Freezing as a Storage Process for Aqueous Polymer Solutions

M. P. Escudier*, J. Clement-Evans and R. J. Poole

University of Liverpool, Department of Engineering (Mechanical Engineering),
Brownlow Hill, Liverpool, L69 3GH, UK

*Email: escudier@liv.ac.uk
Fax.: +44 151 7944848

Received: 8.10.04, Final version: 22.12.04

Abstract:
There is often a need to perform rheological tests on dilute polymeric liquids at a time long after their initial preparation, for example if a more sensitive or novel method of measuring a material property (such as uniaxial/biaxial extensional viscosity or second normal-stress differences) becomes available. An inexpensive method of storing such fluids which prevents any form of deterioration (e.g. bacteriological) would therefore be of great value. This study explores the potential of freezing as that storage process by investigating whether the freeze-thaw process itself leads to rheological changes. The rheological properties of three polymeric liquids: 0.25 % xanthan gum, 0.125% polyacrylamide and a 0.1 %/0.1 % carboxymethylcellulose / xanthan gum blend commonly used in non-Newtonian fluid flow studies were determined in both shear and oscillation before and after a freeze-thaw process. Within the uncertainty of the rheometer used, the rheological properties of the polymers studied were found to be unaffected by the freeze-thaw process leading to the conclusion that this storage method is indeed a practical possibility.

Zusammenfassung:
Häufig besteht Bedarf, rheologische Messungen mit verdünnten Polymerlösungen lange nach der erstmaligen Probenherstellung durchzuführen, z.B. wenn ein genaueres oder neues Messverfahren einer Materialeigenschaft zur Verfügung gestellt wird (wie uniaxiale/biaxiale Dehnviskosität oder zweite Normalspannungsdifferenz). Eine kostengünstige Methode zur Lagerung solcher Fluide, die jegliche Zerstörung (z.B. bakteriologische) verhindert, würde daher von einem sehr grossen Nutzen sein. Diese Untersuchung erörtet das Potential des Gefrierens als Lagerungsmethode durch Ermittelung, ob das Gefrieren und Tauen zu rheologischen Veränderungen führt. Die rheologischen Eigenschaften von drei polymeren Flüssigkeiten, 0.25% Xanthangummi, 0.125% Polyacrylamid und ein 0.1% / 0.1% Carboxymethylzellulose/Xanthangummi-Blend, die überlicherweise in Untersuchungen über nicht-Newtonsche Flüssigkeiten verwendet werden, wurden in Scherung und Oszillationen vor und nach dem Gefrier- und Tauprozess bestimmt. Es wurde gefunden, dass die rheologischen Eigenschaften dieser Polymere im Rahmen der Messgenauigkeit der verwendeten Rheometer von dem Gefrier- und Tauprozess nicht beeinflusst wurden, was zur Schlussfolgerung hat, dass diese Lagermethode in der Tat eine Anwendungsmöglichkeit darstellt.

Résumé:
Il y a souvent un besoin d’effectuer des tests rhéologiques sur des liquides polymères dilués à un temps long après leur préparation initiale, par exemple lorsque une méthode plus sensible ou bien plus récente de mesurer une propriété du matériau (comme la viscosité extensionnelle uniaxiale/biaxiale ou la seconde différence de contraintes normales) devient disponible. Une méthode bon-marché pour conserver de tels fluides et qui empêche toute forme de détérioration (par exemple bactériologique) serait alors de grande valeur. Cette étude explore la congélation comme moyen de conservation en recherchant si le procédé congélation-décongélation lui-même conduit à des changements rhéologiques. Les propriétés rhéologiques de trois liquides polymères: 0.25% de gomme de xanthane, 0.125% de polyacrylamide et un mélange à 0.1%/0.1% de carboxyméthyle cellulose/gomme de xanthane, communément utilisés dans les études d’écoulement de fluides non-Newtoniens, ont été déterminées en cisaillement et en oscillation avant et après le procédé de congélation-décongélation. Dans la limite du domaine d’incertitude du rhéomètre utilisé, les propriétés rhéologiques des polymères étudiés se sont avérées être non affectées par le procédé de congélation-décongélation, ce qui conduit à la conclusion que cette méthode de conservation est de fait une possibilité pratique.

Key words: Freeze/thaw process, long-term storage for polymer solutions

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org

4.2 OSCILLATORY TESTS

To minimise the effects of inertia, the 60 mm diameter, 2° acrylic cone geometry was used to provide the oscillation data. A linearity check was conducted for each fluid to determine the linear viscoelastic region prior to each frequency sweep. Frequency sweeps were performed at two different shear-stress values, both within the linear viscoelastic region, and always showed good agreement, confirming that the viscoelastic properties observed were independent of the shear-stress value.

The storage modulus, G', and loss modulus, G'', for fresh and thawed samples are shown in Fig. 3. The smooth curves in Figs. 3a - 3c represent the results of fitting a four mode Maxwell model to the *G'* and *G''* data:

$$G' = \sum_{i=1}^{4} \frac{\eta_i \lambda_i \omega^2}{1+(\lambda_i \omega)^2} \tag{4a}$$

$$G'' = \sum_{i=1}^{4} \frac{\eta_i \omega}{1+(\lambda_i \omega)^2} \tag{4b}$$

In agreement with the viscometric-viscosity data (Fig. 1), the influence of the freeze-thaw process on all three samples was found to be negligible. This is illustrated by the characteristic relaxation time λ for each data set (shown in Table 2) estimated using the following expression:

$$\lambda = \frac{\sum_{i=1}^{4} \lambda_i \eta_i}{\sum_{i=1}^{4} \eta_i} \tag{5}$$

As can be seen in Table 2 there is no systematic influence of the freeze-thaw process on the parameter λ. In addition, for each fluid the λ values determined for fresh, thawed and combined data sets agree to within better than 4 %. Also included in Table 2 are the standard deviations σ_I and σ_C as well as the (1 - *R*) values for the *G'* and *G''* fits, these statistical measures being defined in much the same way as those for the viscosity fits. As can be seen, the standard deviations are only marginally higher than those in Table 1. With two exceptions, the (1 – R) values are also higher but still well within the limits for the correlations to be regarded as good. As has been found previously, in oscillation (Walters et al (1990)) the CMC/XG blend is the least viscoelastic (*G''* > *G'*), then 0.25% XG (at low frequencies *G''* > *G'* and at high frequencies *G'* > *G''* with a crossover frequency of 0.35 rads^{-1}) and that PAA is the most viscoelastic as *G'* > *G''*.

4.3 CONCLUDING REMARKS

The conclusion of this work is that for the test polymer solutions, polyacrylamide, xanthan gum and a blend of carboxymethylcellulose/xanthan gum, the freeze-thaw process has no measurable effect on either the viscometric viscosity or the storage and loss moduli. Importantly, as the freeze-process does not impart rheological changes, this allows the possibility of cheap long-term storage for polymer solutions at a temperature of about –25°C. We are unaware of any alternative method for long-term storage of such polymer solutions. Further investigation is required before it may be safely concluded that these polymer solutions can be stored indefinitely as frozen samples. In addition, we shall be undertaking further research into the possible effect of the freeze/thaw process on the exten-

	PAA			CMC/XG			XG		
	FR	TH	BOTH	FR	TH	BOTH	FR	TH	BOTH
λ (s)	22.1	20.7	21.5	6.1	6.1	6.1	14.0	14.5	14.2
σ_I (%)	4.00	4.62	4.66	2.73	2.65	3.22	4.37	4.44	5.21
σ_C (%)	4.36	4.95	4.66	3.27	3.18	3.22	5.20	5.22	5.21
$(1 - R)\cdot 10^3$	1.49	1.49	1.71	0.38	0.42	0.49	1.11	1.22	1.41

Table 2: Characteristic relaxation times based on Maxwell model fit and corresponding statistical parameters.

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org

sional viscosity and on the first-normal stress difference for polymer solutions of higher concentration than those considered here.

NOTATION

a	constant in Carreau-Yasuda model
G'	storage modulus (Pa)
G''	loss modulus (Pa)
n	power-law index
N	number of data points in sample
R	Pearson correlation coefficient
$\dot{\gamma}$	shear rate (s^{-1})
λ	relaxation time (s)
λ_i	relaxation time in Maxwell model(s)
η_i	dynamic viscosity in Maxwell model (Pa·s)
λ_{CY}	time constant in Carreau-Yasuda model (s)
μ	shear viscosity (Pa·s)
μ_{CY}	Carreau-Yasuda viscosity (Pa·s)
μ_M	measured viscosity (Pa·s)
μ_o	zero-shear-rate viscosity (Pa·s)
μ_∞	infinite-shear-rate viscosity (Pa·s)
σ	standard deviation
σ_C	standard deviation between individual measured data set and fit to combined data set (i.e. 'BOTH')
σ_I	inherent standard deviation between individual measured data set and fit to that data set
ω	angular frequency (rad·s^{-1})

REFERENCES

[1] Dontula P, Pasquali, L.E. Scriven LE, C.W. Macosko CW: Can extensional viscosity be measured with opposed-nozzle devices? Rheol. Acta 36 (1997) 429-448.

[2] Escudier MP, Presti F, Smith S: Drag reduction in the turbulent pipe flow of polymers. J. Non-Newt. Fluid Mech. 81 (1999) 197-213.

[3] McKinley GH, Tripathi A: How to extract the Newtonian viscosity from capillary breakup measurements in a filament rheometer, J. Rheol. 44 (2000) 653-670.

[4] Hetzel F, Nielsen J, Wiesner S, Brummer R: Dynamic mechanical freezing points of cosmetic o/w emulsions and their stability at low temperatures. Appl. Rheol. 10 (2000) 114-118.

[5] White PJ, Abbas IR, Johnson LA: Freeze-thaw stability and refrigerated-storage retrogradation of starches. Starch 41 (1989) 176-180.

[6] Ferrero C, Zaritzky NE: Effect of freezing rate and frozen storage on starch-sucrose-hydrocolliod systems. J. Sci. Food Agric. 80 (2000) 2149-2158.

[7] Kuntz LA: Freeze-thaw stability. Food Product Design 5 (1995) 52-59.

[8] Poole RJ, Escudier MP: Turbulent flow of non-Newtonian liquids over a backward-facing step: Part II Viscoelastic and shear-thinning liquids. J. Non-Newt. Fluid Mech. 109 (2003) 193-230.

[9] den Toonder JMJ, Hulsen MA, Kuiken GDC, Nieuwstadt FTM: Drag reduction by polymer additives in a turbulent pipe flow: numerical and laboratory experiments. J. Fluid Mech. 337 (1997) p193-231.

[10] Rudman M, Blackburn HM, Graham LJW, Pullum L: Turbulent pipe flow of shear-thinning fluids. J. Non-Newt. Fluid Mech. 118 (2004) 33-48.

[11] Gampert B, Braemer T, Dietmann T, Bialas M: Experimental study on effect of elasticity on turbulent properties in turbulent channel flow of dilute polymer solutions. Proceedings of the XIVth International Congress on Rheology, Soeul, Korea (2004).

[12] Pereira AS, Pinho FT: Turbulent characteristics of shear-thinning fluids in recirculating flows. Exp Fluids 28 (2000) 266-278.

[13] Escudier MP, Gouldson IW, Pereira AS, Pinho FT, Poole RJ: On the reproducibility of the rheology of shear-thinning liquids. J. Non-Newt. Fluid Mech. 97 (2001) 99-124.

[14] Yasuda K, Armstrong RC, Cohen RE: Shear flow properties of concentrated solutions of linear and star branched polystyrenes. Rheol. Acta 20 (1981) 163-178.

[15] Weiss NA, Hassett MJ: Introductory statistics, Addison Wesley, New York (1991).

[16] Syed Mustapha SMFD, Philips TN, Price CJ, Moseley LG, Jones TER: Viscometric flow interpretation using qualitative and quantitative techniques, Eng. Appl. Art. Intell. 12 (1999) 255-272.

[17] Walters K, Bhatti AQ, Mori N: The influence of polymer conformation on the rheological properties of aqueous polymer solutions, Recent Developments in Structured Continua, Vol 2, Eds: D De Kee and P N Kaloni, Pitman, Longman Scientific and Technical, Harlow, U.K.

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org