

HIGH PRESSURE RHEOLOGY

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Summary

High-pressure rheology plays an important role in many areas of science and technology. For instance, the accurate determination of the pressure-temperature-viscosity relationship is very important in lubrication science and in the polymer industry. In spite of its importance, the influence that pressure exerts on materials mechanical properties has been less studied than the influence of temperature, mainly due to the well-known difficulty to develop reliable rheological equipment for conducting rheological tests under pressure. High-pressure rheology combines conventional experimental techniques on rheometry with those specific for high-pressure analysis. The pressure-temperature behavior of Newtonian simple materials, such as organic low molecular weight liquids, is well described by simple expressions of viscosity as a function of pressure and temperature. For time-dependent non-Newtonian materials, such as complex mixtures, suspensions, emulsions, high molecular weight polymer solutions and melts, etc., the effect of pressure on the rheological behavior is much more complex. Consequently, more sophisticated analysis, such as, for instance, reduced variables and time-pressure-temperature superposition methods, are necessary.

1. Introduction

High-pressure rheology plays an important role in many areas of science and technology. For instance, the accurate determination of the pressure-temperature-viscosity relationship is very important in lubrication science, because the liquid lubricant is submitted to high pressures, and large shear rates, over a wide range of

temperature. In the polymer industry, processing parameters such as pressure and temperature are essential in order to obtain the desired quality in products made by extrusion, injection molding, compression molding, etc.

The effect of pressure on viscosity is quite small for most organic liquids. Generally, the viscosity approximately doubles its value when the pressure is increased from atmospheric pressure to 100 MPa. On the contrary, for lubricating liquids, pressures of the order of 1 GPa in the point of contact may increase the viscosity of the lubricant in several decades. For polymer injection molding, pressures of about 0.1 GPa may increase between 10-100 times the viscosity of the melts, depending on polymer molecular weight. It is worth pointing out that water, at ambient temperature, is an exception to the general evolution of viscosity with pressure. Thus, water viscosity decreases as pressure increases up to about 0.1 GPa (Barnes, 2000).

In spite of the importance of pressure in many processes and phenomena, the influence that pressure exerts on materials mechanical properties has been less studied than the influence of temperature, mainly due to the well-known difficulty to develop reliable rheological equipments for conducting rheological tests under pressure. Simple materials, such as organic low molecular weight liquids, are well characterized by its Newtonian viscosity. Their pressure-temperature behavior is well described by simple expressions of viscosity as a function of pressure and temperature. For time-dependent non-Newtonian materials, such as complex mixtures, suspensions, emulsions, high molecular weight polymer solutions and melts, etc., the effect of pressure on the rheological behavior is much more complex. Consequently, more sophisticated analysis, such as, for instance, reduced variables and time-pressure-temperature superposition methods, are necessary.

2. Experimental Techniques for High-pressure Rheology

High-pressure rheology combines conventional experimental techniques on rheometry with those specific for high-pressure analysis. Working under a pressurized medium implies a deep knowledge of high-pressure methods. Thus, for instance, for the piston-cylinder system, the classical theory of elastic and plastic deformation of the cylinder is of paramount importance in order to give an insight into the deformation and stresses in high-pressure cells. The effect of temperature on high-pressure equipments must be also taken into account, since high-pressure rheology studies may be accomplished in the low and/or high temperature regions. Finally, reliable techniques for detecting pressure values, transmitted torque, and measured deformation in systems that operate at high pressure are necessary in order to obtain useful rheological parameters.

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Bibliography

Ashare, E., Bird, R.B. and Lescarboursa, J.A., (1965) "Falling Cylinder Viscometer for non-Newtonian Fluids", *A.I.Ch. E. Journal*, (11) 5, 910–916. [Determination of the non-Newtonian viscosity by analyzing the velocity of a falling cylinder].

Audonnet, F. and , A. A.H. Pádua. (2001) Simultaneous measurement of density and viscosity of n-pentane from 298 to 383 K and up to 100 MPa using a vibrating-wire instrument. *Fluid Phase Equilibria* 181 147–161. [Simultaneous determination of density and viscosity using the vibrating-wire technique].

Bair S, Jarzynski J, Winer WO. (2001) The temperature, pressure and time dependence of lubricant viscosity. *Tribol Inter* 34 461–468. [Modeling of the evolution of viscosity with temperature and pressure based on the glassy state properties].

Bair S, Khonsari M, Winer WO. (1998) High-pressure rheology of lubricants and limitations of the Reynolds equation. *Tribol Inter.* 31 573–586. [Study of the relationship between the Reynolds number and the piezoviscous behavior for lubricants].

Bair S. (2001) The high-pressure, high-shear stress rheology of polybutene. *J Non-Newtonian Fluid Mech* 97: 53-65. [Study of the effect of pressure on the rheology of a low molecular weight liquid using the Couette geometry].

Bair, S.S., (2007) *High pressure rheology for quantitative elastohydrodynamics*, Elsevier, Amsterdam. [An excellent comprehensive text on high-pressure rheology that covers both theoretical and experimental approaches].

Barnes, H.A. (2000) *A Handbook of Elementary Rheology*, University of Wales. Institute of Non-Newtonian Fluid Mechanics, Aberystwyth. [An introductory text to rheology].

Barus C. (1893) Isothermals, isopiestic and isometrics relative to viscosity. *Am J Sci*; 45 87-96. [A description of the viscosity-pressure relationship].

Berthe D, Vergne Ph. (1990) High pressure rheology for high pressure lubrication: A review. *J Rheol* . 34:639-655. [A review on high pressure viscometry and rheology applied to EHL problems].

Bridgman, P.W., (1970) *The Physics of High Pressure*, Dover, New York. [A comprehensive old text on high pressure techniques and equipments].

Bridgman. P.W., (1926) "The Effect of Pressure on the Viscosity of Forty-Three Pure Liquids", *Proc. Amer. Acad.*, 61, 57–99. [Study of the effect of pressure on viscosity using a falling body viscometer].

Caudwell, D.R., Trusler, J.P.M., Vesovic, V. and Wakeham, W.A., (2004) "The Viscosity and Density of n-Dodecane and n-Octane at pressures up to 200 MPa and Temperatures up to 473K", *Int. J. Thermophys.*, Vol. 25(5) 1339–1351. [Study of viscosity and density measurements using the vibrating-wire technique].

Cohen, R.E. and Tschoegl, N.W., (1976) 'Comparison of the dynamic mechanical properties of two SBS triblock copolymers with 1,2- and 1,4-polybutadiene central blocks', *Trans. Soc. Rheol.* 20 153–169. [A discussion on the applicability of the time-temperature superposition principle].

Comings, E.W., (1956) *High Pressure Technology*, McGraw-Hill, New York. [A book devoted to high pressure techniques].

Cook RL. , HE King, DG Peiffer, (1992) High-pressure Viscosity of Dilute Polymer Solutions in Good, Solvents *Macromolecules*, 25, 2928-2934. [Study of the effect of pressure on the intrinsic viscosity of dilute polymer solutions].

Cook, R.L., Herbst, C.A. and King, H.E., (1993) "High-Pressure Viscosity of Glass Forming Liquids Measured by the Centrifugal Force Diamond Anvil Cell Viscometer", *J. Phys. Chem.*, Vol. 97(10) 2355–2361. [Study of the application of diamond anvil cells to viscosity measurements at high pressures].

Dandridge, A. and Jackson, D.A., (1981) "Measurements of Viscosity under Pressure: A New Method",

J. Phys. D: Appl. Phys., 14 829–831. [Improvement of a falling body viscometer].

Doolittle AK, Doolittle DB. (1957) Studies in Newtonian flow. Further verification of the free-space viscosity equation. *J Appl Phys* 28 901-905. [Study of the free-volume theory].

Eremets, M.I., (1996) *High Pressure Experimental Methods*, Oxford Univ. Press, Oxford. [A book on the experimental methods used in high pressure tests].

Ferry, J.D. and Stratton, R.A., (1960) 'The free volume interpretation of the dependence of viscosities and viscoelastic relaxation times on concentration, pressure, and tensile strain', *Kolloid-Z.* 171 107–111. [A modelization of the pressure dependence of viscosity based on the free-volume theory].

Ferry, J.D., (1980) *Viscoelastic Properties of Polymers*, 3rd edn., John Wiley and Sons, New York. [A classical book on the viscoelastic properties of polymeric materials].

Fesko, D.G. and Tschoegl, N.W., (1974) 'Time-temperature superposition in styrene/butadiene/styrene block copolymers', *Internat. J. Polym. Mater.* 3, 51–79. [Study of the application of the time-temperature superposition principle].

Fesko, D.G. and Tschoegl, N.W., (1971) 'Time-temperature superposition in thermorheologically complex materials', *J. Polym. Sci., Part C, Symposia* 35, 51–69. [A comprehensive analysis on the applicability of the time-temperature superposition principle]

Fillers RW, Tschoegl N.W., (1977) The Effect of Pressure on the Mechanical Properties of Polymers. *Trans Soc Rheol*, 21, 51-100. [Study of the effect of pressure on the mechanical properties of some polymer using dilatometry].

Freeman, B.D., Bokobza, L. and Monnerie, L., (1990) 'The effect of hydrostatic pressure on local polymer dynamics in polyisoprene', *Polymer* 31, 1045–1050. [Modeling the evolution of viscosity with pressure at low and moderate pressures].

Galvin, G. D., J. F. Hutton, and B. Jones, (1981) "Development of a high-pressure, high shear rate capillary viscometer," *J. Non-Newt. Fluid Mech.* 8, 11-28. [A description of a single-piston high-pressure capillary rheometer].

Geerissen, H., F. Gernandt, B. A. Wolf, and H. Lentz, (1991) "Pressure dependence of viscometric relaxation times measured with a new apparatus—WLF behavior of moderately concentrated solutions of poly-nbutylmethacrylate s in 2-propanol," *Makromol. Chem.* 192, 165–176. [A description of a pressure cell magnetically coupled to a rotational viscometer].

Gross, B., (1969) 'Time-temperature superposition principle in relaxation theory', *J. Appl. Phys.* 40, 3397. [An application of the time-temperature superposition principle].

Gross, B., (1968) *Mathematical Structure of the Theories of Viscoelasticity*, Hermann et Cie., Paris. [A book on the theory of viscoelasticity].

Hersey, M.D., (1916) "The Theory of the Torsion and the Rolling Ball Viscometers and their Use in Measuring the Effect of Pressure on Viscosity", *J. Washington Acad. Sci.*, 6 525–530. [In this study, an electrical method is used at both ends of a falling body viscometer for detecting the position of the body].

Hutton, J.F. and Phillips M.C., "High Pressure Viscosity of a Polyphenyl Ether Measured with a New Couette Viscometer", *Nature Phys. Sci.*, 245 15-16 (1973). [Study of the improvement of a Couette high-pressure viscometer].

Irving, J.B. and Barlow, A.J., (1971) "An Automatic High Pressure Viscometer", *J. Phys. E.*, 4(3) 232–236. [A description of an improved falling body viscometer using inductance coils].

Izuchi, M. and Nishibata, K., (1986) "A High Pressure Rolling-Ball Viscometer up to 1 GPa", *Japanese J. Appl. Phys.*, Vol. 25(7) 1091–1096. [A description of an improved falling body viscometer using variable differential transformers].

Kadijk, S. E. and B. H. A. A. van den Brule, (1994) "On the pressure dependence of the viscosity of molten polymers," *Polym. Eng. Sci.* 34, 1535-1546. [Study of the pressure dependence of viscosity for polymers, using a capillary with double piston].

Kaplan, D. and Tschoegl, N.W., (1974) 'Time-temperature superposition in two-phase polyblends', *Polym. Engrg. Sci.* 14, 43–49. [Study of the applicability of the time-temperature superposition principle]

to polymers blends].

King, H.E., Herbolzheimer, E. and Cook, R.L., (1992) "The Diamond-Anvil Cell as a Viscometer", *J. Appl. Phys.*, Vol. 71(5) 2071–2081. [Study of the application of diamond anvil cells to viscosity measurements at high pressures].

Kinzl, M., Lufta, G., Horst, R., Wolf, B. A. (2002) Viscosity of solutions of low-density polyethylene in ethylene as a function of temperature and pressure, *J. Rheol.* 47(4), 869-877. [Use of a pressure cell magnetically coupled to a rotational viscometer for conducting viscosity-pressure measurements on polymer solutions].

Koran, F. and Dealy, J. M. (1999) "A high pressure sliding plate rheometer for polymer melts" *J. Rheol.* 43 (5) 1279-1290. [Description of a high pressure sliding plate rheometer].

Lamb J, (1977) Viscoelasticity and Lubrication: A Review of Liquid Properties, *J. Rheol.* 22 317-347. [A general review that covers some aspects of the high pressure rheology for lubricants].

Lohrenz, J., Swift, G.W. and Kurata, F., (1960) "An Experimentally Verified Study of the Falling Cylinder Viscometer", *A.I.Ch. E. Journal*, 6(4) , 547–550. [Study of the determination of the non-Newtonian viscosity by analyzing the velocity of a falling cylinder].

Mackley, M. R., R. T. J. Marshall, and J. B. A. F. Smeulders, (1995) "The Multipass Rheometer", *J. Rheol.* 39(6), 1293-1309. [A description of the multipass rheometer].

Martín-Alfonso, M.J., Martínez-Boza, F., Partal, P., Gallegos, C. (2006) Influence of pressure and temperature on the flow behavior of heavy fuel oils, *Rheologica Acta* 45(4), pp. 357-365. [Study of the effect of pressure on fuel oil viscosity using a modified Couette pressure cell].

Martín-Alfonso, M.J., Martínez-Boza, F.J., Navarro, F.J., Fernández, M., Gallegos, C. (2007) Pressure-temperature-viscosity relationship for heavy petroleum fractions, *Fuel* 86 (1-2), pp. 227-233. [Modeling pressure-temperature-viscosity relationship for heavy oils using the FMT model and PVT data].

McLachlan, R.J., (1976) "A New High Pressure Viscometer for Viscosity Range 10 to 106 Pa s", *J. Phys. E.*, 9 391–394. [A description of an improved falling body viscometer using LVDT].

Moonan, W.K. and Tschoegl, N.W., (1983) 'The effect of pressure on the mechanical properties of polymers. 2. Expansivity and compressibility measurements', *Macromolecules* 16, 55–59. [Study of the effect of pressure on the mechanical properties of polymers focused on expansivity and compressibility measurements].

Moonan, W.K. and Tschoegl, N.W., (1984) 'The effect of pressure on the mechanical properties of polymers. 3. Substitution of the glassy parameters for those of the occupied volume', *Internat. Polym. Mater.* 10, 199–211. [Study of the effect of pressure on the mechanical properties of polymers focused on the free volume approach].

Moonan, W.K. and Tschoegl, N.W., (1985) 'The effect of pressure on the mechanical properties of polymers. IV. Measurements in torsion', *J. Polym. Sci., Polym. Phys. Ed.* 23, 623–651. [Study of the effect of pressure on the mechanical properties of polymers using torsion data].

Murnaghan, F.D., (1951) *Finite Deformation of Elastic Solids*, John Wiley and Sons, New York, [A book on the theory of elasticity focused on the evolution of expansivity and compressibility with temperature and pressure].

Norton, A.E., Knott, M.J. and Muenger, J.R., (1941) "Flow Properties of Lubricants under High Pressure", *ASME Trans.*, Vol. 63(7) 631–643. [Control of pressure drop in a capillary viscometer by attaching a long capillary to the end].

Novak, J.D. and Winer, W.O., (1968) "Some Measurements of High Pressure Lubricant Rheology", *ASME J. Lubr. Techn.*, Vol. 90(3) 580–591. [Some ingenious procedures for controlling the pressure drop in a high-pressure capillary rheometer].

O'Reilly, J.M., (1962) 'The effect of pressure on glass temperature and dielectric relaxation time of polyvinyl acetate', *J. Polym. Sci.* 57, 429–444. [Modeling the evolution of viscosity with pressure at low and moderate pressures].

Piermarini, G.J., Forman, R.A. and Block, S., (1978) "Viscosity Measurements in the Diamond Anvil

Cell”, *Rev. Sci. Instrum.*, Vol. 48(8) 1061–1066. [A description of the diamond anvil cell for conducting viscosity measurements at high pressure].

Quiñones-Cisneros, S. E.; Zeberg-Mikkelsen, C. K.; Stenby, E. H. (2000) The Friction Theory (f-theory) for Viscosity Modeling. *Fluid Phase Equilib.* 169, 249. [Study of the friction theory applied to viscosity modeling].

Quiñones-Cisneros, S.E. and Deiters, U.K. (2006) Generalization of the Friction Theory for Viscosity Modeling. *J. Phys. Chem. B*, 110, 12820-12834. [Study on the generalization of the friction theory for viscosity modeling applications].

Ramos, A.R, Kovacs, A.J., O’Reilly, J.M., Tribone, J.J. and Greener, J., (1988) ‘Effect of combined pressure and temperature changes on structural recovery of glass forming materials. I. Extension of the KAHR model’, *J. Polym. Sci., Polym. Phys. Ed.* 26, 501–513. [Expression of the shift factor as a function of compressibility].

Royer, J. R.; Gay, Y. J.; DeSimone, J. M.; Khan, S. A., (2000) High-Pressure Rheology of Polystyrene Melts Plasticized with CO₂: Experimental Measurement and Predictive Scaling Relationships *J Polym Sci Part B: Polym Phys* 38, 3168–3180. [Study of the high-pressure rheology of polymers plasticized with gas].

Sargent, L. B., (1983) “Pressure-viscosity coefficients of liquid lubricants,” *A.S.L.E. Trans.* 26 (1), 1-10. [Empirical correlation of pressure-viscosity data].

Sawamura, S., Takeuchi, N., Kitamura, K. and Tangiguchi, Y., (1990) “High Pressure Rolling-Ball Viscometer of a Corrosion-Resistant Type”, *Rev. Sci. Instrum.*, Vol. 61(2) 871–873. [A description of an improved falling body viscometer using light detectors].

Schmidt A, Gold PW, Aßmann C, Dicke H, Loos J., (2000) Viscosity-Pressure-Temperature Behavior of Mineral and Synthetic Oils. 12th International Colloquium Tribology 2000 – Plus, Stuttgart/Ostfildern, Germany, January 11-13.[Study of the viscosity-pressure-temperature relationship for lubricant oils].

Soave, G. (1972) Equilibrium Constants from a Modified Redlich-Kwong Equation of State. *Chem. Eng. Sci.* 27, 1197-1203. [Focused on the SRK EOS].

Stryjek, R.; Vera, J. H. (1986) PRSV: An Improved Peng-Robinson Equation of State for Pure Compounds and Mixtures. *Can. J. Chem. Eng.*, 64(2), 323-333. [Focused on the PRSV EOS].

Retsina T, S.M. Richardson, W.A. Wakeham, (1986) The theory of a vibrating-rod densimeter, *Appl. Sci. Res.* 43 127–158. [Theoretical analysis of the mechanics of oscillation of a wire surrounded by a fluid].

Retsina T, S.M. Richardson, W.A. Wakeham, (1987) The theory of a vibrating-rod viscometer, *Appl. Sci. Res.* 43 325–346. [Theoretical analysis of the mechanics of oscillation of a wire surrounded by a fluid].

Tait, P., (1900) *Physics and Chemistry of the Voyage of H.M. Ship Challenger*, Vol. II, Cambridge University Press, Cambridge. [A book on pressure-volume-temperature relationships].

Thomas, B.W., Ham, W.R. and Dow, R.W., (1939) “Viscosity-Pressure Characteristics of Lubricating Oils”, *Ind. Eng. Chem.*, Vol. 31(10) 1267–1270. [Description of a pressurized rotational viscometer with the motor inside of the pressure vessel].

Tribone, J.J., O’Reilly, J.M. and Greener, J., (1989) ‘Pressure-jump volume-relaxation studies of polystyrene in the glass transition region’, *J. Polym. Sci.: Part B: Polym. Phys.* 27, 837–857. [Modeling of the evolution of viscosity with pressure at low and moderate pressures].

Tschoegl NW, Knauss WG, Emri I. (2002) The Effect of Temperature and Pressure on the Mechanical Properties of Thermo- and/or Piezorheologically Simple Polymeric Materials in Thermodynamic Equilibrium – A Critical Review. *Mech of Time-Dependent Mat* 6 53–99. [A excellent review on high-pressure rheology].

Westover, R. E. (1961) “Effect of hydrostatic pressure on polyethylene melt rheology,” *Sot. Plastics Eng. Trans.* 1, 14-20. [Study of the pressure dependence of polymer viscosities using a capillary with double piston].

Williams, M.L., Landel, R.F. and Ferry, J.D., (1955) ‘The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids’, *J. Amer. Chem. Soc.* 77, 3701–

3707. [Temperature dependence of the relaxation mechanics for different materials].

Yasutomi S, Bair S. Winer W. (1984) An application of a free volume model to lubricant rheology. *ASME J Tribol* 106 291–303. [Description of pressure-temperature-viscosity relationships based on the free model volume and the glassy state].

Biographical Sketches

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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.