

## RHEOLOGY

### **Crispulo Gallegos**

*Complex Fluid Engineering Laboratory. Departamento de Ingeniería Química.  
University of Huelva. 21071 Huelva, Spain*

### **Kenneth Walters**

*Institute of Mathematical and Physical Sciences, Aberystwyth University, U.K.*

**Keywords:** rheology, rheometry, materials, processes, theoretical, viscosity, viscoelasticity, shear, extensional

### **Contents**

- 1 What is Rheology?
- 2. The major components of rheology discussed in this book
  - 2.1. Basic concepts on Rheology: an overview
  - 2.2. Rheometry
  - 2.3. Rheological materials
  - 2.4. Rheological processes
  - 2.5. Theoretical rheology
- 3. Conclusion
- Glossary
- Bibliography
- Biographical Sketches

### **Summary**

The aim of this overview is to outline and summarize the comprehensive information on “Rheology” contained in the remaining 23 chapters on this subject which make up the contents of this Encyclopedia. To facilitate the task, we have chosen to divide the chapters into five main areas, namely, basic concepts of rheology; rheometry; rheological materials, rheological processes and theoretical rheology. Of course, many of the chapters contain material from more than one general area. This to be expected and supports the view that rheology is an interdisciplinary subject which embraces many aspects of mathematics, physics, chemistry, engineering and biology.

All the sub-areas mentioned above are described in this overview. Furthermore, for obvious reasons, the collection of chapters begins with one on “The History of Rheology”, written by one of the authors of this general introduction (K. Walters)

### **1. What is Rheology?**

“Rheology” is not a subject which is on everybody’s lips! Indeed, some well known dictionaries do not even include a definition of the term. So, for example, the small Collins Gem Dictionary is quite happy to inform its readers that a “rhea” is a “three-toed South American ostrich”, whilst at the same time offering no definition for

“rheology”! Why is that so? Is it because rheology is a relatively recent science, which only came into prominence in the second half of the 20<sup>th</sup> Century? Is it because rheology is a truly interdisciplinary science and, as a result, does not fit easily into any of the established scientific disciplines?

It is probably a combination of these and related factors, but there are some encouraging signs that the subject is being taken seriously by the publishers of modern dictionaries. For example, the Concise Oxford Dictionary defines rheology as the “study of flow and deformation of matter”.

Having said that, there are some disturbing signs that the message is still not receiving universal acceptance. So, for example, some respectable computer “spell checks” (like the one we are currently using to type this text within a “Microsoft Word” framework) alert users to a “spelling error” when the term rheology is included in the text. Interestingly, the “spelling and grammar” facility suggests that “rheology” must be a misprint for “theology”.

There may be some excuse for this conclusion, since on the conventional QWERTY keyboard, the letter “r” and the letter “t” are next to each other. What is clear is that over-zealous proof readers in the publication business have often come to the conclusion that rheology must be a misprint for theology, with an obvious consequence – “theology” is spread liberally throughout the rheological literature with a frequency which is most definitely outside any acceptable criterion of randomness!

We suggest that this preamble provides ample evidence that the current book is very timely! However, we need to address the subject in hand.

The term “rheology” was invented by Professor Eugene Bingham of Lafayette College in Easton, Pennsylvania on the advice of a colleague, the Professor of Classics. It was meant to mean “the study of the deformation and flow of matter”, which is of course consistent with the dictionary definition given above.

This definition was accepted when the (American) Society of Rheology was founded in Washington DC in 1929. That first meeting contained papers on the properties and behavior of such widely differing materials as asphalt, lubricants, paints, plastics and rubber, which gives some idea of the scope of the subject and also the numerous scientific disciplines that are likely to be involved. Nowadays, the scope is even wider with Biorheology (the study of body fluids) and the incredible growth in the synthetic fiber and plastics industries. There are now thriving national Societies of Rheology in many countries, divided into three major groupings, namely Europe, the Americas, and the so-called Pacific Rim. In many ways, rheology has come of age!

In this book, various experts will elaborate on what rheology is all about and how it differs from classical continuum mechanics, i.e. solid and fluid mechanics – subjects associated with the names of Hooke, Newton, Navier and Stokes.

Notice that we have already referred to *solids* and *liquids*, without defining what we mean by these terms. We assume that, when we refer to a solid or a liquid, the reader

will know exactly what we mean. If asked for definitions, we would probably get a variety of answers, but they would all contain the same basic ideas. A *liquid* is a material that flows under its own weight; it finds its own level when placed in a beaker. A *solid* is a material that suffers from “homesickness”, once stresses are removed, it has a strong desire to return to its original configuration. When a solid is dropped on the floor, it bounces; it has elastic properties.

These would be acceptable answers and most people would not expect any ambiguity to arise from the respective definitions. This is however a gross over-simplification of what is a complex situation.

To emphasize the point, we ask the reader to consider the popular material known as Silicone, which is sometimes used for packing electronic equipment, which is used in physiotherapy, and which is often sold as a childrens’ toy.

On the basis of popular definitions of solid-like and liquid-like behavior, the silicone is a *liquid*, although usually a very viscous one. It will find its own level when placed in a container, given sufficient time, i.e. it flows! But this is not the whole story, because the silicone is often nicknamed “Bouncing Putty”. In its capacity as a children’s toy, it is sometimes sold as “the real solid liquid” and this does not violate any Trades Description Act! For interest, we show in Figure 1 the publicity material for a similar product called *Wonder putty*, which clearly has some of features referred to above.

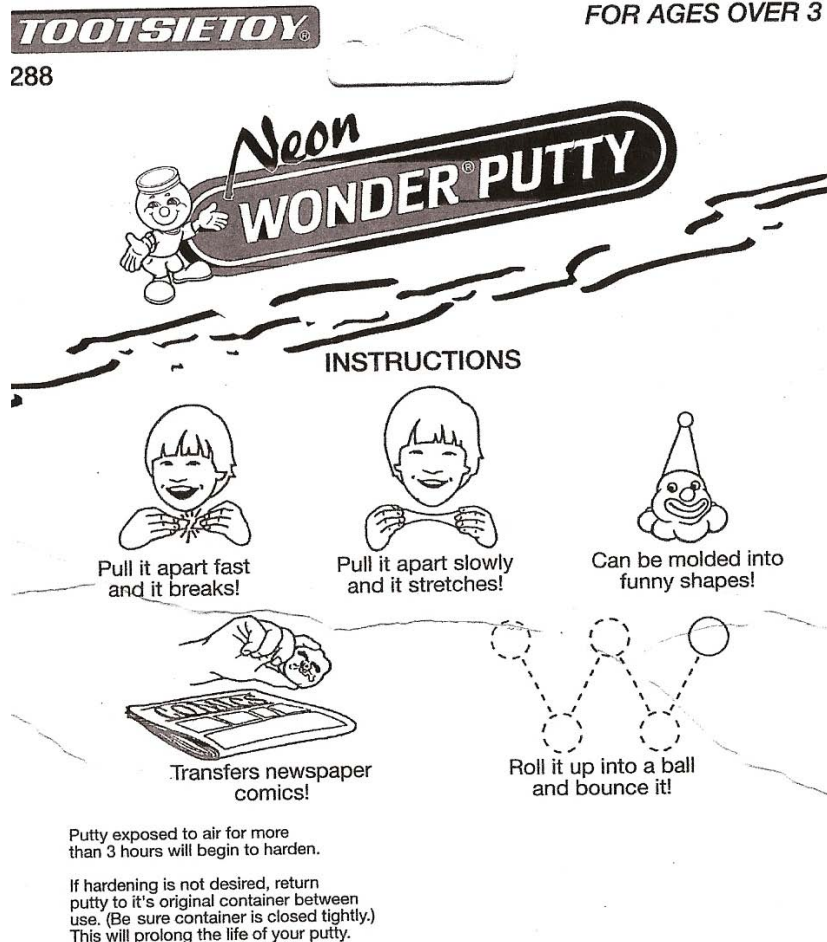


Figure 1. Publicity material supplied with the *Wonder putty* children's toy product.

It is not difficult to argue that a material like silicone is a liquid, but one which possesses some of the properties we usually associate with solids. Rheologists call it an *elastico-viscous liquid* or simply an *elastic liquid*. The most common examples of elastic liquids are the polymer solutions and melts used in the synthetic fiber and plastics industries, liquid detergents, multigrade oils, and many “body fluids”, but this list is by no means complete. Little wonder then that there is a general belief amongst rheologists that their science should be better known by non-experts than it is!

At this point it is informative for us to give further consideration to some of the simple tests that can be carried out on the silicone material we discussed above. So, in a *slow* flow process, the material behaves like a liquid – it finds its own level in a container. When it is extended *slowly*, it shows ductile fracture, which is a liquid characteristic. However, when the silicone is extended on a shorter time scale, it exhibits brittle fracture, which is a *solid* characteristic. Under the severe and sudden deformation experienced as the material strikes the ground, it bounces, which is again a *solid* characteristic.

*So, a given material can behave as a solid or a liquid depending on the time scale of the deformation process.*

In this connection, Marcus Reiner, who was one of the organizers of the original 1929 meeting in Washington DC, introduced the helpful concept of the *Deborah number*. This he based on an Old Testament scripture from the Book of Judges, Chapter 5, verse 5, where Reiner said the text should read “The mountains flow before the Lord”. The idea is that “*everything flows if you wait long enough*”.

On the basis of the Bible reference, Reiner defined the so-called Deborah number,  $De$ , through the equation:

$$De = \lambda/T \quad (1)$$

where  $T$  is a characteristic time of the deformation process and  $\lambda$  is a characteristic time of the material. The symbol  $\lambda$  can be viewed as a “measure of the material’s memory”. This would be infinite for a perfectly elastic solid and zero for a purely-viscous (Newtonian) liquid. In fact, for water  $\lambda$  is typically quoted in the  $10^{-13}$  seconds range. For many lubricating oils,  $\lambda$  is of the order of  $10^{-6}$  seconds, and for the polymer melts used in the plastics industries, the characteristic times can be as high as a few seconds.

High Deborah numbers correspond to solid-like behavior and low Deborah numbers to liquid-like behavior. A material can appear solid-like either because it is, i.e. it has an infinite characteristic time, or because the deformation process that is in use is very fast. One obvious consequence of this is that even mobile liquid systems with very low characteristic times can behave like elastic solids when exposed to a very-fast deformation process.

As we shall see in later chapters, the Deborah number concept has significant utility in many rheological studies, especially since it highlights the fact that it is not only the relaxation time  $\lambda$  which determines material behavior, but also the time scale of the deformation process.

In the foregoing discussion, we have argued that there are liquids that possess solid-like characteristics. What needs to be stressed at this point is that there are also solid-like materials that will flow for a time. Such materials are invariably called *viscoelastic solids*.

Interestingly, it seems that the rheological term *viscoelasticity* is slowly entering into every-day usage and we show in Figure 2 a recent “Pillow menu” provided by a Spanish hotel.

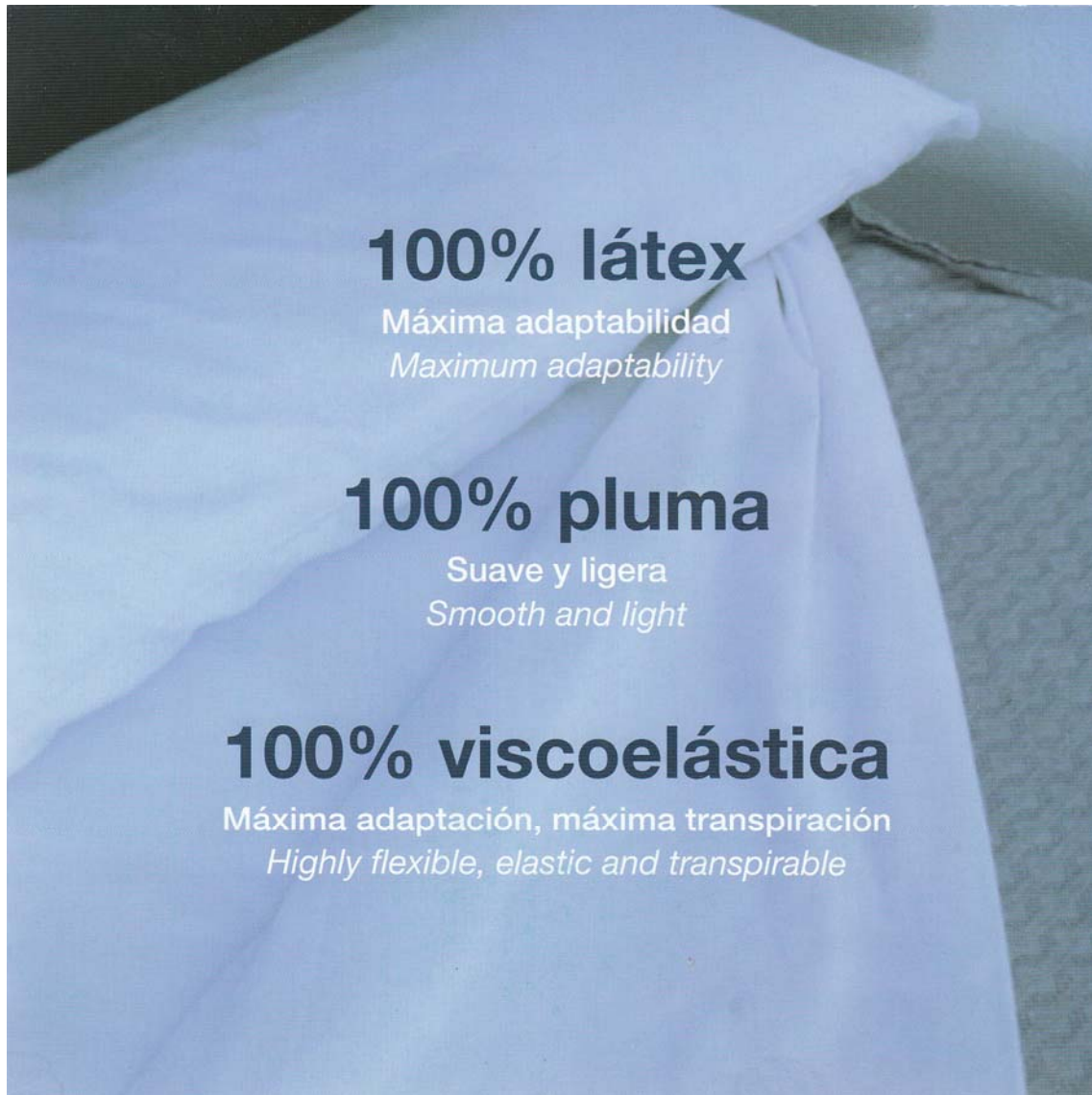


Figure 2. The “Carta de almohadas” taken from the bedroom of a Spanish hotel.

To complete this particular part of the story, it is important to refer to two further issues and material types. The first concerns an important sub-class of materials that appear solid-like under small stresses and liquid-like above some critical value called the *yield stress*. These are invariably called *plastic materials*.

The second sub-set of materials we need to reference can be loosely classified as “time-dependent”. Such materials can be conveniently introduced in the following way:

In addition to the change in material properties that can be brought about by changes in the time-scale of a deformation process and by the strength of that process, there are also changes which can be brought about in some materials by simply waiting long enough! The stirring of some materials at a constant rate can result in a substantial lowering of the viscosity, with a gradual return to the initial viscosity when the stirring

is stopped. This effect is called *thixotropy* and has been actively encouraged in some paints.

Some materials show the opposite type of response, with an *increase* in viscosity as time progresses. In the scientific literature, this phenomenon is known by at least three terms: *anti-thixotropy*, *negative thixotropy*, and *rheopexy*, although the last of these is now seen as being inappropriate.

Many of the fascinating and distinctive features of material behavior mentioned above have been captured in a 20 min CD presentation entitled “Non-Newtonian Fluids”. This was constructed by the Institute of Non-Newtonian Fluid Mechanics (Wales) and copies are still available for distribution, as are copies of related presentations on the “History of Rheology”, “Boger Fluids”, “Extravagant Viscoelastic Effects” and “Yield Stress”. These films are recommended as useful learning tools for newcomers to the field of rheology.

We hope that this section has “set the scene” for the detailed and focused aspects of rheology, which will occupy the remainder of this volume.

-  
-  
-

TO ACCESS ALL THE 14 PAGES OF THIS CHAPTER,  
Visit: <http://www.eolss.net/Eolss-sampleAllChapter.aspx>

### Bibliography

Barnes H.A. and Walters K. (1985) *The yield stress myth?* *Rheological Acta* **24**, 323-326. [A short provocative paper which questions the yield-stress concept.]

Barnes, H.A., Hutton, J.F. and Walters, K. (1989) *An introduction to rheology*. Elsevier, Amsterdam (Holland). [A very popular introductory text on Rheology].

Barnes H.A. (1999) *The yield stress – a review*. *J. non-Newtonian Fluid Mechanics* **81**, 133-178. [A comprehensive review of the yield-stress debate.]

Barnes, H.A. (2000) *A handbook of elementary Rheology*. Institute of Non-Newtonian Fluid Mechanics-University of Wales, Aberystwyth (Wales, UK). [General and relevant text book on rheology].

Bingham E.C. (1922) *Fluidity and plasticity*. McGraw Hill, New York. [The introduction of the most famous equation for yield-stress materials.]

Boger D.V. (1977/78) *A highly elastic constant-viscosity fluid*. *J. non-Newtonian Fluid Mechanics* **3**, 87-91. [The first reference to the so-called Boger fluid.]

Boger D.V. and Walters K. (1993) *Rheological Phenomena in Focus*. Elsevier. [Contains a comprehensive set of flow-visualization pictures for non-Newtonian fluids.]

Boltzmann L. (1874) *Sitzber Kgl Akad Wiss Wien, Math-Naturw Classe* **70**, 275-306. (1877) *Sitzber Kgl Akad Wiss Wien* **76**, 815-842. (1878) *Wied Ann* **5**, 430-432. [A series of papers related to the famous Boltzmann integral equations for linear viscoelasticity.]

- Broadbent J.M., Kaye A., Lodge A.S. and Vale D.G. (1968) *Possible systematic errors in the measurement of normal stress differences in polymer solutions in steady shear flow*. *Nature* **217**, 55.
- Coleman B.D. and Noll W. (1960) *An approximate theorem for functionals with applications in continuum mechanics*. *Arch. Rat. Mech. Anal.* **36**, 355-370. [Derivation of the hierarchy equations for slow flow of elastic liquids.]
- Crochet M.J., Davies A.R. and Walters K. (1984) *Numerical simulation of non-Newtonian flow*, Elsevier. [The first text book to be devoted to Computational Rheology.]
- Dealy, J.M. and Wissbrun, K.F. (1995) *Melt rheology and its role in plastic processing*. Chapman & Hall, London (UK). [General and relevant text book on polymer viscoelasticity].
- Doi M. and Edwards S.F. (1978) *Dynamics of concentrated polymer systems* Parts 1-4. *J. Chem. Soc. Faraday Trans.* **74**, 1789-1801, 1802-1817, 1818-1832, **75**, 38-54. (1986) *The theory of polymer dynamics*, Clarendon Press, Oxford. [Contains important work on the application of reptation ideas for polymeric systems.]
- Ferry, J.D. (1980) *Viscoelastic properties of polymers*. John Wiley & Sons, New York (USA). [General and relevant text book on polymer viscoelasticity].
- Fröhlich H. and Sack R. (1946) *Theory of the rheological properties of dispersions*. *Proc Roy. Soc.* **A185**, 415-430. [Derivation of the (linear) equations for a dilute suspension of rigid spheres in a Newtonian fluid.]
- Hooke R. (1676) *A description of helioscopes and some other instruments*. London. Printed by T.R. for John Martyn. [The introduction of the famous linear law for elastic solids – introduced as a Latin anagram!] This was followed by a more comprehensible paper in 1678 – “*De potential restitutiva*”. J.Martyn, London.
- Jaumann G. (1905) *Grundlagen der bewegungslehre* “Springer, Leipzig (1911) *Sitz Akad Wiss Wien* **120**, 385-530. [Introduction of a non-linear time derivative for non-Newtonian fluids – sometimes known as the Jaumann derivative and also the corotational derivative.]
- Lodge A.S. (1956) *A network theory of flow birefringence and stress in concentrated polymer solutions*. *Trans. Faraday Soc.* **52**, 120-130. [Derives constitutive equations for the so-called “rubber-like liquid”.]
- Macosko, C. W. (1994) *Rheology principles, measurements and applications*, VCH Publishers, New York (USA). [General and relevant text book on rheology]
- McLeish T.C.B. and Larson R.G. (1998) *Molecular constitutive equations for a class of branched polymers: The pom-pom polymer*. *J. Rheol.* **42**, 81-110. [An important paper in polymer melt rheology.]
- Mezger, T. (2006) *The Rheology handbook*, Vincentz Network, Hannover (Germany). [An engineering textbook on rheology with detailed advice for experimental rheology].
- Oldroyd J.G. (1950) *On the formulation of rheological equations of state*. *Proc. Roy. Soc.* **A200**, 523-541. [A very important paper on the construction of constitutive equations for elastic liquids.]
- Oldroyd J.G. (1953) *The elastic and viscous properties of emulsions and suspensions*. *Proc. Roy. Soc.* **A218**, 122-132. [Derivation of the (linear) equations for dilute emulsions.]
- Perera M.G.N. and Walters K. (1977) *Long-range memory effects in flows involving abrupt changes in geometry*. *J. non-Newtonian Fluid Mechanics* **2**, 49-81, 191-204. [The first successful attempt(s) to apply (finite-difference) numerical schemes in the case of long-range memory effects and complex geometries.]
- Phan Thien N. and Tanner R.I. (1977) *A new constitutive equation derived from network theory*. *J. non-Newtonian Fluid Mechanics* **2**, 191-204. [This paper saw the introduction of a constitutive equation which is still popular.]
- Poynting J.H. and Thomson J.J. (1902) *Properties of Matter*, London: Charles Griffin and Co. Ltd. [Contains the first reference to mechanical models.]
- Reiner M. (1945) *A mathematical theory of dilatancy*. *Amer. J. Math.* **67**, 350-362. [The paper derives the equations for the so-called Reiner-Rivlin fluid.]



Reiner M. (1964) The Deborah number. *Physics Today* **17**, 62. [Contains a popular introduction to the concept of the Deborah number.]

Rivlin R.S. (1948) *The hydrodynamics of non-Newtonian fluids Part 1*. *Proc. Roy. Soc* **A193**, 260-281. [The paper derives the equations for the so-called Reiner-Rivlin fluid.]

Tanner, R.I. (1985). *Engineering Rheology* Clarendon Press, Oxford (UK). [General and relevant text book on rheology applied to engineering].

Tanner R.I. and Walters K. (1998) *Rheology: An historical perspective*. Elsevier. [Recommended reading for those who wish to know more about historical developments in Rheology.]

Thomson W. (1865) *Proc. Roy. Soc.* **14**, 289-297. (1878). *Elasticity and heat in Encyclopedia Britannica 9<sup>th</sup> Edition*. [Introduces what is often referred to as the Kelvin-Voigt model for viscoelastic solids. Thomson is better known as Lord Kelvin.]

Trouton F.T. (1906) *On the coefficient of viscous traction and its relation to that of viscosity*. *Proc. Roy. Soc.* **77**, 426-440. [An influential paper on *extensional* flow, limited in this case to Newtonian fluids.]

Tshoegl, N.W. (1989) *The phenomenological theory of linear viscoelastic behavior*. Springer Verlag, Berlin (Germany). [General and relevant text book on linear viscoelasticity].

Walters K. and Webster M.F. (2003) *The distinctive CFD challenges of computational rheology*. *Int. J. for Numerical Methods in Fluids* **43**, 577-596. [An example of many of the recent reviews on developments in Computational Rheology.]

### Biographical Sketches

**Crispulo Gallegos** is Professor of Chemical Engineering and Chair at the University of Huelva (Spain). He received his PhD from the University of Seville in 1982. From 1985-1997 he was Professor of Chemical Engineering at the University of Seville (Spain). He has also been Visiting Professor at several universities, including the University of Cambridge (UK) and Université Laval (Canada). His research interests lie in rheology, microstructure and processing of complex fluids. Professor Gallegos is the author of more than 200 papers in scientific journals and books, and author of more than 200 contributions to international and national conferences. He is co-inventor in 8 patents. He is member of the Editorial Boards of different scientific journals. Dr. Gallegos has been Scientific Coordinator of the Food Technology Area of the National Agency for Evaluation and Prospective of the Spanish Ministry for Science and Technology (2001-2004). Since 2009, he is President of the European Society of Rheology.

**Professor Ken Walters** was appointed Professor at the University of Wales Aberystwyth (now Aberystwyth University) in 1973. He was awarded a DSc degree in 1985. He is a former President of the British Society of Rheology and received their gold medal in 1984. He was elected a Fellow of the Royal Society in 1991 and is a Foreign Associate of the National Academy of Engineering of the United States. In 1998, he was awarded an Honorary Doctorate by the Université Joseph Fourier in Grenoble, France and received the Weissenberg Award of the European Society of Rheology in 2002.

Professor Walters is the author of several books on rheology, rheometry and non-Newtonian fluid flow. He was Executive Editor of the *Journal of Non-Newtonian Fluid Mechanics* from its launch in 1976 until the publication of Volume 100 in 2002. From 1996-2000, Professor Walters was the first President of the European Society of Rheology, and from 2000-2004, he was Chairman of the International Committee on Rheology.