

# A Simplified Nonlinear Model for Describing the Viscoelastic Properties of Wheat Flour Doughs at High Shear Strain<sup>1</sup>

B. LAUNAY<sup>2</sup>

## ABSTRACT

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Shear stress relaxation properties of wheat flour doughs were analyzed with an equation derived from Lethersich's analogical model, i.e., a Kelvin body ( $G$  and  $\eta_K$ ) in series with a dashpot  $\eta$ . Assuming  $\eta_K \ll \eta$ , the relaxation curves may be described by considering that  $\eta$  alone varies with the shear stress  $\sigma$  according to a power law. The corresponding constant shear modulus  $G$  decreases when the shear strain increases.  $G$  does not depend strongly on flour strength, dough water content, mixing time, or temperature, except at temperatures beyond 45–50°C, where  $G$  strongly increases. The addition of urea or sodium sulfite does not appear to

alter  $G$  significantly. It is inferred that hydrophobic interactions play a major role in dough elastic properties. Results published by Bloksma and Meppelink are shown to be consistent with an almost invariable value of  $G$  at a given shear strain and with decreasing values of  $G$  when the shear strain increases. The power-law model is compared with Peleg's equation and with the theory of cooperative flow proposed by Bohlin and Carlson. The stress relaxation kinetics derived from this theory is similar to the one predicted by the power-law model, but the fitting parameters do not have the same physical meaning.

The viscoelastic behavior of wheat flour doughs is of great significance in the baking industry. For example, the rate at which internal stresses induced by mechanical treatment relax during a rest period depends on both viscosity and dough elasticity. Relaxation effects are also shown by the changing dimensions of dough pieces after punching or molding as a function of time. It is therefore understandable that several workers have devoted a great deal of effort to characterizing dough elasticity using transitory rheological measurements: creep (constant stress) and recovery or stress relaxation (constant strain). Several studies have been made of uniaxial extension, following the pioneering work of Scott-Blair and co-workers more than 50 years ago (Schofield and Scott-Blair 1933, Halton and Scott-Blair 1936). Simple shear has been used more recently in studies of creep and recovery (Bloksma 1962, 1972; Yoneyama et al 1970; Bloksma and Meppelink 1973; Hibberd and Parker 1979) and for stress relaxation measurements (Launay and Buré 1974a,b; Bohlin and Carlson 1981). Frazier et al (1973) also studied stress relaxation after compressing a dough ball between two plates with an Instron universal testing machine under conditions where the deformation was not precisely defined. They observed that the relaxation rate depends on several parameters and, in particular, on mixing work input, but they had no way of separating the effects on viscous and elastic properties.

The aim of this paper is to give a detailed account of a simple nonlinear viscoelastic model developed previously (Launay and Buré 1974b) that is also applicable to biaxial stress relaxation (Launay 1987).

<sup>1</sup>These results have been presented in part at the AACC 64th Annual Meeting, Washington, DC, October 1979; the AACC 73rd Annual Meeting, San Diego, CA, October 1988; and the 8th International Cereal and Bread Congress, Lausanne, Switzerland, 1988.

<sup>2</sup>Professor, Département Science de l'Aliment, ENSIA, 91305 Massy, France.

## MATERIALS AND METHODS

### Flours and Doughs

Four commercial flour samples were studied: two of them classified as strong flours, f4 (13.1% protein, dry matter basis) and f5 (13.2% protein), and two flours used for French bread baking, f6 (9.9% protein) and f8 (10.0% protein). Doughs containing 0.83% NaCl (dough basis) were mixed in the alveograph kneader or in the farinograph (75 rpm) for a given time. Water contents are expressed as total water percent dough weight. Doughs were allowed to rest 20 min at about 20°C in a closed plastic box before measurement. Recent creep and recovery studies on flour-water doughs having various consistencies showed that their rheological properties were fairly stable for approximately 20–40 min (Launay, unpublished results).

### Rheological Measurements

A cone-plate viscometer was used (Haake Rotovisko, BV type) with a speed reducer (reducer 100), the MK 5000 measuring head, and the PK 1 cone (2.8 cm,  $5.47 \times 10^{-3}$  radian). Plate temperature was regulated by thermostated water circulation. When the temperature was different from that of the laboratory, actual dough temperature was measured (in an earlier experiment) by inserting a thermocouple between cone and plate. Up to 10 different shear rates, from 0.574 to 93.01 sec<sup>-1</sup>, were used, and the shear stress versus time curves were recorded (MECI Speedomax).

Steady deformation at constant shear rate  $\dot{\gamma}$  was stopped after an elapsed time  $t_i$  corresponding to a predetermined shear strain  $\gamma_i = \dot{\gamma}t_i$ , and the relaxation curve  $\sigma(t)$  was recorded. Three values of  $\gamma_i$  were studied (Fig. 1): 123.6 ( $\gamma_1$ ), 206.0 ( $\gamma_2$ ), and 288.3 ( $\gamma_3$ ). Therefore, the results presented here pertain to high shear strains. Other details are presented elsewhere (Launay and Buré 1973, 1974a).

## RESULTS AND DISCUSSION

### The Model

Bloksma (1962) showed that the creep and recovery curves of wheat flour doughs are characteristic of a viscoelastic liquid; at a constant stress, creep never stops, and there is only partial elastic recovery when the stress is removed. In addition, Bloksma clearly established that the behavior is nonlinear; in particular, the compliance ( $\gamma/\sigma$ ) is an increasing function of  $\sigma$  rather than being independent of it. This observation was subsequently confirmed by Hibberd and Parker (1979), who tried to take into account nonlinear effects. Linear models are still frequently used to analyze experimental curves (e.g., Yoneyama et al 1970), but, contrary to common expectations, even a good agreement between experimental values and theoretical curves is not sufficient to prove that linear models are valid. In addition, the fitted parameters must be independent of the stress in the linear domain.

We also find that the flow behavior of dough is strongly nonlinear and may be described by a power law in the shear rate range from 0.6 to 93  $\text{sec}^{-1}$  (Launay and Buré 1973):

$$\sigma = K\dot{\gamma}^\alpha \quad (1)$$

with  $K$  decreasing when  $\dot{\gamma}$  increases from  $\dot{\gamma}_1$  to  $\dot{\gamma}_3$ . From equation 1,  $\eta$  may be also calculated as a function of  $\sigma$ :

$$\eta = \sigma/\dot{\gamma} = K^{1/\alpha}\sigma^{1-1/\alpha} \quad (2)$$

Typical values of the power-law exponent are  $\alpha = 0.3 \pm 0.1$  (for a linear, i.e., Newtonian, viscosity  $\alpha = 1$ ). This behavior has also been observed at much lower shear rates ( $6.5 \times 10^{-4} \text{ sec}^{-1}$  to  $2 \times 10^{-2} \text{ sec}^{-1}$ ) by Bloksma and Nieman (1975), and we recently confirmed that the power-law still applies at least from  $\dot{\gamma} = 4 \times 10^{-4} \text{ sec}^{-1}$  (unpublished results). Taking into account these strongly nonlinear properties at very low shear rates, it is not consistent to fit the relaxation curves with one or several linear Maxwell models. As pointed out by Bloksma (1972) the simplest model that may qualitatively describe stress relaxation and partial elastic recovery is Lethersich's model (Fig. 2). With this model stress relaxation is complete, and its rate depends on  $(\eta + \eta_K)$ , but steady flow properties are solely defined by

$\eta$ . The equation corresponding to this model is:

$$\sigma = G\gamma_{el} + \eta_K \dot{\gamma}_{el} = \eta \dot{\gamma}_v \quad (3)$$

With  $\gamma_{el}$ , elastic deformation, and  $\dot{\gamma}_v$  viscous (irrecoverable) deformation.

For nonlinear viscous properties,  $\eta_K$  and  $\eta$  are functions of the absolute values of  $\dot{\gamma}_{el}$  and  $\dot{\gamma}_v$ , respectively. During the relaxation process  $\dot{\gamma} = \dot{\gamma}_{el} + \dot{\gamma}_v = 0$ , i.e.,  $|\dot{\gamma}_{el}| = |\dot{\gamma}_v|$  and, therefore,  $\eta_K$  and  $\eta$  are functions of the same shear rate values. In the case of creep curves, the slope  $\dot{\gamma} = d\gamma/dt$  is always much steeper close to  $t = 0$  than at longer times when steady viscous flow is attained (Bloksma 1962, 1972): this result indicates that  $\eta_K(\dot{\gamma}) \ll \eta(\dot{\gamma})$ . By example, Yoneyama et al (1970), using a linear (Burgers') model, found that  $\eta_K$  is smaller than  $\eta$  by one order of magnitude. Hence, equation 3 may be reduced to:

$$\sigma = G\gamma_{el} = \eta \dot{\gamma}_v \quad (4)$$

Another working hypothesis may be introduced by assuming that  $G$  is constant during the relaxation process, that is,  $G$  does not depend on  $\sigma$ . In other words, we will examine whether it is possible to attribute the nonlinear relaxation behavior to nonlinear viscous properties. In the earliest studies, the elastic properties in uniaxial extension were observed to be less dependent on stress than the viscous ones (Schofield and Scott-Blair 1933, Halton and Scott-Blair 1936). In simple shear, the same conclusion may be drawn from creep and recovery curves (Bloksma 1962, 1972) and from stress-versus-time curves at constant shear rate (Bloksma and Nieman 1974). This hypothesis of constant  $G$  is then not unreasonable. Stress relaxation is governed by the following equation, deduced from equation 4:

$$\dot{\gamma} = \dot{\gamma}_{el} + \dot{\gamma}_v = \dot{\sigma}/G + \sigma/\eta = 0 \quad (5)$$

and, by replacing  $\eta$  by its value as a function of  $\sigma$  (eq. 2):

$$\dot{\sigma}/G + K^{-1/\alpha}\sigma^{1/\alpha} = 0 \quad (6)$$

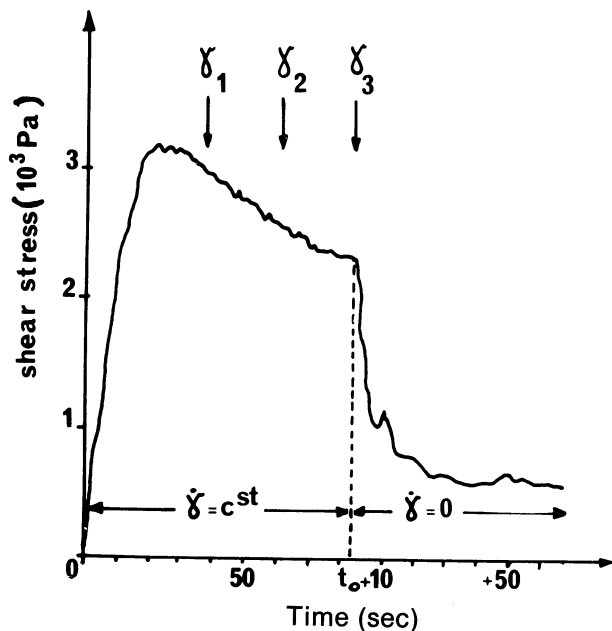


Fig. 1. Shear stress versus time at  $\dot{\gamma} = 3.45 \text{ sec}^{-1}$  and at  $\dot{\gamma} = 0$  from  $t = t_0$  (stress relaxation). Arrows correspond to the three values of shear strain  $\gamma_i$  used in this study. Experimental conditions: sample f6, 40% mc, alveograph 6 min, measured at 23.8°C.

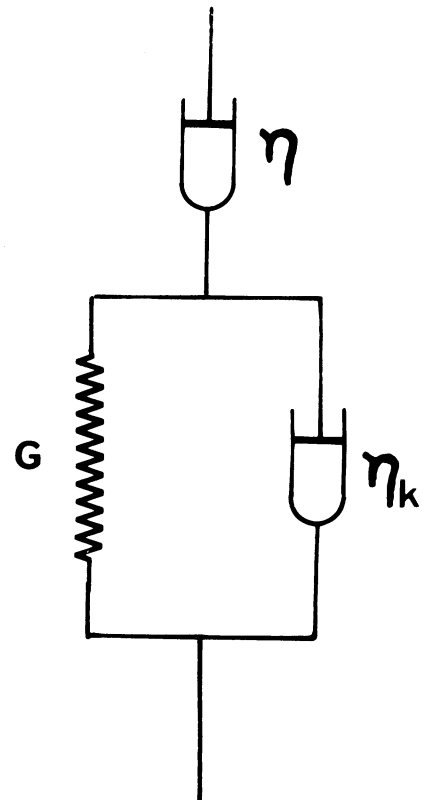


Fig. 2. Lethersich's analogical model.

By integration, putting  $\sigma = \sigma_0$  and  $t = 0$  when stress relaxation starts ( $t = t_0$  on Fig. 1), one obtains:

$$(\sigma_0/\sigma)^{n-1} = 1 + pt \quad (7)$$

where  $n = 1/\alpha$  and  $p = (n-1)G\sigma_0^{n-1}K^{-n}$ .

Equation 7 predicts, at sufficiently long times, a power law relationship between  $\sigma$  and  $t$  that corresponds to numerous experimental observations. The value of the half-relaxation time ( $\sigma/\sigma_0 = 0.5$ ) is easily deduced from equation 7:

$$t_{1/2} = [(2^{n-1}-1)/(n-1)] \cdot (K^n/G\sigma_0^{n-1}) \quad (8)$$

The half-relaxation time decreases when  $\sigma_0$  increases ( $n = 1/\alpha > 1$ ), as observed by Launay and Buré (1974a), and a power-law relationship between  $t_{1/2}$  and  $\sigma_0$  is also predicted.

#### Experimental Valuation of the Model

Figure 3 indicates that the power-law relationship predicted at long times by equation 7 is verified on at least a log unit. Generally, it was not possible to follow stress relaxation curves for much longer than about 1 min, because the quality of the signal was not sufficient (Fig. 1) and dough dehydration was not controlled. However, a few experiments have shown that the power-law still applies over about two log units. From the slopes of the linear parts of the curves [ $= 1/(1-n)$ ], equation 7 may be evaluated in the full experimental range (Fig. 4). As  $n$  and  $K$  (consistency index, eq. 1) are known, the shear modulus  $G$  is obtained from the value of the slope  $p$ . A good agreement between experimental and fitted relaxation curves is observed in Figure 5. In addition, Figure 6 demonstrates that equation 8 is well suited to describe the relationship between the half-relaxation time  $t_{1/2}$  and the initial stress  $\sigma_0$ . A decay ratio other

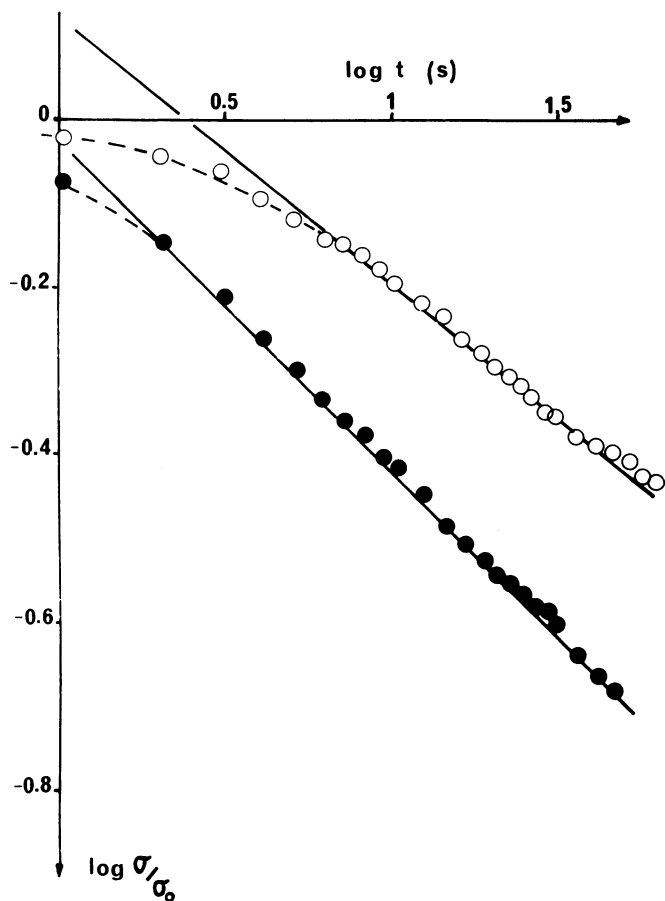


Fig. 3. Shear stress relaxation in log scales: sample f6, 40% mc, farinograph 6 min, measured at 12°C,  $\sigma_0 = 9.9 \times 10^3$  Pa (○), and 16.1°C,  $\sigma_0 = 8.8 \times 10^3$  Pa (●),  $\gamma_1 = \gamma_3$ .

than  $\sigma/\sigma_0 = 0.5$  could be chosen on practical grounds; the same type of results would be obtained with only a change in the value of the ordinate at the origin. It may also be noted that the effect of the shear strain  $\gamma$  is only of second order on the stress relaxation rate, as already mentioned (Launay and Buré 1974a). This property has also been stated by Bohlin and Carlson (1981) at much lower shear strains ( $\gamma$  from 0.1 to 1). From the slopes of the least-square lines corresponding to equation 8 in log scales and from the value of  $K$ , it is easy to calculate  $G$ . Both methods

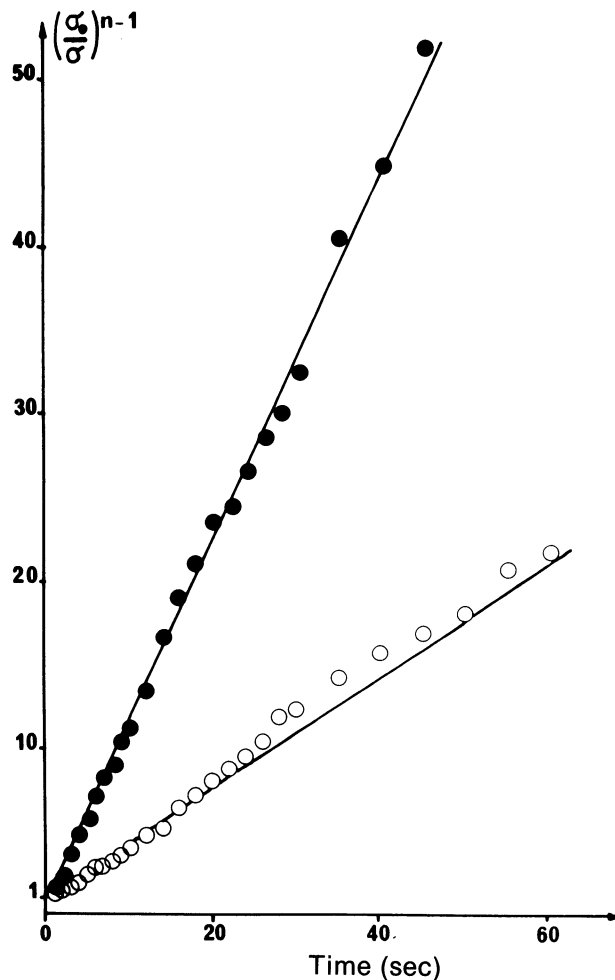


Fig. 4. Results of Fig. 3 linearized using equation 7.

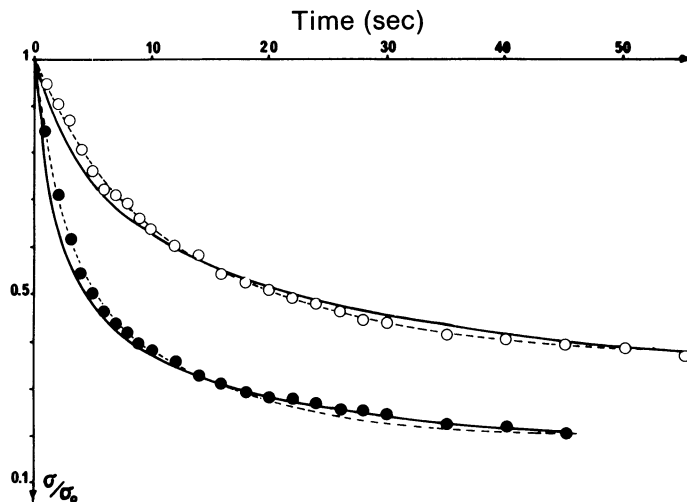


Fig. 5. Experimental stress relaxation curves (○ and ● as in Fig. 3) and fitted kinetics: equation 7 (continuous lines) and Peleg's equation (eq. 10, dashed lines).

were used to obtain the results given in Table I. As will be shown later, dough temperature did not have a statistically significant effect on  $G$  in the range considered here, and elastic moduli obtained at different temperatures were pooled in Table I. The only significant differences at the 5% probability level are related to the effect of shear strain and, in particular, equations 7 and 8 lead to values of  $G$  that are not significantly different at this level. If all the values obtained at the same shear strain  $\gamma$  are also pooled, the difference between the elastic moduli at  $\gamma = \gamma_2$  and  $\gamma = \gamma_3$  is very highly significant ( $<0.1\%$ ). In the following we determined  $G$  from  $t_{1/2}$  for two reasons: easier computation and smaller variability in resulting  $G$ .

The model also predicts that  $n$  (eq. 7 or 8) should be equal to  $\alpha^{-1}$  (eq. 1 or 2). This was verified, as shown in Figure 7; the least-square line is very close to the theoretical relationship  $n = \alpha^{-1}$ . In conclusion, the proposed model satisfactorily describes stress relaxation.

### Relationship Between Dough Characteristics and $G$

In addition to type of flour, the following factors were studied: dough water content, mixing time, and temperature of measurement. Urea (1.6% flour basis) or sodium sulfite (0.15% flour basis) were also incorporated in the dough. All these factors have been shown to affect the flow properties of dough and, in particular, they modify  $\alpha$  and  $K$  (Launay and Buré 1973). The results were split following the shear strain  $\gamma$  at which they were obtained and the type of flour used (strong flours f4 and f5 or bread flours f6 and f8). Equation 8 gives a straight line  $\log \sigma_0 = f(\log t_{1/2})$  with a slope  $1/(1-n)$  and an ordinate at the origin given by equation 9:

$$(\log \sigma_0)_{t_{1/2}=1} = [1/(n-1)] \cdot \log[(2^{n-1} - 1)/(n-1)] + [1/(n-1)] \cdot (n \log K - \log G) \quad (9)$$

TABLE I  
Comparison of the Values of  $G$  Derived from  $\sigma(t)$  (eq. 7) or from  $t_{1/2}$  (eq. 8)

Sample/ Treatment	Shear Strain $\gamma_2$		Shear Strain $\gamma_3$	
	Eq. 7	Eq. 8	Eq. 7	Eq. 8
Flour 5				
alveograph 6 min				
42% mc, 5-37.7°C	435	436	328	299
Flour 6				
farinograph 6 min				
40% mc, 8.5-22°C	...	...	285	302
43.2% mc, 8.5-21.2°C	...	...	249	265

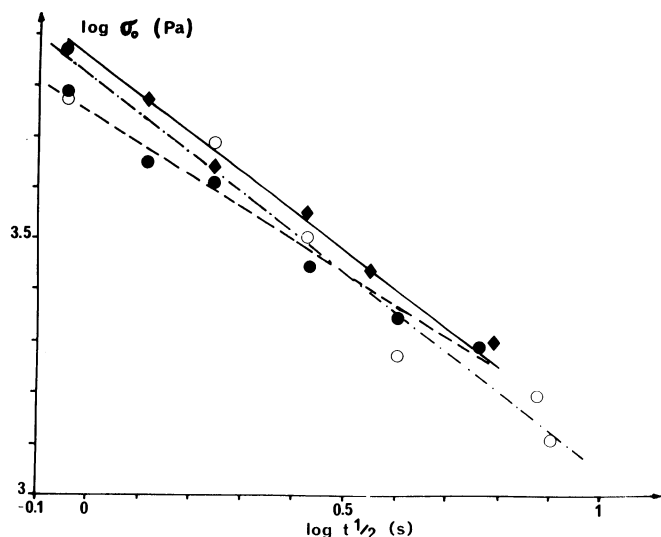


Fig. 6. Power-law relationships between half-relaxation time  $t_{1/2}$  and initial stress  $\sigma_0$  predicted by equation 8: sample f4, 43.2% mc, alveograph 6 min, measured at 24.7°C at  $\gamma_1 = \gamma_1$  ( $\blacklozenge$ ),  $\gamma_2$  ( $\bullet$ ), and  $\gamma_3$  ( $\circ$ ).

Figures 8-11 show the relationship between  $(n \log K - \log G)$ , as calculated from equation 9, and  $n \log K$ , where  $n$  and  $K$  are deduced from equations 8 and 1, respectively. As it has been shown that  $n$  and  $1/\alpha$  are closely related (Fig. 7),  $n \log K$  is mainly dependent on dough flow properties. On the other hand ( $n \log K - \log G$ ) is entirely deduced from stress relaxation curves (eq. 9). Thus, the relationships observed between  $n \log K$  and  $(n \log K - \log G)$  mean that  $\log G$  is a function of  $n \log K$ , whatever the dough water content, temperature or mixing time. In addition, as these relationships are straight lines with slopes not significantly different from 1 (Table II),  $\log G$  may be

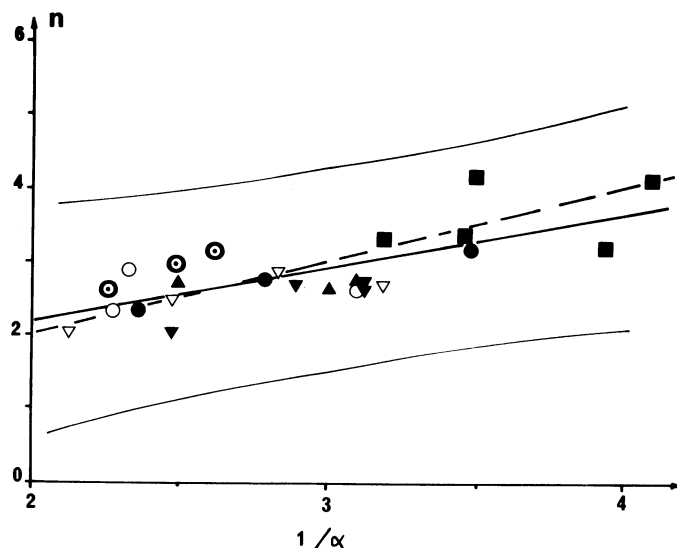


Fig. 7. Comparison of experimental results with the theoretical prediction  $n = \alpha^{-1}$  (dashed line). The power-law exponent  $n$  is calculated as shown on Fig. 6. Experimental conditions: sample f4, 43.2% mc, alveograph 6 min, measured at 24.7-33.3°C at  $\gamma_1$  ( $\circ$ ),  $\gamma_2$  ( $\circ$ ), and  $\gamma_3$  ( $\bullet$ ); sample f5, 42-45% mc, alveograph 6 min, measured at 24.7°C at  $\gamma_2$  ( $\nabla$ ) and  $\gamma_3$  ( $\blacktriangledown$ ); sample f6, 42-45% mc, alveograph 6 min, measured at 23.8°C at  $\gamma_3$  ( $\blacktriangle$ ); sample f6, 40% mc, 6 min in farinograph, measured at 8.5-22.1°C at  $\gamma_3$  ( $\blacksquare$ ). Continuous lines: linear least squares regression  $n = f(\alpha^{-1})$  and 5% confidence limits for a predicted  $n$  at any given value of  $\alpha^{-1}$ .

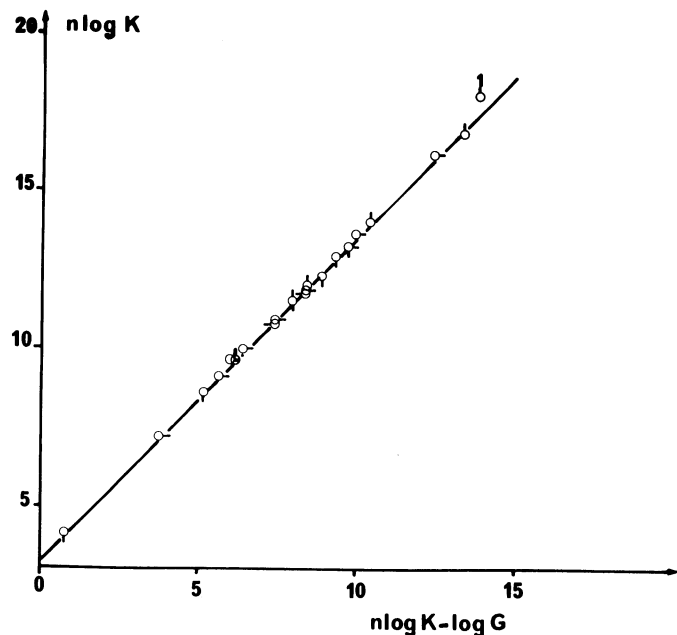


Fig. 8. Determination of  $G$  at  $\gamma_1 = \gamma_3$  for strong flours: sample f4, 43.2% mc, alveograph 6 min, measured at 17.8-36.8°C ( $\circ$ ) and 46.3°C ( $\blacksquare$ ); sample f4, 43-45% mc, 15 min in farinograph, measured at 24.7°C ( $\circ$ ); sample f5, 42% mc, alveograph 6 min, measured at 4.8-37.7°C ( $\circ$ ); sample f5, 40-47% mc, alveograph 6 min, measured at 24.7°C ( $\circ$ ).  $K$  in 0.1 Pa s<sup>n</sup>,  $G$  in 0.1 Pa.

considered to be independent of  $n \log K$ , i.e., of dough viscous properties. Doughs from the strong flours f4 and f5 have the same elastic modulus for dough water contents varying between 40 and 47%, for 6 min of mixing in the kneader of the alveograph or 15 min in the farinograph, and at temperatures from 5 to 37°C (Figs. 8–10). At a more elevated dough temperature (46.3°C),  $G$  seems to be much higher—about three times more than its mean value. It has also been shown that the flow behavior is completely altered above about 50°C (Launay and Buré 1973), but the variation of  $\alpha$  and  $K$  with temperature was not anomalous up to 46.3°C:  $\alpha$  increased and  $K$  decreased. However, in this case as at 36.8°C, it was noticed that  $n$  is much too high compared with  $1/\alpha$ , and the two corresponding points have been omitted

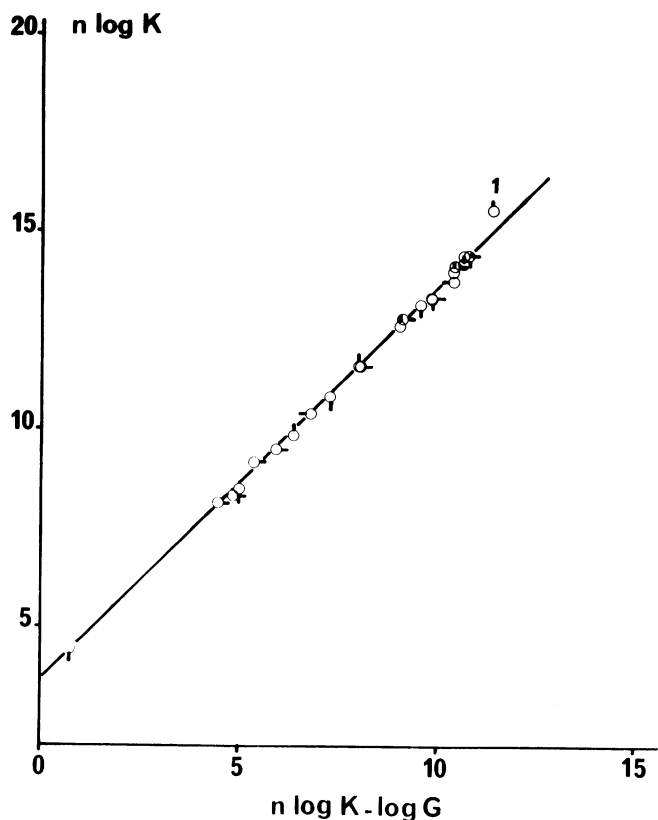


Fig. 9. Determination of  $G$  at  $\gamma_1 = \gamma_2$  for strong flours; compare Fig. 8.

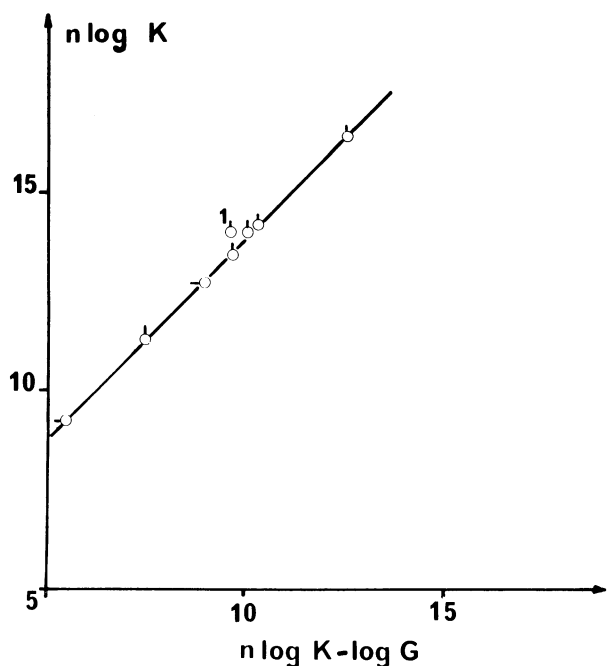


Fig. 10. Determination of  $G$  at  $\gamma_1 = \gamma_1$  for strong flours; compare Fig. 8.

for the computation of the linear relationship represented in Figure 7. This discrepancy may be an effect of dehydration, as dough becomes drier towards the end of the rheological test, i.e., during stress relaxation. But, because  $G$  does not appear to depend much on dough water content, a major error would be introduced by using an underestimated value of  $K$  that did not take into account dough dehydration. Consequently, the increase of  $G$  with temperature would be also underestimated. In addition to dough temperature beyond 45–50°C, the only factor that significantly modifies the value of  $G$  is the shear strain  $\gamma$ ; Table II shows that  $G$  decreases when  $\gamma$  increases. In Table II the confidence intervals for  $G$  at  $\gamma = \gamma_2$  and at  $\gamma = \gamma_3$  overlap, but it was shown previously (Table I) that the mean values of  $G$  differ at a very highly significant level.

An analogous conclusion may be drawn for bread flour f6 (Fig. 11); the least-square line has a slope equal to 1 (Table II) and, therefore, dough water content (40–45%) and temperature (8.5–22.1°C) have no significant effects on  $G$ . This conclusion is also valid for mixing times, which varied from 3 to 60 min

TABLE II  
Mean Values of  $G$  Deduced from Figures 8–11

Sample/ Shear Strain	Slope <sup>a</sup>	$G$ (Pa) <sup>b</sup>
Flours 4 and 5		
$\gamma_1$	$1.012 \pm 0.031$	$575 \pm 85$
$\gamma_2$	$0.992 \pm 0.022$	$375 \pm 51$
$\gamma_3$	$1.061 \pm 0.110$	$302 \pm 176$
Flours 6 and 8		
$\gamma_3$	$1.010 \pm 0.018$	$297 \pm 34$

<sup>a</sup> $n \log K$  versus  $(n \log K - \log G)$ , confidence interval at 5%.

<sup>b</sup>At  $n \log K - \log G = 10$ , confidence interval at 5%.

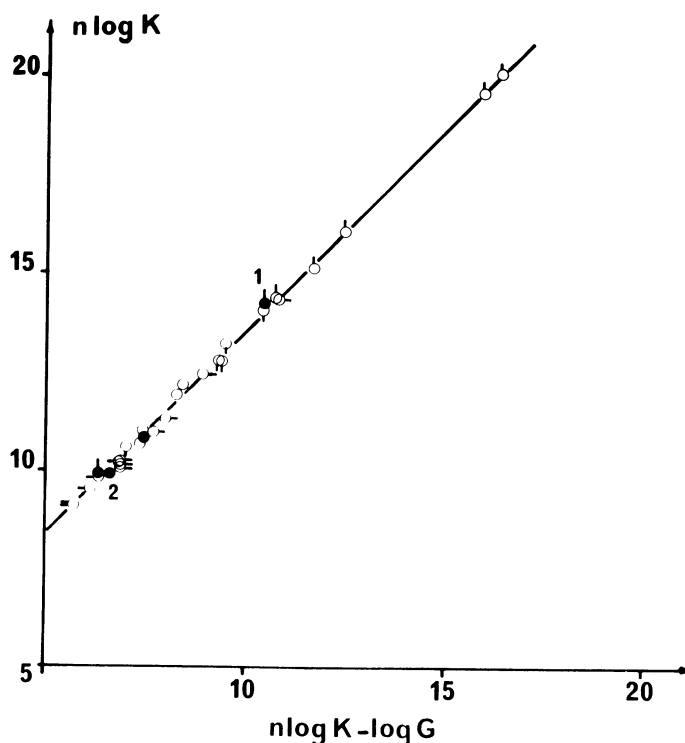


Fig. 11. Determination of  $G$  at  $\gamma_1 = \gamma_3$  for bread flours: sample f6, 40–45% mc, alveograph 6 min, measured at 23.8°C (○); sample f6, 40% mc, farinograph 6 min, measured at 8.5–22.1°C (◊); sample f6, 43.2% mc, farinograph 6 min, measured at 8.5–21.3°C (◐); sample f6, 42% mc, 3–60 min in the farinograph, measured at 21.5°C (◑); sample f6, 42% mc, farinograph 60 min, measured at 9.8–21.5°C (◒); sample f6, 40% mc, farinograph 6 min, measured at 23.8°C with and without (1) 0.15% sodium sulfite (●); sample f8, 43.2% mc, alveograph 6 min, measured at 24.8°C with and without (2) 1.6% urea (●). The straight line corresponds to the results of Fig. 8 (strong flours f4 and f5).

in the farinograph bowl. The effect of two chemicals was also examined: urea (1.6%, flour basis) and sodium sulfite (0.15%, flour basis), rupturing agents of hydrogen and disulfide bonds, respectively. Urea and, even more efficiently, sodium sulfite decrease dough viscosity (Launay and Buré 1973) but they don't appear to modify  $G$  (Fig. 11).

The line drawn on Figure 11 is the one corresponding to f4 and f5 at the same shear strain  $\gamma_3$  (Fig. 8); however, it fits the experimental points very well. As shown in Table II,  $G$  has the same value for both flour types; at least at  $\gamma = \gamma_3$ , doughs could not be distinguished by their elastic properties according to flour strength.

### Other Viscoelastic Models

If, following the arguments previously presented, linear viscoelastic models are discarded, there are not many alternatives that may be used to describe relaxation curves. A very simple empirical equation was proposed by Peleg (1980):

$$\sigma_0/(\sigma_0 - \sigma) = a + (kt)^{-1} \quad (10)$$

where  $k$  is a rate constant of the relaxation process. If, after a sufficiently long time ( $t \gg k^{-1}$ ), the stress relaxes to  $\sigma = 0$ , it follows immediately from equation 10 that  $a = 1$ . Therefore, a viscoelastic liquid is characterized by  $a = 1$  and a viscoelastic solid by  $a > 1$  with the asymptotic value of the stress given by  $\sigma_{lim} = (1 - a^{-1})\sigma_0$ . Figure 12 shows that the stress relaxation curves of wheat flour doughs may be linearized with equation 10. In Figure 5 it may be seen that the agreement between the experimental points and the curve fitted with equation 10 is very good and even better than with equation 7. However, Peleg's equation suffers from two drawbacks here. First, it is not possible to relate the rate constant  $k$  to dough rheological properties, as has been done for  $p^{-1}$  in equation 7. Secondly, the values calculated for the parameter  $a$  (1.16 and 1.30) correspond to those of a solid, with values of  $\sigma_{lim}$  equal to about two-thirds of the last experimental ones. These asymptotic values are undoubtedly overestimated; if a longer time scale were used, a lower asymptotic value (lower  $a$ ) and a smaller rate constant  $k$  would be obtained. In the case of solid foods, it has been shown that there is a close relationship between  $\sigma_{lim}$  and the last experimental value of the stress, indicating that  $\sigma_{lim}$  strongly depends on the time scale (Launay and Cantoni 1987). This is a serious weakness, even if Peleg's equation is very easy to apply and fits a large number of stress relaxation results. In the present case, the calculated asymptotic stresses were very high (1,200 Pa at 16.1°C and 2,300 Pa at 12°C, see Fig. 5) and they would not correspond to realistic estimates of a hypothetical yield stress. Even if a yield stress in dough is sometimes assumed, its value in shear is certainly several orders of magnitude lower than these results. For the

doughs tested by Bloksma (1962), the yield stresses could not exceed 14 Pa, and Hibberd and Parker (1979) have shown that viscous flow may be observed in creep down to 10 Pa. In contrast, the model we propose predicts stress relaxation without residual stress. With equation 7, the time necessary to reach 5% of the initial stress  $\sigma_0$  may be easily calculated. In the cases represented on Figure 5 it would take about 27 min at 16.1°C and more than 8 hr at 12°C to attain 440 and 495 Pa, respectively. Therefore, if a yield stress amounting to a few pascals really exists, it cannot be evaluated on the basis of these results and, in any case, the simplifying hypothesis  $\sigma_{lim} = 0$  is justified in practice.

Bohlin and Carlson (1981) proposed an analysis of stress relaxation of wheat flour dough and gluten based on a theory of flow as a cooperative process. They obtain the following rate equation:

$$\dot{\sigma} = -\sigma(\sigma/\sigma_0 + \epsilon)^z/\tau \quad (11)$$

where  $\tau$  is a relaxation time,  $z$  is the coordination number of flow units and  $\epsilon$  is a measure of the strength of the cooperation. Because  $\epsilon$  is very small ( $\epsilon < 7 \times 10^{-3}$ ), it follows immediately that integrating equation 11 leads to a result identical to equation 7, where

$$z = n + 1,$$

$$\text{and } \tau = K^n G^{-1} \sigma_0^{1-n} = (n-1)/p = (n-1)t_{1/2}/(2^{n-1} - 1).$$

Using this interpretation, our results would imply a variation range for  $z$  (Fig. 7), instead of a constant value ( $z = 4.2 \pm 0.2$ ), as proposed by the authors. In addition, they give no information on  $\tau$ , which, at constant  $z$ , is proportional to  $t_{1/2}$  and should consequently depend much on dough characteristics (Launay and Buré 1974a). At longer times, for  $\sigma \approx 0.25 \sigma_0$ , Bohlin and Carlson (1981) observed a second relaxation process characterized by a smaller value of  $z$  ( $2.2 \pm 0.2$ ). As we did not obtain, in most cases, relaxation curves beyond  $\sigma \approx 0.2 \sigma_0$ , we cannot discard this long time process. Following our model, it would correspond to larger values of the power-law exponent  $\alpha$  ( $0.71 \leq \alpha \leq 1$ ), indicating that the flow behavior tends to become Newtonian. Taking into account the low maximum strain (0.4) and stress (400 Pa) levels used in the cited work, such a result is not unlikely. In conclusion, it seems that the results obtained by Bohlin and Carlson (1981) could be fruitfully reexamined along the lines of our model.

## DISCUSSION

The Lethersich model with  $\eta_K \ll \eta$  (Fig. 1) may be used to describe shear stress relaxation in wheat flour dough, the nonlinear

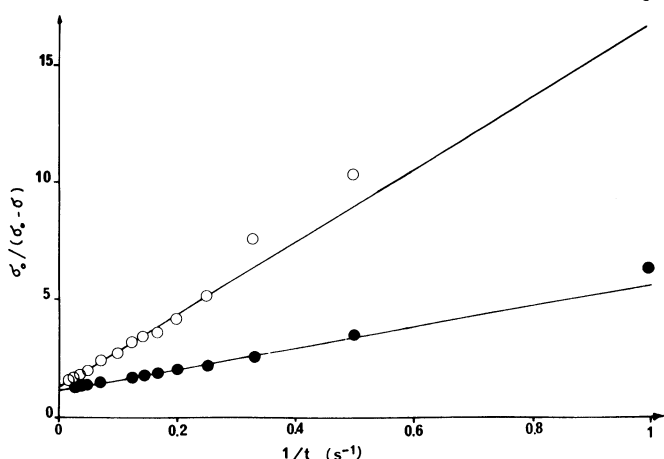


Fig. 12. Shear stress relaxation following Peleg's equation in linearized form (eq. 10). Experimental conditions as in Fig. 3.

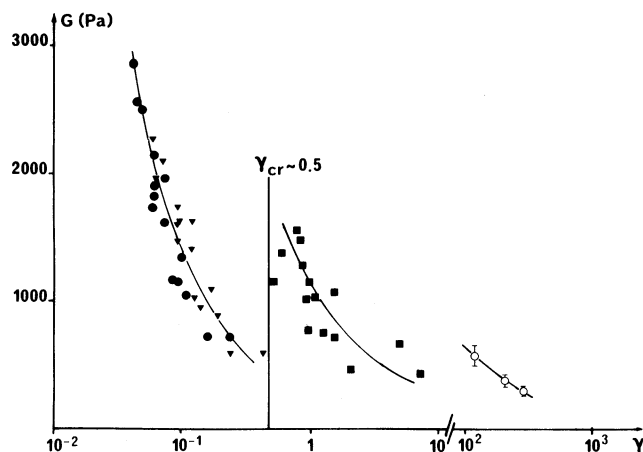


Fig. 13. Shear modulus  $G$  versus deformation. Comparison of the results of this work ( $\circ$ , 5% confidence intervals) with those calculated (eq. 12) from the method of Bloksma and Meppelink (1973) at three creep times: 18 sec ( $\bullet$ ), 60 sec ( $\blacktriangledown$ ), and 900 sec ( $\blacksquare$ ).

behavior being entirely attributed to viscous properties. However, Jeffrey's model (nonlinear), consisting of a Maxwell unit in parallel with a dashpot  $\eta_k$ , will give exactly the same result if  $\eta_k \ll \eta$ . We have seen that the elastic modulus  $G$  does not depend significantly on flour strength, dough water content, temperature, and at least as a first approximation, on mixing time (Launay and Buré 1974b). Also, the addition of sodium sulfite and urea does not seem to bring any change in  $G$ . However, beyond 45–50°C,  $G$  appears to increase. As the importance of hydrophobic interactions in the development of dough rheological properties is now well established, it may be assumed that these interactions, which are reinforced by an increase in temperature, play a key role in dough elasticity. In this regard, it would be interesting to study the effect of anions of the Hofmeister series on the value of  $G$ , as has been done by Kinsella and Hale (1984) for farinograph consistencies. In summary, all the factors examined in this work act on rheological properties of dough essentially through their effect on its viscosity, except shear strain and temperature beyond a critical value.

Published values of  $G$  are of the same order of magnitude as those deduced from our model; Bloksma (1972) gave a range of 500–7,000 Pa for  $G$ , and Smith and Tschoegl (1970) found  $E (= 3G) = 3,700$  Pa in the linear elastic domain. We have also shown that  $G$  decreases when the shear strain  $\gamma$  increases (Tables I and II), and this result deserves further discussion. Bloksma and Meppelink (1973) published the creep and recovery properties of dough samples made with a number of pure wheat varieties and kneaded for 5 min in a GRL mixer at a water content giving a farinograph consistency of 500 BU. On the basis of the model in Figure 2,  $G$  may be calculated from the value of the elastic deformation  $\gamma_{el}$ :

$$G = (\sigma - \sigma_k) / \gamma_{el} \approx \sigma / \gamma_{el} \quad (12)$$

if the stress  $\sigma_k$  in the dashpot  $\eta_k$  is neglected, as has been assumed previously ( $\eta_k \dot{\gamma}_{el} \ll G\gamma_{el}$ , eq. 3 and 4). Using equation 12 and creep data after 18, 60, and 900 sec, the corresponding elastic moduli were calculated with the results given by Bloksma and Meppelink (1973) in tabulated form. They are represented on Figure 13 as a function of the total shear strain  $\gamma$ . It appears that  $G$  does not vary much from one dough sample to another at a given value of  $\gamma$ , but here too  $G$  decreases when  $\gamma$  increases. The values of  $G$  obtained at the same shear strain  $\gamma$  after 18 or 60 sec creep time are not different; this indicates that the previous approximation (eq. 12), which assumes steady state flow behavior, is verified. On the other hand, there is a gap in this curve implying a sharp increase of  $G$  at  $\gamma_{cr} \approx 0.5$ . This gap is related to the occurrence of an inflection point on the creep curve that has been observed on several occasions by Bloksma (1962) at about  $\gamma = 0.5$  and which has been confirmed in our laboratory (*unpublished results*). A similar gap could also exist between  $\gamma \approx 10$  and  $\gamma \approx 100$ , but we don't have any experimental results in this range. Our values of  $G$  seem to be consistent with those deduced from the work of Bloksma and Meppelink (1973), although they have been obtained with two independent methods and at very different shear strains. It may be assumed that during a viscosity measurement or during a creep test, there is a progressive disruption of a shear-sensitive elastic network. Following disruption, a new elastic network could be called into

play at a critical shear strain  $\gamma = 0.5$ . It is possible that similar phenomena take place during dough mechanical treatments. The model developed in this work could help to clarify the relationships between parameters playing a key role in baking technology and viscoelastic properties of dough which, though generally considered to be essential, are most often unquantified.

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