The Effect of Temperature on the Rheological Behavior of Polyethylene Oxide (PEO) Solutions

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Received: 31.5.2012, Final version: 25.9.2012

Abstract:
The rheological properties of polyethylene oxide (PEO) solutions were investigated, at different temperatures, using small and large deformation rheological methods. Steady-state flow measurements showed that the flow behavior of the PEO solutions is well described by the Cross model, which yields the critical concentrations c^* (from the dilute regime to semidilute regime) and c^{**} (from the semi-dilute regime to the concentrated regime). In the range of the temperatures investigated here, the apparent viscosity is found to obey the Arrhenius equation below a critical temperature we believe corresponds to the cloud point temperature. Above the cloud point temperature, the viscosity increased with temperature. Similarly below the cloud point, both transient and dynamic tests showed that PEO solutions exhibit viscoelastic behavior, where both the elastic G' and viscous G'' modules increased with the increase in concentration and with the decrease in temperature. The Cox-Merz rule was found to apply to the PEO solutions at temperatures lower than the cloud point temperature, whilst divergence was reported after phase separation. The frequencies at which $G' = G''$, i.e. the reciprocal of the relaxation times of the temporary polymer network, was found to increase (the relaxation times decline) with decreasing polymer concentration, in agreement with the relaxation times, derived from the Cross model. In essence, this study demonstrates that it is possible to monitor accurately the cloud point temperature of PEO solutions by viscometric analysis.

Zusammenfassung:
Die rheologischen Eigenschaften von Polyethylenoxid (PEO)-Lösungen wurden bei verschiedenen Temperaturen mit Hilfe rheologischer Messungen bei kleinen und großen Deformationen untersucht. Stationäre Fließmessungen zeigten, dass das Fließverhalten der PEO-Lösungen gut durch das Cross-Modell beschrieben wird, das zu der kritischen Konzentration c* (vom verdünnten zum halbverdünnten Regime) und zu der kritischen Konzentration c** (vom halbverdünnten zum konzentrierten Regime) führt. In dem untersuchten Temperaturbereich folgt die scheinbare Viskosität unterhalb einer kritischen Temperatur einem Arrhenius-Gesetz, die nach unserer Vermutung dem Trübpunkt entspricht. Oberhalb des Trübpunkts nimmt die Viskosität mit der Temperatur zu. Unterhalb des Trübpunkts zeigen sowohl dynamische als auch transiente Messungen, dass die PEO-Lösungen viskoelastisches Verhalten aufweisen, wobei der Speicher- und der Verlustmodul mit höherer PEO-Konzentration und niedrigerer Temperatur zunehmen. Die Cox-Merz-Regel wurde unterhalb des Trübpunkts durch die PEO-Lösungen erfüllt, wohingegen eine Divergenz nach der Phasenseparation auftrat. Die Frequenz, bei der G'=G'' gilt, i.e. die reziproke Relaxationszeit des temporären Polymernetzwerks, nahm mit abnehmender Polymerkonzentration zu, d. h. die Relaxationszeit nahm ab. Dies ist in Übereinstimmung mit den Relaxationszeiten, die sich aus dem Cross-Modell ergeben. Diese Studie zeigt, dass es möglich ist, die Temperatur des Trübpunkts für Polymerlösungen mit Hilfe rheologischer Methoden genau zu messen.

Résumé:
Les propriétés rhéologiques de solutions de polyéthylène oxyde (PEO) ont été étudiées, à différentes températures dans les gammes des faibles et des grandes déformations. Les mesures en régime stationnaire ont montré que le comportement rhéologique des solutions de polymères est décrit de manière satisfaisante par le modèle de Cross qui permet la 3 détermination des concentrations critiques c^* (transition du régime dilué au régime semidilué) et c^{**} (transition du régime semi-dilué au régime concentré). Dans la gamme des températures étudiées, l'évolution de la viscosité suit la loi d'Arrhenius en dessous d'une température critique qui correspondrait

© Appl. Rheol. 23 (2013) 13435 DOI: 10.3933/ApplRheol-23-13435

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REFERENCES

[1] Bailey FE, Koleske JV:Poly(ethylene oxide), Academic Press, New York (1976).

[2] Toms BA: Some observations on the flow of linear polymer solutions through straight tubes at large Reynolds numbers, Proc. of the 1st International Congress on Rheology, North-Holland, Amsterdam (1949).

[3] Kobets G: Explanation of the Toms effect in terms of the viscosity anisotropy of the solution, J. Appl. Mech. Tech. Phys. 10 (1969) 108 – 112.

[4] Khoultchaev K: Temperature dependent behavior of polyethylene oxide in papermaking suspensions, AIChE J 43 (1997) 2353 – 2358.

[5] Muller R, Bouquey M, Mauguiere F, Schlatter G, Serra C, Terrisse J: Rheology of reactive polymer blends: separation of mixing and reaction steps, Appl. Rheol. 11 (2001) 141 – 152.

[6] Powell R, Schwarz W: Rheological properties of aqueous poly (ethylene oxide) solutions in parallel superposed flows, Trans. Soc. Rheol. 19 (1975) 617 – 643.

[7] Powell RL, Schwarz WH: Rheological Properties of Aqueous Poly(ethylene Oxide) Solutions in Parallel Superposed Flows, J. Rheol. 19 (1975) 617 – 643.

[8] Powell R, Schwarz W: Nonlinear dynamic viscoelasticity, J. Rheol. 23 (1979) 323 – 352.

[9] Molyneux P:Water-soluble synthetic polymers: properties and behavior: CRC Press, Boca Raton (1983).

[10] Lance-Gomez E, Ward T: Viscoelastic character of poly (ethylene oxide) in aqueous solutions: Effect of shear rate, concentration, salt, and anionic surfactant, J. Appl. Polymer Sci. 31 (1986) 333 – 340.

[11] Oliveira MSN, Yeh R, McKinley GH: Iterated stretching, extensional rheology and formation of beads-on-a-string structures in polymer solutions, J. Non-Newtonian Fluid Mech. 137 (2006) 137 – 148.

[12] Ortiz M, De Kee D, Carreau PJ: Rheology of concentrated poly(ethylene oxide) solutions, J. Rheol. 38 (1994) 519 – 539.

[13] Rodd LE, Scott TP, Cooper-White JJ, McKinley GH: Capillary break-up rheometry of low-viscosity elastic fluids, Appl. Rheol. 15 (2005) 12 – 27.

[14] Kwon KC, Park YK, Floyd T, Vahdat N, Jackson E, Jones P: Rheological Characterization of Shear-Thinning Fluids with a Novel Viscosity Equation of a Tank-tube Viscometer, Appl. Rheol. 17 (2007) 51413.

[15] Briscoe B, Luckham P, Zhu S: Rheological study of poly (ethylene oxide) in aqueous salt solutions at high temperature and pressure, Macromolecules 29 (1996) 6208 – 6211.

[16] Gentile L, De Luca G, Antunes FE, Rossi CO, Ranieri GA: Thermogelation analysis of F127-water mixtures by physical chemistry techniques, Appl. Rheol. 20 (2010) 52081.1 – 9.

[17] Abraham T, Ratna D, Siengchin S, Karger Kocsis J: Rheological and thermal properties of poly (ethylene oxide)/multiwall carbon nanotube composites, J. Appl. Polymer Sci. 110 (2008) 2094 – 2101.

[18] Gauri V, Koelling KW: Extensional rheology of concentrated poly(ethylene oxide) solutions, Rheol. Acta 36 (1997) 555 – 567.

[19] Kalashnikov VN: Shear-rate dependent viscosity of dilute polymer solutions, J. Rheol. 38 (1994) 1385 – 1403.

[20] Hashmi S, Kitano T: Effects of state change of liquid crystalline polymer on dynamic visco-elasticity of its blends with polyethylene-terephthalate, Appl. Rheol. 17 (2007) 64510.

[21] Dong A, Zhai Y, Xiao L, Qi H, Tian Q, Deng L, Guo R: Thermosensitive behavior of poly(ethylene glycol)/poly(2-(N,N-dimethylamino)ethyl methacrylate) double hydrophilic block copolymers, J. Polymer Sci. B: Polymer Phys. 48 (2010) 503 – 508.

[22] Bain MK, Bhowmik M, Maity D, Bera NK, Ghosh S, Chattopadhyay D: Control of thermo reversible gelation of methylcellulose using polyethylene glycol and sodium chloride for sustained delivery of ophthalmic drug, J. Appl. Polymer Sci. 118 (2010) 631 – 637.

[23] Antunes FE, Gentile L, Tavano L, Rossi CO: Rheological Characterization of the Thermal Gelation of Poly (n-isopropyl-acrylamide) and Poly (n-isopropylacrylamide) Co-acrylic Acid Gum Hydrogels, Appl. Rheol. 19 (2009) 42064.

[24] Persson J, Johansson HO, Tjerneld F: Biomolecule separation using temperature-induced phase separation with recycling of phase-forming polymers, Ind. Eng. Chem. Res. 39 (2000) 2788 – 2796.

[25] James DF, Saringer JH: Flow of dilute polymer solutions through converging channels, J. Non-Newtonian Fluid Mech. 11 (1982) 317 – 339.

[26] Tirrell M: Phase behavior of flowing polymer mixtures, Fluid Phase Equilibria 30 (1986) 367 – 380.

[27] Klenin VI, Kolnibolotchuk NK, Solonina NA: Phase analysis of the system poly (ethylene oxide)-water in a hydrodynamic field, Polymer Sci. 35 (1993) 552 – 554.

[28] Ataman M: Properties of aqueous salt solutions of poly(ethylene oxide). Cloud points, q temperatures, Colloid Polymer Sci. 265 (1987) 19 – 25.

[29] Sharma R, Bahadur P: Effect of different additives on the cloud point of a polyethylene oxide-polypropylene oxide-polyethylene oxide block copolymer in aqueous solution, J. Surf. Deter. 5 (2002) 263 – 268.

[30] Patel K, Bahadur P, Guo C, Ma JH, Liu HZ, Yamashita Y, Khanal A, Nakashima K: Salt induced micellization of very hydrophilic PEO-PPO-PEO block copolymers in aqueous solutions, Eur. Polymer J. 43 (2007) 1699 – 1708.

[31] Inoue T, Misono T: Cloud point phenomena for POE-type nonionic surfactants in a model room

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http://www.appliedrheology.org

temperature ionic liquid, J. Colloid Interface Sci. 326 (2008) 483–489.
[32] Inoue T, Misono T: Cloud point phenomena for POE-type nonionic surfactants in imidazolium-based ionic liquids: Effect of anion species of ionic liquids on the cloud point, J. Colloid Interface Sci. 337 (2009) 247–253.
[33] Pang P, Englezos P: Kinetics of the aggregation of polyethylene oxide at temperatures above the polyethylene oxide-water cloud point temperature, Colloids Surf. A: Physicochem. Eng. Aspects 204 (2002) 23–30.
[34] Ebagninin KW, Benchabane A, Bekkour K: Rheological characterization of poly(ethylene oxide) solutions of different molecular weights, J. Colloid Interface Sci. 336 (2009) 360–367.
[35] Graessley WW: Polymer chain dimensions and the dependence of viscoelastic properties on concentration, molecular weight and solvent power, Polymer 21 (1980) 258–262.
[36] Benchabane A: Rheological behavior study of a clay-polymer mixture: Effects of polymer addition, Ph.D. Thesis, Université de Strasbourg (2006).
[37] Clasen C, Kulicke W-M: Determination of viscoelastic and rheo-optical material functions of water-soluble cellulose derivatives, Prog. Polymer Sci. 26 (2001) 1839–1919.
[38] Dunstan DE, Hill EK, Wei Y: Direct measurement of polymer segment orientation and distortion in shear: semi-dilute solution behavior, Polymer 45 (2004) 1261–1266.
[39] Benchabane A, Bekkour K: Rheological properties of Carboxymethylcellulose (CMC) solutions, Colloid Polymer Sci. 286 (2008) 1173–1180.
[40] Li H, Hou W, Zhang Y: Rheological properties of aqueous solution of new exopolysaccharide secreted by a deep-sea mesophilic bacterium, Carbohyd. Polymers 84 (2011) 1117–1125.
[41] Liu W-H, Yu TL, Lin H-L: Shear thickening behavior of dilute poly(diallyl dimethyl ammonium chloride) aqueous solutions, Polymer 48 (2007) 4152–4165.
[42] Cross MM: Rheology of non-Newtonian fluids: a new flow equation for pseudoplastic systems, J. Colloid Sci. 20 (1965) 417–437.
[43] Aluigi A, Vineis C, Varesano A, Mazzuchetti G, Ferrero F, Tonin C: Structure and properties of keratin/PEO blend nanofibres, Eur. Polymer J. 44 (2008) 2465–2475.
[44] Daoust H, St-Cyr D: Microcalorimetric study of poly (ethylene oxide) in water and in water-ethanol mixed solvent, Macromolecules 17 (1984) 596–601.
[45] Malcolm G, Rowlinson J: The thermodynamic properties of aqueous solutions of polyethylene glycol, polypropylene glycol and dioxane, Trans. Faraday Soc. 53 (1957) 921–931.
[46] Kjellander R, Florin E: Water structure and changes in thermal stability of the system poly (ethylene oxide)–water, J. Chem. Soc., Faraday Trans. 177 (1981) 2053–2077.
[47] Chopra D, Haynes C, Hatzikiriakos SG, Vlassopoulos D: Modeling the shear-induced structural changes in polymeric fluids, J. Non-Newtonian Fluid Mech. 82 (1999) 367–385.
[48] Rangel-Nafaile C, Metzner AB, Wissbrun KF: Analysis of stress-induced phase separations in polymer solutions, Macromolecules 17 (1984) 1187–1195.
[49] Bodvik R, Dedinaite A, Karlson L, Bergstrom M, Baverback P, Pedersen JS, Edwards K, Karlsson G, Varga I, Claesson PM: Aggregation and network formation of aqueous methylcellulose and hydroxypropylmethylcellulose solutions, Colloids Surf. A: Physicochem. Eng. Aspects 354 (2010) 162–171.
[50] Saeki S, Kuwahara N, Nakata M, Kaneko M: Upper and lower critical solution temperatures in poly (ethylene glycol) solutions, Polymer 17 (1976) 685–689.
[51] Wolf B: Improvement of polymer solubility: Influence of shear and of pressure, Pure Appl. Chem. 69 (1997) 929–933.
[52] Inokuchi K: Rheology of Surface Films. IV. Viscoelastic Properties of 6-Nylon Films at Air/Water Interface, Bull. Chem. Soc. Japan 20 (1955) 453.
[53] Klein J, Luckham PF: Forces between two adsorbed poly (ethylene oxide) layers in a good aqueous solvent in the range 0–150 nm, Macromolecules 17 (1984) 1041–1048.
[54] Briscoe B, Luckham P, Zhu S: Pressure influences upon shear thickening of poly (acrylamide) solutions, Rheol. Acta 38 (1999) 224–234.
[55] Cox WP, Merz EH: Correlation of dynamic and steady flow viscosities, J. Polymer Sci. 28 (1958) 619–622.
[56] Kulicke W, Porter R: Relation between steady shear flow and dynamic rheology, Rheol. Acta 19 (1980) 601–605.
[57] Alves VD, Freitas F, Costa N, Carvalheira M, Oliveira R, Gonçalves MP, Reis MAM: Effect of temperature on the dynamic and steady-shear rheology of a new microbial extracellular polysaccharide produced from glycerol byproduct, Carbohyd. Polymers 79 (2010) 981–988.
[58] Xu C, Willfor S, Holmlund P, Holmbom B: Rheological properties of water-soluble spruce O-acetyl galactoglucomannans, Carbohyd. Polymers 75 (2009) 498–504.

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