Carbohydrate Polymers 40 (1999) 9–16

Carbohydrate Polymers

Nonlinear viscoelastic solution properties of oat-based β-glucan/amylodextrin blends[☆]

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Received 25 November 1998; received in revised form 9 February 1999; accepted 9 February 1999

Abstract

The rheological properties of several (1,3; 1,4)-β-D-glucan/amylodextrin blends, designated as OATRIM, were investigated. OATRIM containing 10% by weight (1,3; 1,4)-β-D-glucan, was found to exhibit a region of shear-thickening behavior at 25°C above a critical shear rate of 30 s^{-1}. The shear-thickening behavior was also found to be dependent on the temperature of the suspension with the magnitude of the observed shear-thickening region decreasing with temperature and finally being eliminated at a temperature of 60°C. When the level of (1,3; 1,4)-β-D-glucan in the OATRIM sample was reduced to 5% by weight, the shear-thickening region was not observed. When the (1,3; 1,4)-β-D-glucan level was increased to 24% by weight, two regions of shear thickening were observed with critical shear rates of 30 and 100 s^{-1}. In addition, a double stress overshoot was observed during the start-up of steady-state shear at a shear rate of 100 s^{-1}. These observations indicate that the shear-thickening behavior is due, in part, to interactions between the (1,3; 1,4)-β-D-glucans and the amylodextrins that make up OATRIM. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Viscoelastic properties; Nonlinear; *beta;*-Glucan/amylodextrin blends; Shear-thickeneing

1. Introduction

The utilization of various soluble fibers in dietary applications has been an area of active research over the past several years. This is largely as a result of a number of studies that have shown that soluble fibers from cereal grains such as oats provide beneficial contributions to human health, including lowering blood cholesterol levels (Uusitupa, Ruuskanen & Makinen, 1992; Malkki, Autio & Hanninen, 1992; Topping, 1991; American Heart Association Committee Report and Circulation, 1980; Food and Drug Administration, 1997). The soluble fiber obtained from oats is designated as (1,3; 1,4)-β-D-glucan and is well known to provide health benefits in human nutrition (Inglett, 1997). A patented method has introduced a product entitled OATRIM to the marketplace as a viable commercial source of soluble (1,3; 1,4)-β-D-glucan and amylodextrins. (Inglett, 1991). Preliminary studies on OATRIM have revealed that the biological properties of the material are retained (Inglett & Newman, 1994). Later research has indicated that consumption of OATRIM is associated with health benefits related to disease control, glucose, insulin responses, and weight control (Behall, Scholfield & Clark, 1993; Hallfrisch, Scholfield & Behall, 1997; Scholfield, Behall & Armero, 1993).

Given the importance of β-glucan-containing blends in food applications, many unanswered questions remain concerning the physical and rheological properties of these materials. A limited number of studies on the viscoelastic properties of β-glucan-containing materials have been reported in literature (Wood, 1984; Autio, Myllymaki & Malkki, 1987; Autio, Myllymaki, Suortti, Saastamoinen & Poutanen, 1992; Doublier & Wood, 1995; Autio, 1988; Zhang, Doehlert & Moore, 1998). In general, solutions of oat gums have been found to display shear-thinning behavior over shear rates ranging from 0 to 1500 s^{-1}. Oscillatory shear viscoelastic properties of oat (1,3; 1,4)-β-D-glucan appear to display classic non-Newtonian flow behavior. A recent study of the rheological properties of OATRIM-10, a mixture of 10% by weight (1,3; 1,4)-β-D-glucan and

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[☆] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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PII: S0144-8617(99)00031-4

Table 1
Composition of OATRIM samples

Material	Weight percent (1,3; 1,4)-β-D-glucan	Weight percent amylodextrins	Weight percent ash	Weight percent proteins	Weight percent crude fat
OATRIM-5	5	86	4	4	1
OATRIM-10	10	81	4	4	1
OATRIM-24	24	67	4	4	1

amylodextrins, noted a region of shear-thickening behavior (Carriere & Inglett, 1998). Studies focused on the rheological response to the interactions of (1,3; 1,4)-β-D-glucans with other biopolymers have not been reported.

In the research reported herein, investigations of the viscoelastic solution properties of OATRIM are reported. The data presented in this work are obtained using thixotropic loop and steady-state shear experiments. The effects of shear rate, temperature, (1,3; 1,4)-β-D-glucan content, and aging on the rheological properties are reported. Of particular note, is the finding of two different shear rate regions of shear-thickening behavior for OATRIM when the (1,3; 1,4)-β-D-glucan level was 24% by weight. This is the first report of such behavior for (1,3; 1,4)-β-D-glucan-containing materials.

2. Materials and methods

2.1. Materials and sample preparation

The procedure to produce the OATRIM samples used in this study has been discussed in the literature (Inglett, 1993; Inglett & Newman, 1994). Four kilograms of oat bran were slurried in 28 l of water containing 50 ppm of calcium. The pH of the slurry was adjusted in the range 5–8 and then passed through a steam jet cooker and collected in a 30-gal steam-heated kettle. An α-amylase enzyme preparation was added to the slurry (Inglett, 1993). The solution was stirred at 80–90°C for 5 min. Passing the slurry through a steam injection cooker deactivated the enzyme. The slurry was

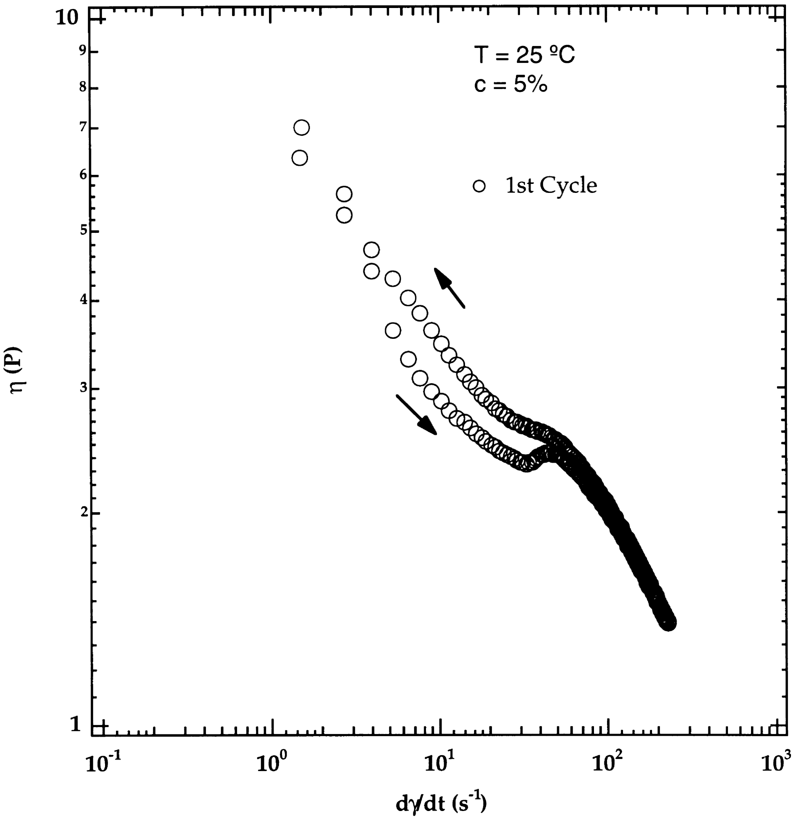

Fig. 1. The effect of shear rate on the measured shear viscosity during a complete cycle of a thixotropic loop experiment for OATRIM-10 at 25°C is displayed. The region of shear-thickening behavior for OATRIM-10 is evident starting at a critical shear rate of 30 s^{-1}. The arrows indicate the direction of the applied thixotropic loop.

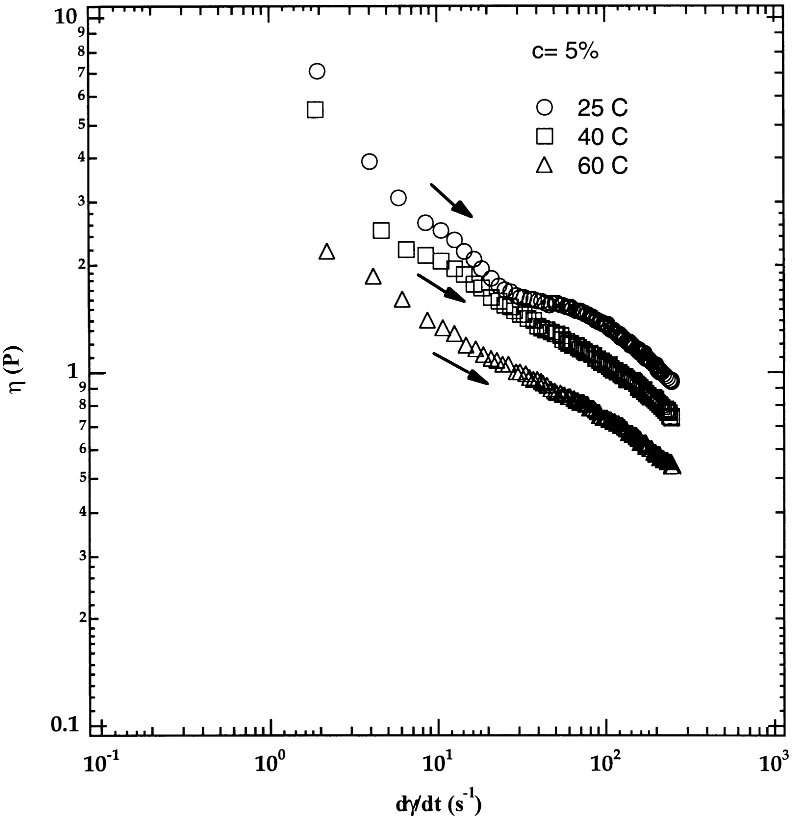

Fig. 2. The effect of temperature on the shear viscosity of OATRIM-10. The data displayed were obtained during the upward cycle of a thixotropic loop experiment. The arrows indicate the direction of the applied shear rate.

then centrifuged at 15 000 rpm to separate the soluble and insoluble components. The soluble materials were isolated and the water was removed by freeze-drying the solution. The resulting material is designated as OATRIM. All of the materials discussed in this work were produced in the pilot plant facilities of the National Center for Agricultural Utilization Research (Peoria, IL).

The degrees of polymerization and the number average molecular weights of the amylodextrins produced by the enzymatic treatment are summarized in the literature (Inglett, 1993). The number on the end of the OATRIM label designates the weight percent of β-glucan in the material. The compositions of the various OATRIM samples used in this study are summarized in Table 1.

Samples for the rheological experiments were prepared by dispersing OATRIM in water at a concentration of 5% by weight. The suspension was agitated by hand and then heated to near boiling on a hot plate. The sample was then cooled to room temperature and used in the experiments. Fresh samples were made daily to ensure that the material had not undergone decomposition.

2.2. Rheological measurements

Rheological properties were measured using a CarriMed® CSL^2 500 controlled-stress rheometer with a cone-and-plate fixture. All rheological studies were conducted using a 6-cm diameter, 4° cone. The temperature of the sample was controlled using a Peltier plate, which enabled the chamber of the viscometer to be controlled to within ± 0.1°C. Prior to the start of each experiment the rheometer inertia was calibrated and the instrument was zeroed. All the data presented in this study were analyzed using TA DATA rheological software.

The thixotropic loop experiments were conducted over a shear rate range of 0–250 s^{-1}. The upward and downward time segments of the thixotropic loop were kept equal for all the experiments discussed in this report, typically four minutes per loop. The downward cycle was initiated immediately after the conclusion of the upward cycle of the loop. Measurements of the shear viscosity were obtained throughout the course of the experiment.

Start-up of steady-state shear experiments were conducted by accelerating the cone to a pre-determined shear rate and then maintaining that shear rate over a specific time period. The time period was chosen to allow the sample to obtain a constant shear stress. Measurements of the shear stress versus time were obtained throughout the course of the experiment.

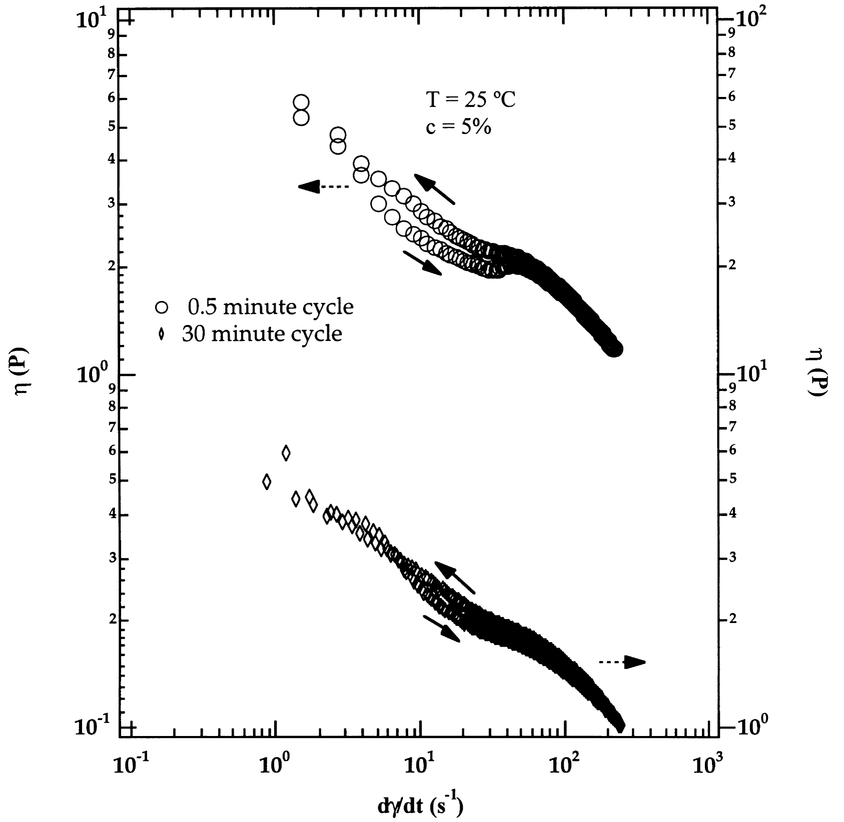

Fig. 3. The effect of cycle time on the measured shear viscosity of OATRIM-10 at 25°C. The data were obtained during a thixotropic loop experiment conducted over a shear rate range of 0–250 s^{-1} with a total cycle time of 0.5, or 30 min. The solid arrows indicate the direction of the applied thixotropic loop. The dashed arrows indicate the ordinate associated with the curve.

3. Results and discussion

The response of OATRIM-10 to a thixotropic loop experiment from 0 to 250 s^{-1} at 25°C is illustrated in Fig. 1. As has been previously noted (Carriere & Inglett, 1998), the suspension displayed a counterclockwise loop. From 0 to 30 s^{-1} the suspension displayed shear-thinning behavior. Starting at a critical shear rate, $\dot{\gamma}_c$, of 30 s^{-1} a region of shear-thickening behavior was observed ending at 50 s^{-1}. Above 50 s^{-1}, the suspension again displayed shear-thinning behavior till the end of the experimental range of 250 s^{-1}. The downward cycle of the thixotropic loop displayed similar behavior to the upward cycle including the region of shear thickening from 50 to 30 s^{-1}. Consequent thixotropic loops displayed similar behavior with the shear-thickening region starting at the same critical shear rate and comparable viscosities. (Carriere & Inglett, 1998).

The effect of temperature on the observed shear-thickening region for OATRIM-10 is illustrated in Fig. 2. The upward cycle of a series of thixotropic loop experiments conducted at 25, 40, and 60°C are displayed in the figure. As the temperature increased the viscosity of the suspension dropped as expected. In addition, the shear-thickening region was depressed as the temperature increased. At 40°C, a slight shear-thickening region was observed starting near 30 s^{-1}. At 60°C, the shear-thickening region was not observed at any of the shear rates examined.

The effect of cycle time on the observed shear-thickening region was investigated and the results are illustrated in Fig. 3. Thixotropic loop experiments were conducted using total cycle times of 0.5, 4, and 30 min. At a 0.5-min cycle time, $\dot{\gamma}_c = 25\ s^{-1}$ while at a cycle time of 30 min, $\dot{\gamma}_c = 30\ s^{-1}$. The difference in the observed critical shear rate was within the error of the experimental measurement. Some of the difference between the critical shear rates observed for the short cycle times and the long cycle times could be as a result of some loss of moisture from the sample over the course of the longer experiment. Many viscoelastic materials will display shear-thickening-like behavior during the course of a thixotropic loop experiment if the cycle time of the loop is much smaller than the relaxation time of the material (Bird & Marsh, 1968; Marsh, 1968). However, if the loop cycle time is increased sufficiently, the observed shear-thickening behavior should be eliminated. Calculation of the longest relaxation time for 5% by weight OATRIM-10 suspensions at 25°C indicates a value of approximately 0.28 s (Carriere & Inglett, 1998). The data obtained at a total loop time of 30 min are outside the range that one could contribute the observed shear-thickening behavior to the

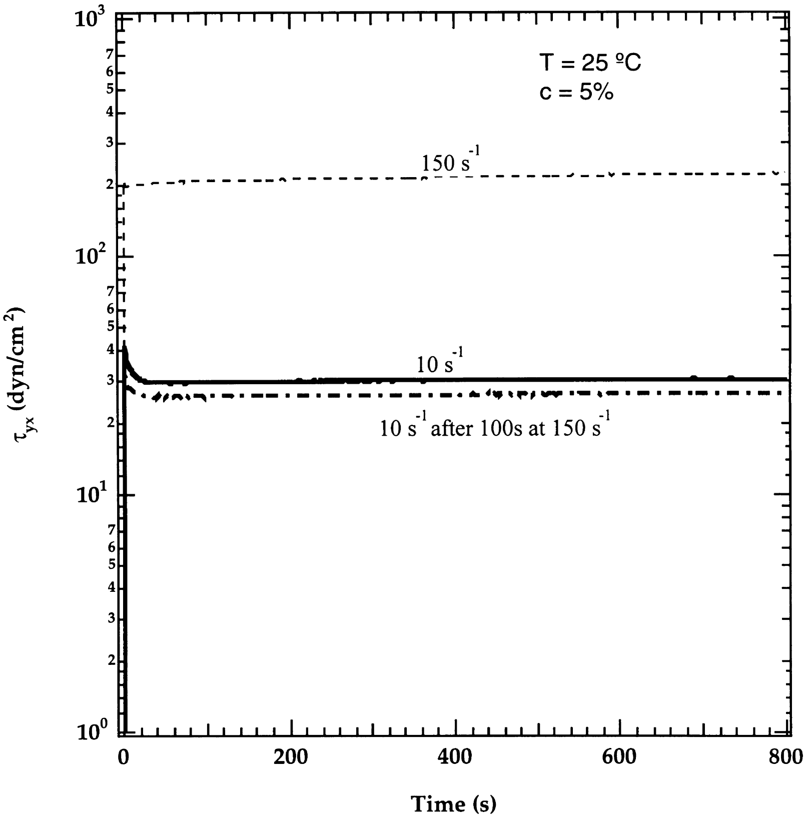

Fig. 4. The effect of shear rate on the measured shear stress versus time plots for OATRIM-10. The data were obtained during the start-up of steady-state shear at 25°C.

incomplete relaxation of the suspension over the time scale of the experiment. These results lead to the conclusion that the shear-thickening behavior is probably a result of an interaction between the components of the materials that make up OATRIM-10. This type of behavior has been observed in other biopolymer systems, notably, semidilute solutions of waxy maize starch (Dintzis & Bagley, 1994, 1995; Dintzis, Berhow, Bagley, Wu & Felker, 1996; Carriere & Loffredo, 1998; Carriere, 1998). However, for waxy maize starch the shear-thickening region creates a stable shear-induced structure in the solution. For OATRIM-10, the shear-thickening region is reversible and the presence of any stable flow-induced structure is not observed.

The effect of aging on the rheological properties of OATRIM-10 was also investigated (data not shown). The response to a thixotropic loop for a sample that was freshly prepared is shown in Fig. 1. Experimental data for samples that had been stored in a refrigerator for 3 and 8 days displayed identical behavior. For each of the samples, a region of shear thickening was observed. The critical shear rate was unaffected by the storage and subsequent aging. The absolute viscosity of each of the materials was within experimental error of one another. These data indicate that OATRIM-10 does not undergo significant aging during 8 days in refrigerated storage.

The response of OATRIM-10 to the startup of steady-state shear flow is illustrated in Fig. 4. In Fig. 4, shear stress is plotted against time for shear rates of 10 and 150 s^{-1}. At 10 s^{-1}, which is below the critical shear rate, the system displayed a slight initial stress overshoot that decayed to a stable plateau after 30 s. At 150 s^{-1}, which is above the critical shear rate, but in the second shear-thinning regime (Fig. 1), there was not any evidence of stress overshoot. The stress decayed rapidly to a stable plateau within the first few seconds. Reducing the shear rate to 10 s^{-1}, after subjecting the sample to a shear rate of 150 s^{-1} for 100 s, produced a curve similar to that obtained at 10 s^{-1} with a fresh sample. The material again displayed a stress overshoot that dropped to a stable plateau after 30 s. The agreement between the two data sets obtained at a shear rate of 10 s^{-1} indicates that the shear-thickening region does not generate any permanent structure in the material. That is, the shear-thickening behavior is reversible, which is in agreement with the behavior seen in during the thixotropic loop experiments.

The effect of (1,3; 1,4)-β-D-glucan level on the shear-thickening behavior in OATRIM-10 is illustrated in Fig. 5. The data for OATRIM-10 displayed the aforementioned region of shear thickening starting at 30 s^{-1} with a counter-clockwise loop. When the amount of (1,3; 1,4)-β-D-glucan was reduced to 5% (OATRIM-5), the observed loop is counter-clockwise, and there was little evidence of shear

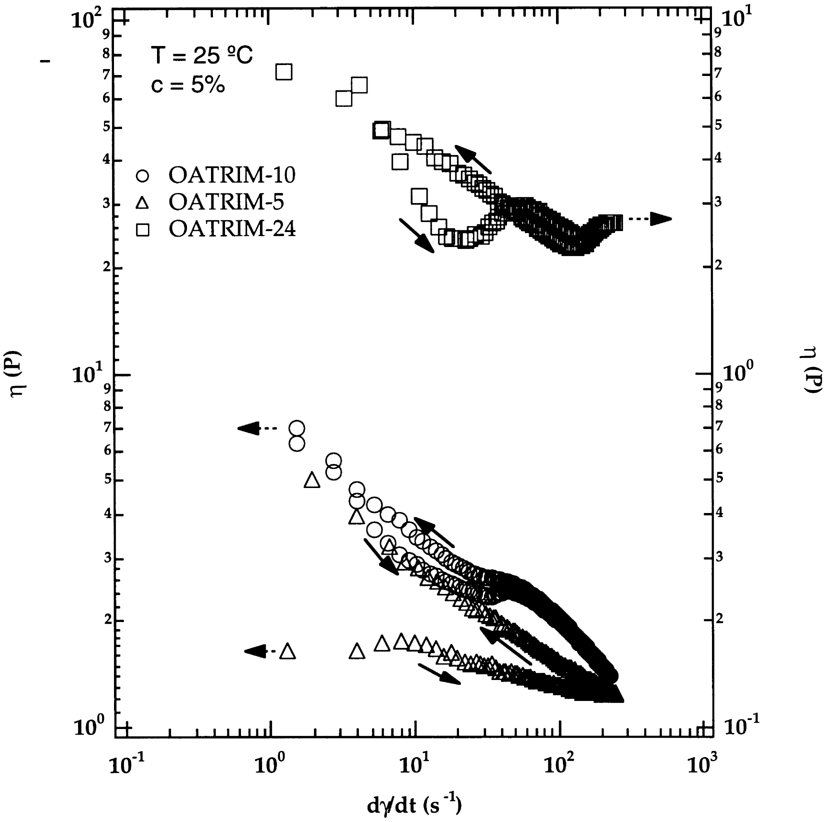

Fig. 5. Effect of (1,3; 1,4)-β-D-glucan on the measured shear viscosity of OATRIM materials at 25°C. The data were obtained during a thixotropic loop experiment conducted over a shear rate range of 0–250 s^{-1}. The solid arrows indicate the direction of the applied thixotropic loops. The dashed arrows indicate the ordinate associated with the curve.

thickening throughout the shear rate range examined. OATRIM-5 displayed only shear-thinning behavior with a marked mismatch between the starting and ending viscosities. Replication of the thixotropic loop (data not presented) experiment produced a curve that followed the downward cycle for the initial thixotropic loop. The initial upward cycle of the thixotropic loop created a shear-dependent, unstable association in the material that caused a transient increase in the viscosity of the suspension. When the shear field was removed the suspension recovered its initial state. As OATRIM-5 does not display the shear-thickening behavior observed in OATRIM-10, it is possible to conclude that the shear-thickening behavior in OATRIM materials is due, in part, to the concentration of (1,3; 1,4)-β-D-glucan. It should be noted that (1,3; 1,4)-β-D-glucan by itself displays strictly shear-thinning behavior (Wood, 1984; Autio *et al.*, 1987; 1992; Doublier & Wood, 1995; Autio, 1988; Zhang *et al.*, 1998). Therefore, the shear-thickening regions are most probably attributed to a complex interaction between the amylodextrins and (1,3; 1,4)-β-D-glucan components that constitute OATRIM once the (1,3; 1,4)-β-D-glucan concentration is above a critical level.

If the amount of (1,3; 1,4)-β-D-glucan was increased to 24% by weight (OATRIM-24), a counter-clockwise thixotropic loop was again observed (Fig. 5). The initial shear-thinning region decreased with increasing shear rate at a more marked degree than was observed in OATRIM-10. A shear-thickening region was observed starting at 30 s^{-1} and extending until 50 s^{-1}. This is the same shear rate range that the shear-thickening region was observed for OATRIM-10. OATRIM-24 then exhibits a region of shear-thinning behavior up to a shear rate of 100 s^{-1}, where a second region of shear thickening was observed. The second shear-thickening region extended up to a shear rate of 200 s^{-1}. As the initial shear-thickening region observed in OATRIM-24 extended over the same range as that observed for OATRIM-10, it is probable that the same interactions that cause the shear-thickening region in OATRIM-10 are also producing the initial shear-thickening region in OATRIM-24. The exact cause of the second shear-thickening region is unknown, but could be as a result of a transient physical network formed by weak associations such as hydrogen bonding as discussed later.

The response of OATRIM-24 to the startup of steady-state shear flow is illustrated in Fig. 6. In Fig. 6, the shear stress is plotted against time for shear rates of 10, 100, and 200 s^{-1}. At 10 s^{-1}, which is lower than the critical shear rate for the initial shear-thickening region, the shear stress was observed to exhibit a large stress overshoot and then gradually decayed to a stable plateau after 30 s. At a shear rate of

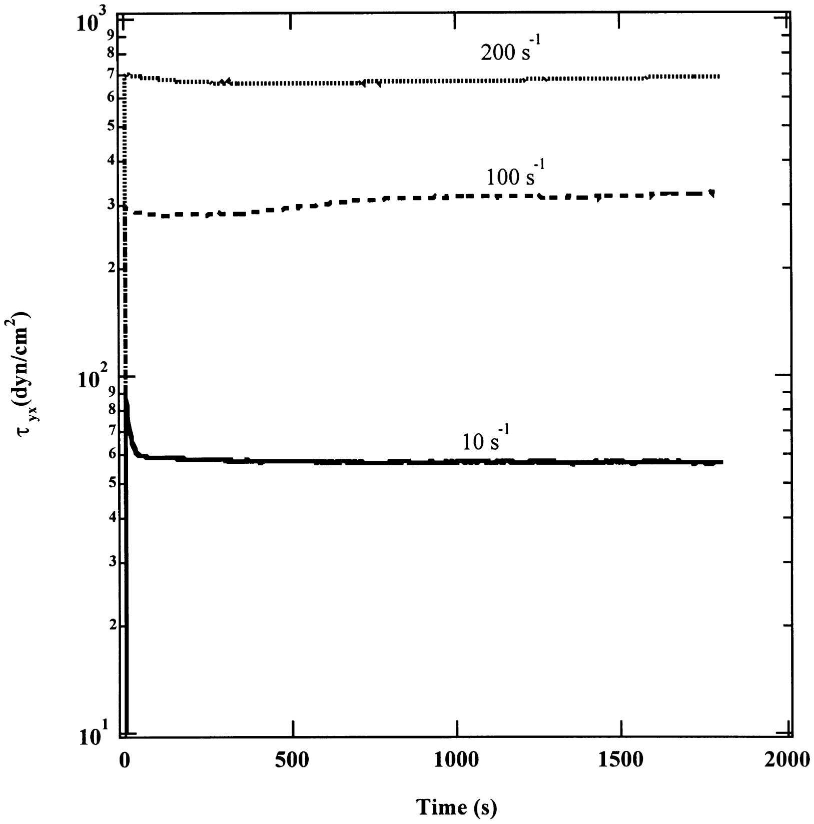

Fig. 6. The effect of shear rate on the measured shear stress versus time plots for OATRIM-24. The data were obtained during the start-up of steady-state shear at 25°C.

200 s^{-1}, which is at the end of the second shear-thickening region, the shear stress was observed to obtain a stable plateau quite quickly without evidence of stress overshoot. At a shear rate of 100 s^{-1}, which is at the start of the second shear-thickening region, the shear stress exhibited a slight initial stress overshoot which decayed to a steady plateau and then a second stress overshoot occurred starting at about 500 s. The second stress overshoot was small in amplitude and decayed at a slower rate than the initial overshoot. Semi-dilute and concentrated solutions of hydrophilic polymers such as polyacrylamide, poly(vinyl alcohol) are known to display unusual phenomenon such as double stress overshoots and maxima in the elongational stress growth function (Kulicke, Klien & Porter, 1979; Kulicke, Kniewske & Klien, 1982; Kulicke & Klien, 1978; Odell, Muller & Keller, 1988; Fergusson, Hudsen, Warren & Tomalarian, 1987). One proposed explanation for these observations is the formation of a transient network caused by weak associations such as hydrogen bonding. A recent physical model has been developed that can reproduce some of these observations (Lele & Mashelkar, 1998). A transient network caused by hydrogen bonding might explain the double stress overshoot as well the two shear-thickening regimes; however, more work is needed to address this issue. From the data presented in Figs. 5 and 6, it is evident that the amount of (1,3; 1,4)-β-D-glucan is critical for the observed shear-thickening behavior exhibited by OATRIM-10 and OATRIM-24.

4. Conclusions

The rheological properties of various OATRIM materials were investigated. OATRIM samples containing 10 and 24% by weight (1,3; 1,4)-β-D-glucan were found to display complicated nonlinear behavior including regions of shear-thickening and stress overshoots. OATRIM samples containing 5% by weight (1,3; 1,4)-β-D-glucan displayed shear-thinning behavior and did not exhibit any evidence of stress overshoot. OATRIM-24 was found to exhibit two distinct regions of shear-thickening behavior as well as two regimes of stress overshoot. This behavior is unusual and unexpected. This result underscores the unique rheological responses of these materials. It is important to note that both (1,3; 1,4)-β-D-glucan and the amylodextrins by themselves exhibit only shear-thinning behavior. The shear-thickening behaviors evidenced by OATRIM-10 and OATRIM-24 are most probably due to complicated interactions between the (1,3; 1,4)-β-D-glucan and amylodextrins that make up the materials.

Acknowledgements

The assistance and support of A. Loffredo, E. Bagley, and R. Greene in the completion of this work is acknowledged with gratitude. This work was supported financially by The United States Department of Agriculture.

References

American Heart Association Committee Report. (1980). *Circulation*, 62, pp. 449A-445A.

Autio, K. (1988). In G. O. Phillips & P. A. Williams & D. J. Wedlock (Eds.), *Gums and stabilizers for the food industry*, (pp. 483). London: Elsevier.

Autio, K., Myllymaki, O., & Malkki, Y. (1987). *J. Food Sci.*, *52*, 1364–1366.

Autio, K., Myllymaki, O., Suortti, T., Saastamoinen, M., & Poutanen, K. (1992). *Food Hydrocoll.*, *5*, 513–522.

Behall, K. M., Scholfield, D. J., Clark, W. M., 1993. International Congress of Nutrition, Adelaide Book 2, Adelaide, Australia: Smith-Gordon, p. 661.

Bird, R. B., & Marsh, B. D. (1968). *Trans. Soc. Rheol.*, *12*, 479–488.

Carriere, C. J. (1998). J. Polym. Sci. *Polymer Physics Edition*, *36*, 2085–2093.

Carriere, C. J., & Loffredo, A. R. (1998). *Polymer Engng. Sci.*, *38*, 1523–1528.

Carriere, C. J., & Inglett, G. E. (1998). *Cereal Chem.*, *75*, 354–359.

Dintzis, F. R., & Bagley, E. B. (1994). *J. Appl. Polym. Sci.*, *56*, 637–640.

Dintzis, F. R., & Bagley, E. B. (1995). *J. Rheol.*, *39*, 1399–1409.

Dintzis, F. R., Berhow, M. A., Bagley, E. B., Wu, Y. V., & Felker, F. C. (1996). *Cereal Chem.*, *73*, 638–643.

Doublier, J. -L., & Wood, P. J. (1995). *Cereal Chem.*, *72*, 335–340.

Fergusson, J., Hudsen, N. E., Warren, B. C. H., & Tomalarian, A. (1987). *Nature*, *325*, 234–236.

Food and Drug Administration, X., Federal Register, 62 1997 3584-3601.

Hallfrisch, J., Scholfield, D. J., & Behall, K. M. (1997). *J. Nutr. Biochem.*, *8*, 497–501.

Inglett, G. E., 1991 U. S. Patent, 4,996,063, February 26.

Inglett, G. E. (1993). *Food Chemistry*, *47*, 133–136.

Inglett, G. E. (1997). *Cereal Foods World*, *42*, 382–385.

Inglett, G. E., & Newman, R. K. (1994). *Plant Foods Hum. Nutr.*, *45*, 53–61.

Kulicke, W. M., & Klien, J. (1978). *Angew. Makromol. Chem.*, *69*, 169–188.

Kulicke, W. M., Klien, J., & Porter, R. S. (1979). *Angew. Makromol. Chem.*, *76/77*, 191–208.

Kulicke, W. M., Kniewske, R., & Klien, J. (1982). *Prog. Polym. Sci.*, *8*, 373–468.

Lele, A. K., & Mashelkar, R. A. (1998). *J. Non-Newtonian Fluid Mech.*, *75*, 99–115.

Malkki, Y., Autio, K., & Hanninen, O. (1992). *Cereal Chem.*, *69*, 647–653.

Marsh, B. D. (1968). *Trans. Soc. Rheol.*, *12*, 489–510.

Odell, J. A., Muller, A. J., & Keller, A. (1988). *Polymer*, *29*, 1179–1190.

Scholfield, D. J., Behall, K. M., & Armero, E. C. (1993). *FASEB J.*, *7*, A738.

Topping, D. L. (1991). *Nutr. Rev.*, *49*, 195–203.

Uusitupa, M. I. J., Ruuskanen, E., & Makinen, E. A. (1992). *J. Am. Coll. Nutr.*, *11*, 651–660.

Wood, P. J. (1984). In V. F. Rasper (Ed.), *Cereal polysaccharides in technology and nutrition*, (pp. 52–57). St. Paul, MN: American Association of Cereal Chemistry.

Zhang, D., Doehlert, D. C., & Moore, W. R. (1998). *Cereal Chem.*, *75*, 433–438.