Influence of Test Times on Creep and Recovery Behavior of Xanthan Gum Hydrogels

M. Dolz[1]*, F. Corrias[2], O. Díez-Sales[2], A. Casanovas[1] and M.J. Hernández[1]

[1] Department de Física de la Terra i Termodinàmica, Universitat de València, 46100 Burjassot, Spain
[2] Departament de Farmàcia i Tecnologia Farmacèutica, Universitat de València,
46100 Burjassot, Spain

* Email: manuel.dolz@uv.es
Fax: x34.96.3544911

Received: 26.9.2008, Final version: 11.2.2009

Abstract:
Rheological creep and recovery tests have been applied at different assay times to xanthan gum hydrogels at several concentrations. The Burger model has been successfully applied to fit the creep data and to analyze results. Increasing the xanthan gum concentration also increases the elastic and viscous components without changing the molecular distribution of these hydrogels. A semi-empirical equation considering the different elements of the Burger model has been proposed to analyze compliance behavior in recovery tests. The dependence of the relative contribution to deformation of the Maxwell and Kelvin-Voigt units upon xanthan gum concentration and recovery assay times has been evaluated. Since the recovery ratio is the same for all hydrogels, we suggest parallel structures with no mutual interactions are formed when increasing concentration.

Zusammenfassung:
Rheologische Kriech- und Erholungs-Versuche wurden bei verschiedenen Konzentrationen und Xanthan Hydrogelen durchgeführt. Das Burger Modell wurde erfolgreich benutzt um die Daten zu reproduzieren. Bei zunehmender Xanthan-Konzentration steigen die elastischen und viskosen Komponenten. Unter Berücksichtigung der verschiedenen Elemente des Burger Modells wird eine semi-empirische Gleichung vorgeschlagen. Der relative Beitrag zum Verziehen des Hydrogels von den Maxwell- und Kelvin-Voigt Teilen des Burgers Modell wird für die Xanthan Konzentrationen und vorliegenden Erholungs-Zeiten ausgewertet. Da das Erholungs-Verhältnis unabhängig von der Art des Hydrogels ist, wird von uns die Bildung paralleler Strukturen ohne gegenseitige Wechselwirkung im Hydrogel vorgeschlagen.

Résumé:
Des tests rhéologiques de fluage et de recouvrance ont été réalisés à différent temps d'essai, sur des hydrogels de gomme Xanthan à différentes concentrations. On a analysé les données expérimentales à l'aide du modèle de Burger de manière satisfaisante. La concentration croissante de la gomme de Xanthan produit un incrément de l'élasticité et de la viscosité des composants du modèle. Nous avons proposé une équation semi-empirique qui prend en compte les différents éléments du modèle de Burger. Nous avons évalué la contribution relative de chacune des unités de Maxwell et de Kelvin-Voigt du modèle de Burger à la déformation des hydrogels, en fonction de la concentration de la gomme et du temps d'essai. Enfin, il est prouvé que le pourcentage final de recouvrance est le même pour tous les hydrogels, ce qui suggère que l'augmentation de la concentration en Xanthan produit la formation de structures moléculaires en parallèle, sans interactions mutuelles.

Key words: creep, recovery, viscoelasticity, Burger model, xanthan gum

1 INTRODUCTION

Xanthan gum [1] is a polymer industrially obtained from the bacterium Xanthomonas campestris. It is one of the most widely used hydrocolloids in the food industry, included in the formulation of salad dressings, creams, sauces, syrups, desserts, beverages, and in prepared and frozen foods [2]. It is also used in lotions, creams, cough syrups, and toothpaste in the cosmetics and pharmaceutical industry [3]. Moreover, it is employed in oils, hydraulic fluid, pesticides, animal fodder, cleaning products, dyes and metal bathings [4]. Many of the applications of xanthan gum are a consequence of its rheological behavior. Under resting conditions, the long xanthan gum molecules combine to form a three-dimensional network. On applying shear to the system, the added energy disrupts these weak bonds, and

© Appl. Rheol. 19 (2009) 34201

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

Table 3: Percentage of deformation associated to the Maxwell dashpot, J_∞, and the Kelvin-Voigt component, J_{KV}.

c (%)	D_∞ (%)	D_{KV} (%)
1.00	38 ± 4	54 ± 2
1.30	42 ± 4	48 ± 3
1.70	34 ± 3	59 ± 2
1.85	42 ± 2	49 ± 4
2.00	34 ± 2	52 ± 2
2.30	34 ± 3	51 ± 4

centage deformation of each of the components of the Burger model, we calculated (Eq. 9)

$$D_\infty(\%) = 100\left(\frac{J_\infty}{J_{Max}}\right) \tag{12}$$

and

$$D_{KV}(\%) = 100\left(\frac{J_{KV}}{J_{Max}}\right) \tag{13}$$

The results are reported in Table 3. Regardless of system concentration, both the relative deformation of Maxwell dashpot and the relative deformation corresponding to the Kelvin-Voigt system remain constant when prolonging test time. This means that although, J_{Max} becomes greater when increasing creep time, the recovery of strain J_{KV} and J_∞ increase in the same proportion and the ratio keeps constant. Comparison of the relative compliance values (Table 3) shows that the deformation experienced by the Kelvin-Voigt element is about 40 % greater than the deformation of the Maxwell dashpot, due to the greater viscosity of the latter.

On the other hand, knowing that $D_{MS} + D_\infty + D_{KV}$ must be 100 %, D_{MS} should be about 10 % since $D_\infty + D_{KV} = 89 \pm 6$ %. Therefore, as we have already indicated when analyzing Eq. 11, it is confirmed now that the time test should be greater than 300 seconds. Most creep and recovery studies published in the literature consider times of this magnitude, or even longer [5, 7, 8, 11]. Finally, we have calculated the total percentage recovery of the system [18], R_T (%) considering sufficiently large recovery times ($t \to \infty$):

$$R_T(\%) = 100\left[\frac{\left(J_{Max} - J_\infty\right)}{J_{Max}}\right] = 100\left[1 - \frac{J_\infty}{J_{Max}}\right] \tag{14}$$

In this way we solve the problem of the particularization of recovery time, which obviously does not necessarily coincide with creep time. The values obtained for RT are independent of the test time and of the gum concentration. Unlike the results obtained with emulsions, where the degree of recovery increases with the concentration of polymer involved [4]. We can say that all the xanthan gum hydrogels recover about 65 % of the structure they initially had, within the linear viscoelastic region. This could mean that approximately 35 % of the links are irreversibly broken during creep test (at least over the test times considered).

4 CONCLUSIONS

Creep tests have shown that the mechanical Burger model is suitable for reproducing the rheological behavior of xanthan gum hydrogels at the concentrations studied. The increase in xanthan gum concentration reinforces the elastic moduli and the viscosities of the Maxwell and Kelvin-Voigt contributions to the Burger model, but exerts no influence upon the molecular distribution of the hydrogels. This is in agreement with the results obtained on analyzing the recovery tests. The relative deformations of the Maxwell dashpot and Kelvin-Voigt system are independent of both xanthan gum concentration and recovery test time. Moreover, the final percentage recovery of the whole system, once the applied stress is removed, is the same for all samples. In our opinion, this means that on increasing concentration, the Burger structures act in parallel, without mutual interactions.

Regarding the test times, we believe the minimum time for creep testing should be about 300 seconds. However, for recovery tests longer assay times imply better definition of the asymptote determining permanent deformation of the system.

REFERENCES

[1] Kang KS and Pettitt DJ: Xanthan, Gellan, Wellan and Rhamsan, in Industrial Gums. Polysaccharides and their Derivatives. Whistler RL and BeMiller JN, San Diego, Academic Press Inc. (1993).

[2] Dolz M, Hernández MJ, Delegido J, Alfaro MC and Muñoz J: Influence of Xanthan gum and Locust Bean gum upon flow and thixotropic behaviour of food emulsions containing modified starch. J. Food Eng. 81 (2007) 179-186.

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

[3] Corrias F, Dolz M, Herráez M and Díez-Sales O: Rheological properties of progesterone microemulsions: Influence of xanthan and chitosan biopolymer concentration. J. Appl. Polym. Sci. 110 (2008) 1225-1235.

[4] Ghannam M: Creep-recovery experimental investigation of crude oil-polymer emulsions. J. Appl. Polym. Sci. 92 (2004) 226-237.

[5] Fitzsimons S M, Tobin TT and Morris ER: Synergistic binding of konjac glucomannan to xanthan on mixing at room temperature. Food Hydrocoll. 22 (2008) 36-46.

[6] Baroudi K, Silikas N and Watts DC: Time-dependent visco-elastic creep and recovery of flowable composites. Europ. J. Oral Sci. 115 (2007) 517-521.

[7] Campo L and Tobar C: Influence of the starch content in the viscoelastic properties of surimi gels. J. Food Eng. 84 (2008)140-147.

[8] Uddin W: Viscoelastic characterization of polymer-modified asphalt binders of pavement applications. Appl. Rheol. 13 (2003) 191-199.

[9] Martinez VY, Nieto AB, Castro MA, Salvatori D and Alzamora SM: Viscoelastic characteristics of Granny Smith apple during glucose osmotic dehydration. J. Food Eng. 83 (2007) 394-403.

[10] Njintang NY, Mbofung C M F, Moates G K, Parker M L, Faulds C B, Craig F, Smith A C and Waldron K W: Functional properties of five varieties of taro flour, and relationship to creep recovery and sensory characteristics of achu (taro based paste). J. Food Eng. 82 (2007) 114-120.

[11] Perissutti GE, Bresolin TMB and Ganter JMLS: Interaction between the galactomannan from Mimosa scabrella and milk proteins. Food Hydrocolloids 16 (2002) 403-417.

[12] Ould Eleya MM and Gunasekaran S: Rheology of barium sulfate suspensions and pre-thickened beverages used in diagnosis and treatment of dysphagia. Appl. Rheol. 17 (2007) 33137.

[13] Tanner RI: Engineering Rheology, 2 Ed. Oxford University Press, New York (2000).

[14] Steefe JF: Rheological Methods in Food Process Engineering, 2 Ed. East Lansing, USA, Freeman Press (1996).

[15] Xia H, Song M, Zhang Z and Richardson M: Microphase separation, strees relaxation, and creep behavior of polyurethane nanocomposites. Journal of Appl. Polym. Sci. 103 (2007) 2992-3002.

[16] Barnes HA, Hutton J F and Walters K: An Introduction to Rheology. Amsterdam, Elsevier Science Publishers (1993).

[17] Nijenhuis K: Thermoreversible networks. Viscoelastic properties and structure of gels, Advances in Polymer Sciences. Berlin, Springer (1997).

[18] Dolz M, Hernández MJ and Delegido J: Creep and recovery experimental investigation of low oil content food emulsions. Food Hydrocoll. 22 (2008) 421-427.

[19] Njintang NY, Parker ML, Moates GK, Faulds CB, Smith AC, Waldron KW, Mbofung CMF and Scher J: Microestructure and creep-recovery characteristics of achu (a taro based paste) made from freeze dried taro chips as affected by moisture content and variety. J. Food Eng. 87 (2008) 172-180.

[20] Deman JM and Beers AM: Fat chrystal networks: Structure and rheological properties. J. Text. Stud. 18 (1987) 303-318.

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