \quad (2.27)$$

In an elastic solid, $\delta = 0$ or $\tan \delta = 0$ as G' dominates G'' completely. However, in a viscous fluid, $\delta = 90^\circ$ or $\tan \delta = \infty$ as G'' dominates G' completely. In viscoelastic materials, $0 \leq \tan \delta \leq \infty$, depending on the time scale and temperature. When the viscous and the elastic behavior are equal to $\delta = 45^\circ$ or $\tan \delta = 1$, the material is making a transition from liquid to solid or vice versa. For example, this occurs during curing of thermosets when the system reaches its gel point. In the liquid state, $\tan \delta > 1$ as $G'' > G'$, and after gelation, $\tan \delta < 1$ as $G' > G''$. As can be seen in Fig. 2.30, the loss factor can be calculated using the dimensions of the resulting right angled triangle.

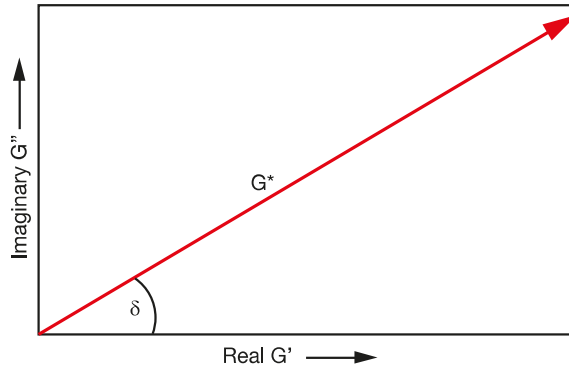


Figure 2.30 Vector representation of the complex shear modulus

Similarly, when the test is regarded from a rheological point of view, a complex viscosity can be computed using the ratio of stress to rate of deformation.

$$\eta^* = \frac{\tau_{xy}(t)}{\dot{\gamma}_{xy}(t)} = \eta' + i\eta'' \quad (2.28)$$

where η' is the viscous component of the complex viscosity, also referred to as the dynamic viscosity, and η'' is the elastic component, also referred to as the out-of-phase component of the complex viscosity. The relation between the complex modulus and complex viscosity components can be described by

$$\eta'' = \frac{G'}{\omega} \quad (2.29)$$

$$\eta' = \frac{G''}{\omega} \quad (2.30)$$

with η'' representing the elastic and η' the viscous behavior. This complex modulus representation is often used in industrial testing.

In 1958, Cox and Merz [15] observed that there is an equivalence between viscosity measured during oscillatory tests at low frequencies and the viscosity measured using a steady shear device at low rates of deformation. The equivalence can be expressed as

$$\eta'(\omega) \Big|_{\omega \rightarrow 0} = \eta(\dot{\gamma}) \Big|_{\dot{\gamma} \rightarrow 0} \quad (2.31)$$

In 1992, Al-Hadithi, Barnes, and Walters [16] defined a similar rule to Cox and Merz's rule, where they related the storage modulus measured by oscillatory tests to the first normal stress difference measured by a steady shear rheometer. Using

$$\frac{G'(\omega)}{\omega^2} \Big|_{\omega \rightarrow 0} = \frac{N_1(\dot{\gamma})}{2\dot{\gamma}^2} \Big|_{\dot{\gamma} \rightarrow 0} \quad (2.32)$$

and trial-and-error, Al-Hadithi et al. established the following relationship

$$N_1(\dot{\gamma}) \approx 2G'(\omega) \left[1 + \frac{(\eta_0 + \eta')G'(\omega)}{2\omega\eta'^2} \right]^{1/2} \quad (2.33)$$

where η_0 is the zero shear rate viscosity. However, in most cases the simple Cox-Merz rule (Eq. 2.31) can be used as long as the test is performed within the linear viscoelastic range, also referred to as small amplitude oscillatory shear (SAOS) test. The linear viscoelastic domain is valid for most polymers when the deformation stays below 10% strain.

Recalling the definition of the Deborah number from Chapter 1, $De = \lambda/t_p$, we recognize that in an oscillatory test the characteristic time can be defined by $1/\omega$, resulting in $De = \lambda\omega$. However, deformation, γ_0 , in conjunction with the Deborah number results in a Weissenberg number, $We = \gamma_0\lambda\omega$, which is a dimensionless number similar to the Deborah number that includes deformation in addition to time scale and relaxation time. Hence, a small Weissenberg number represents a process in the linear viscoelastic domain.

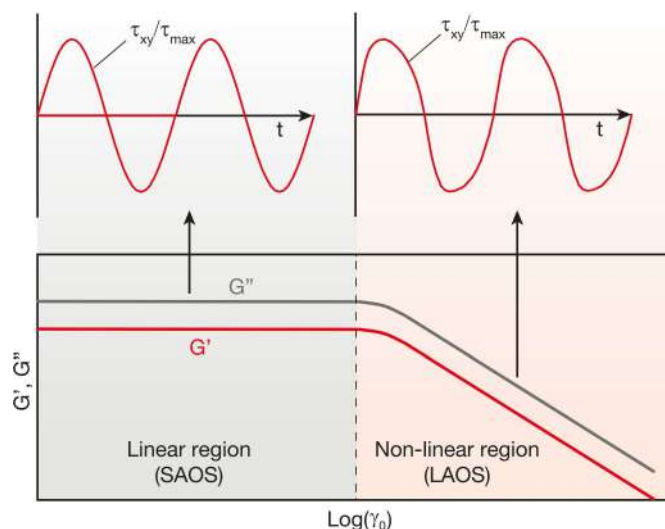


Figure 2.31 Schematic diagram of strain magnitude sweep at a constant test frequency, with visible linear (SAOS) and non-linear (LAOS) viscoelastic responses and their corresponding stress responses.

Once the deformations are large, e.g., $We > 1$, such as those polymer melts are subjected to during processing, the stress response starts exhibiting a non-sinusoidal response, where higher harmonics become evident (Fig. 2.31) [17]. In these cases, the stress response can be represented using

$$\tau_{xy}(t) = \tau_1 \sin(\omega t + \delta_1) + \tau_3 \sin(3\omega t + \delta_3) + \tau_5 \sin(5\omega t + \delta_5) \dots \quad (2.34)$$

A fast Fourier transform of the stress response can be used to determine the contribution of each frequency on the compound stress response. Often, the first two terms, the first and third harmonic, are sufficient to represent the stress wave.

At large deformations, material properties such as storage and loss shear modulus start to exhibit a deformation-dependent behavior caused by molecular disentanglement and molecular orientation. Oscillatory shear tests are referred to as large amplitude oscillatory shear (LAOS). Large deformations are more realistic when analyzing polymer melts because strains that are felt by the material during processing flows can be of several 100%. Figure 2.31 shows a schematic of polymer responses under oscillatory shear caused by small to large deformations.

Example 2.5 Storage and Loss Modulus Measurements Using Oscillatory Shear Tests

Using the same extrusion blow molding grade high density polyethylene as in Example 2.1, measure the storage and loss moduli as functions of frequency and temperature.

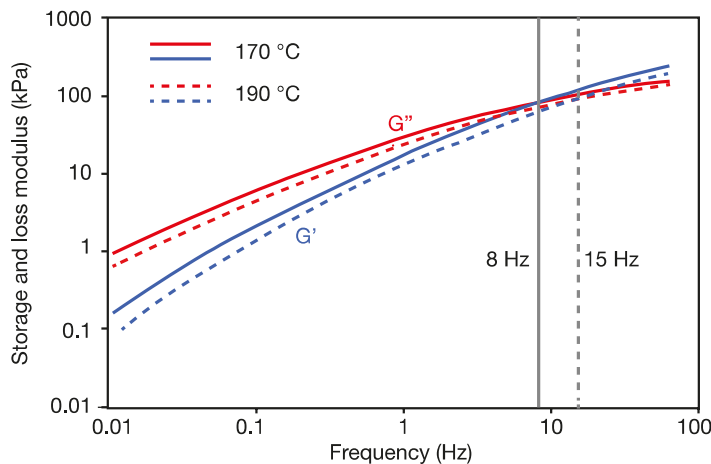


Figure 2.32 Storage and loss moduli for a blow molding grade PE-HD as functions of frequency and temperature.

The storage and loss moduli were measured using a parallel plate rheometer (see Chapter 6) in the linear strain domain, with an applied strain amplitude of 2%. A frequency scan from 0.1 to 70 Hz was performed at 170 °C and 190 °C. The disc size was 25 mm with a distance between the plates of 2 mm. Figure 2.32 shows the results.

Example 2.6 Small and Large Amplitude Oscillatory Shear Tests

Using the same extrusion blow molding grade high density polyethylene as in Example 2.1, measure the stress response when imposing an oscillatory strain input. Repeat the experiment for various shear rates and strain amplitudes.

The same samples used in the previous examples within this chapter were used to impose an oscillatory shear strain for small to large amplitudes, covering the linear and non-linear viscoelastic regimes. Figure 2.33 presents the stress response for a frequency of 7.5 rad/s and a strain amplitude of 0.5. The graph reflects a sinusoidal response, representing a linear behavior. When plotting the stress response as a function of strain input, an elliptical Lissajous curve is generated (Fig. 2.34). The elliptical shape also reflects a linear behavior. It should be noted that the area inside the closed loop represents the volume-specific energy dissipated during one cycle. On the other hand, Fig. 2.35 presents the stress response at a frequency of 10 rad/s and a large strain amplitude of 10. The figure clearly shows a stress response that is not sinusoidal, revealing higher harmonics, as described in Eq. 2.34. Furthermore, the Lissajous loop shown in Fig. 2.36 is no longer elliptical, also reflecting the non-linear behavior at larger strain amplitudes. A full Pipkin diagram (see Chapter 5) is presented in Fig. 2.37, where the linear and nonlinear responses are visible.

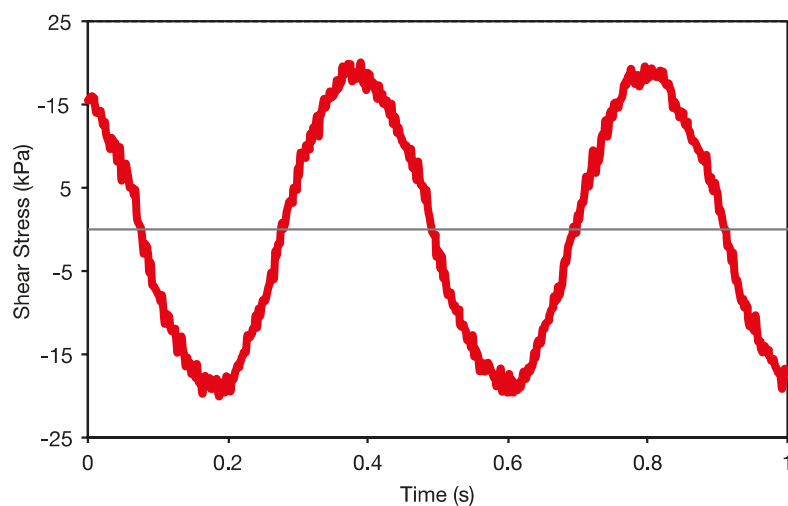


Figure 2.33 Stress response for small amplitude (0.5 strain) deformations and a frequency of 7.5 rad/s of a blow molding grade PE-HD.

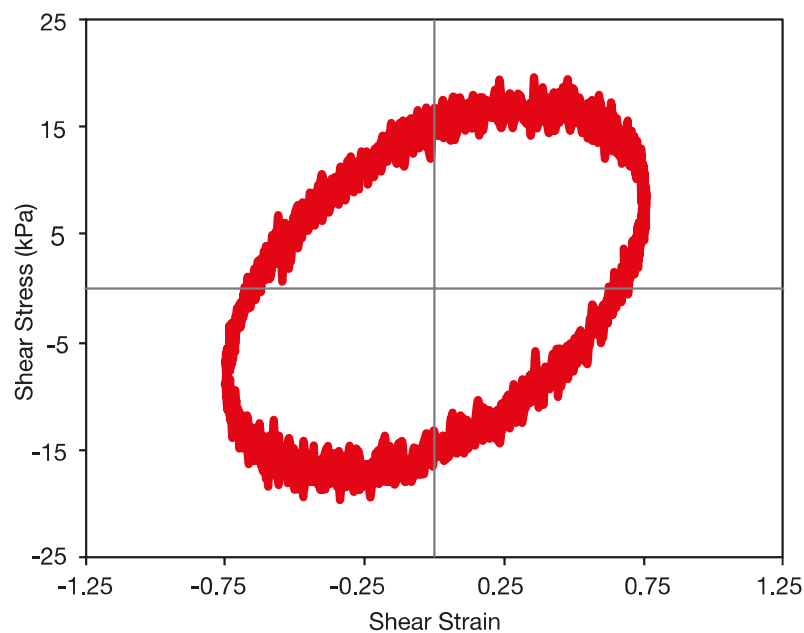


Figure 2.34 Lissajous loop for small amplitude (0.5 strain) deformation and a frequency of 7.5 rad/s of a blow molding grade PE-HD.

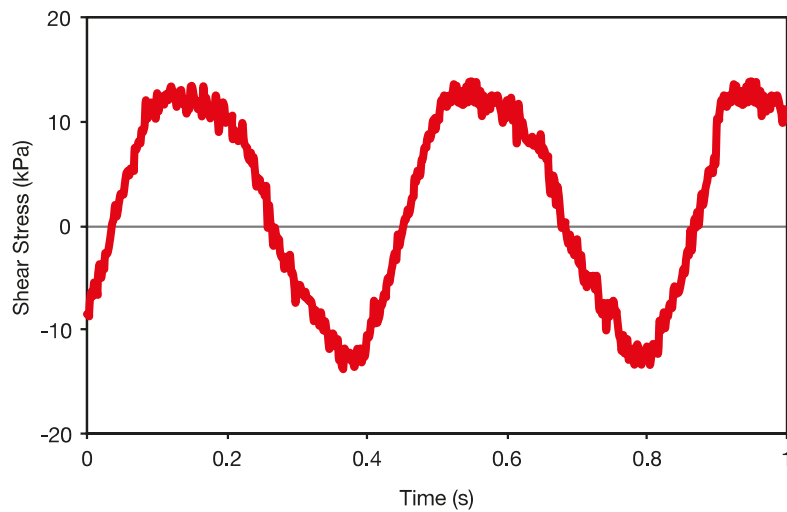


Figure 2.35 Stress response for large amplitude (10 strain) deformations and a frequency of 10 rad/s of a blow molding grade PE-HD.

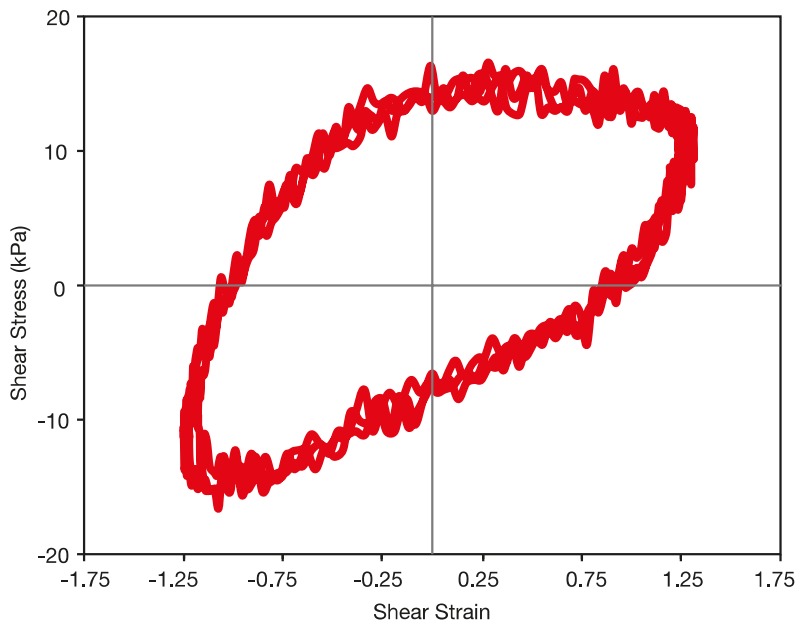


Figure 2.36 Lissajous loop for large amplitude (10 strain) deformations and a frequency of 10 rad/s of a blow molding grade PE-HD.

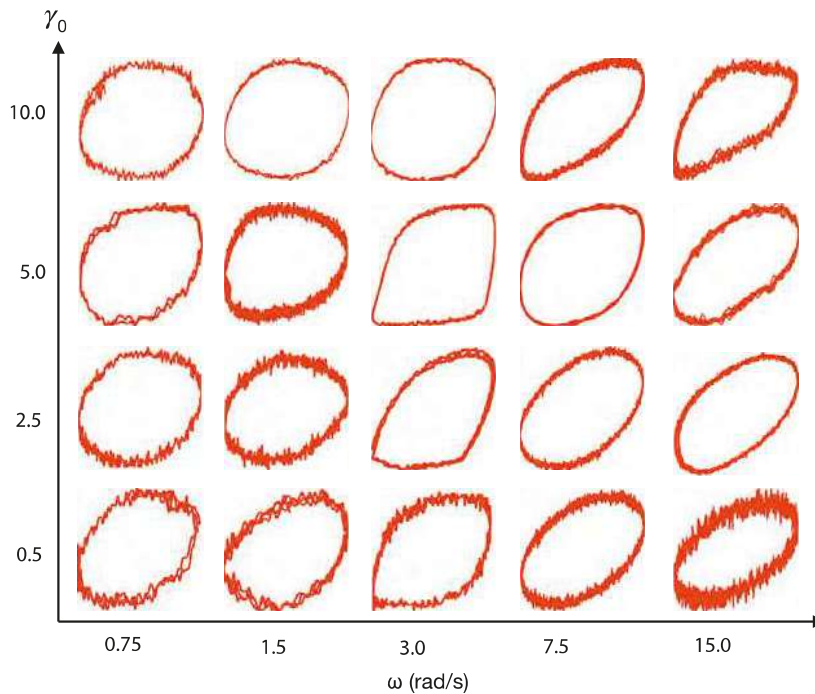


Figure 2.37 Pipkin space for a blow molding grade PE-HD.

■ Problems

- 2.1 Compare the Maxwell model presented in Chapter 1 to the experimental data from the step strain test presented in Example 2.1. How does the Maxwell model's relaxation time, λ , compare to the measured 99% decay value?
- 2.2 Generate a plot of the first normal stress difference coefficient, ψ_1 , for the graphs given in Example 2.2.
- 2.3 Generate a plot of the first normal stress difference coefficient, ψ_1 , using the information given in Figure 10 of the following paper: Baird, D. G., *J. Non-Newtonian Fluid Mech.*, 148, 13–23, (2008).
- 2.4 Compare the results of the stress relaxation test of Example 2.1 and the stress overshoot test of Example 2.4.
- 2.5 Find a function of the form presented in Eq. 2.34 to fit the nonlinear stress response of Example 2.5. Use the first two terms of the equation.

- 2.6** A sliding plate rheometer was used to perform a stress overshoot and relaxation test on a 4 MFI polypropylene copolymer at 190 °C (Fig. 2.38). The relative speed between the two plates was 4.15 mm/s and the separation between the plates was 2.3 mm. At what shear rate was the test performed? What is the viscosity at the given rate of deformation? Compare the time it took to reach a steady state shear stress and the relaxation time after the plates stopped moving. What can you conclude?

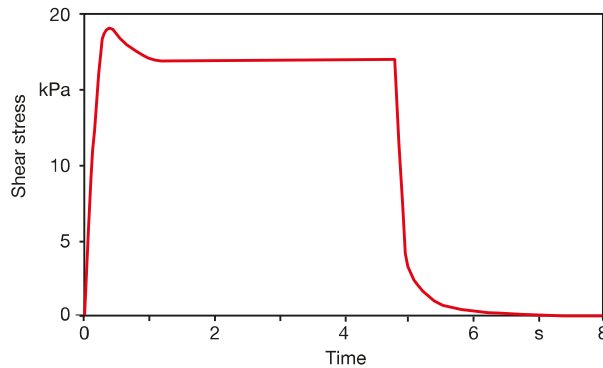


Figure 2.38 Sliding plate rheometer test of a PP copolymer.

- 2.7** Compare the loss modulus measured in Example 2.5 to the viscosity measured in Example 2.2. Use Eq. 2.30 for your comparison.
- 2.8** Use the storage and loss moduli graphs presented in Example 2.5 to discuss the significance of the point where the two graphs cross. How does temperature affect this cross-over point?

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Polymer Rheology

This book is designed to provide a background in polymer rheology to both engineering students and practicing engineers. It is written at an intermediate level with sufficient technical information and practical examples to enable the reader to understand the interesting and complex rheological behavior of polymers, to make the right decisions regarding rheological testing methods, and to troubleshoot rheology related problems encountered in polymer processing. The organization of the book and the practical examples throughout make it an ideal textbook and reference source. Processors and raw material suppliers will find the information within particularly valuable. Rheology is a rapidly growing and industrially important field, playing a significant role not only in polymer processing, but also in food processing, coating and printing, and many other manufacturing processes.

Topics covered:

- Historical background
- Structure and properties of deforming polymers
- Generalized Newtonian fluid (GNF) models
- Transport phenomena in rheometric flows
- Linear viscoelasticity
- Non-linear viscoelasticity
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