Rheol Acta 34:622–625 (1995)

SHORT COMMUNICATION

Sophie Berland
Bernard Launay

Shear softening and thixotropic properties of wheat flour doughs in dynamic testing at high shear strain

Received: 24 January 1995
Accepted: 22 September 1995

S. Berland · Prof. B. Launay (✉)
Laboratoire de Biophysique
du Département Sciences de l'Aliment
Ecole Nationale Supérieure
des Industries Alimentaires
1, avenue des Olympiades
91305 Massy, France

Abstract Shear softening and thixotropic properties of wheat flour doughs are demonstrated in dynamic testing with a constant stress rheometer. This behaviour appears beyond the strictly linear domain (strain amplitude $\gamma_0 \geq 0.2\%$), G', G'' and $|\eta^*|$ decreasing with γ_0, the strain response to a sine stress wave yet retaining a sinusoidal shape. It is also shown that G' recovers progressively in function of rest time. In this domain, as well as in the strictly linear domain, the Cox-Merz rule did not apply but $\eta(\dot{\gamma})$ and $|\eta^*(\omega)|$ may be superimposed by using a shift factor, its value decreasing in the former domain when γ_0 increases. Beyond a strain amplitude of about 10–20%, the strain response is progressively distorted and the shear softening effects become irreversible following rest.

Key words Wheat flour dough – dynamic properties – power law – linear range – Cox-Merz rule – shear softening – thixotropy

Introduction

The methods used for the rheological characterization of wheat flour doughs have been under constant development during the last few decades. Their main purpose is to evaluate the baking value of flours for bread and biscuit making and to assess the rheological effects of formulation and processing parameters: water content, improver addition, mixing intensity, dough temperature, by example. Most often, empirical instruments specifically designed to test wheat flour doughs are used, as the Farinograph (ICC Standard No. 115/1, 1972) (a recording dough mixer), the Extensigraph (ICC Standard No. 114/1, 1972) or the Alveograph (ICC Standard No. 121, 1973; Faridi et al., 1987), the last two instruments inducing uniaxial or biaxial extension, respectively. The results, even if limited to empirical correlations with flour quality, provided a great deal of practical information. However, it is generally accepted that the fundamental rheological properties of wheat flour doughs are essential to understand dough handling behaviour during processing.

Dynamic testing methods are now in current use for evaluating viscoelastic properties of foods, including doughs. The problem of linearity of the behaviour of wheat flour doughs has been discussed by several authors. In a pioneering work, Hibberd and Wallace (1966) found at very low strains, below 0.1%, approximately linear properties, the measured values of the moduli becoming almost independent of the strain amplitude. At higher strains, non-linearity, corresponding to strain softening effects, was pronounced. In further studies, Hibberd and Parker (1975a, 1975b) found that the viscoelastic behaviour was not rigorously linear, even at the smallest reachable strain. However, at low strain amplitudes (<0.22%), the errors introduced by applying the linear theory were found negligible in comparison with the experimental uncertainties. Later, Navickis et al. (1982) concluded that nonlinear effects may well exist even at the smallest strain amplitude that could be achieved (≈0.25%). In more recent works, it was admitted that the behaviour is linear unto strain amplitudes of about 0.2% (Dus and Kokini, 1990), about 0.25% (Weipert, 1990) or about 0.5% (Amemiya and Menjivar, 1992). Lindhal and

Eliasson (1992) have claimed that the behaviour is linear with a fairly good approximation at a strain amplitude lower than 0.8%, and when the magnitude of the strain steps is below 0.05%. It is likely that the critical strain amplitude may vary from one dough to another, and depends in particular on water content. Frequency sweep tests have been performed by several authors, in the linear domain, or at low strain amplitude: G' and G'' follow power laws, with $G'>G''$ and a rather low dependence of G' and G'' on frequency is observed (Hibberd, 1970b; Smith et al., 1970; Amemiya and Menjivar, 1992).

The first aim of this work is to discuss the effects of strain amplitude on the dynamic properties of wheat flour dough.

Experimental

Dough preparation

Baking wheat flour (see Table 1) was kindly supplied by Grands Moulins de Paris (France). Doughs were composed with flour, water (46.2%, total weight dough basis) and sodium chloride (2.2%, total weight flour basis). They were mixed at 25 °C and 60 rpm during 6 min in the small bowl (50 g) of the Brabender Farinograph. At the end of mixing, "consistency" (mixing torque) was equal to 450 Brabender units (1 B.U. = 100 g·cm). Before testing, doughs were stored 1 h in a closed chamber at room temperature, to allow stresses developed during mixing to relax.

Rheological measurements

A controlled stress rheometer Carrimed CSL 100 and a cone-and-plate geometry (truncated cone 4°, 40 mm diameter) were used for flow and dynamic tests. The temperature was 25 °C in all measurements. A dough sample (≈1.5 g) was deposited on the plate and rested 5 min between cone and plate before the stress was applied. It is necessary to prevent the dough from drying during the test: therefore, we used a solvent-trap filled with water, and a lid over the cone for creating a chamber saturated by steam. In practice, during dynamic tests, the maximum stress applied (σ_0) was fixed by the computer in order that the strain amplitude (γ_0) did not go beyond a target value at ±3%.

Viscoelastic properties

Analysis of the output signal: definition of the range where the computation of G' and G'' is valid.

With a controlled Stress rheometer, the sample is submitted to a sinusoidally varying applied torque and the resulting displacement is measured. To get proper results from the computer data analysis, it has to be assumed that the sample behaves as a linear viscoelastic material. Therefore, a sinusoidal stress versus time input shall produce a sinusoidal strain versus time output.

The stress input is:

$$\sigma = \sigma_0 \cos \omega t \ , \qquad (1)$$

where σ_0 is the stress amplitude within each cycle and ω the angular frequency. In the linear domain the corresponding strain output is:

$$\gamma = \gamma_0 \cos(\omega t - \delta) \qquad (2)$$

For a strictly linear viscoelastic behavior σ_0 and γ_0 are proportional to each other and the frequency $\omega/2\pi$ is the same: therefore, G', G'' and $|\eta^*|$ are independent of γ_0. We have examined the shape of the output signal, according to the maximum strain applied, from 0.2 to 30%. A sinusoidal function was fitted to the experimental points, its parameters (amplitude, phase lag, frequency) being calculated according to the Simplex method. The residual function (difference between experimental and fitted points) was calculated, and the quality of fitting was estimated with two criteria: the sum of squares of the resid-

Table 1 Main characteristics of the flour

Composition	Brabender Farinograph	Chopin Alveograph[b]
Water (%): 15.2 Ash (% dry matter): 0.6 Titratable acidity (% dry matter): 0.04	Hydration (%)[a]: 46.2	P (mm): 97 P/L: 1.5 G ($cm^{3/2}$): 18.1 W (10^{-4} J/g): 223

[a] % water (total weight basis) corresponding to a maximum dough consistency equal to 500 BU (ICC Standard, No. 115/1, 1972)
[b] Dough water content 43.2% (total weight basis) (Faridi et al., 1987)

Rheologica Acta, Vol. 34, No. 6 (1995)

Table 2 Quality of the fitting of a sinusoidal function to the experimental values of $\gamma(t)$

Strain (%)	Sum of squares of the residual function	Number of sign changes in the residual function	Frequency of the fitted function ($rad \cdot s^{-1}$)[a]
0.2	0.034	17	6.3
1	0.017	14	6.4
10	0.014	16	6.3
20	0.064	6	6.4
30	0.095	6	6.4

[a] Frequency of the stress input: 6.3 rad/s

ual function, and the number of sign changes of the residues (Table 2).

When the strain amplitude is equal to 1 or 10%, the fitting of experimental points to a sinusoidal curve is good (see Fig. 1A). In this case, the sum of squares is minimum, while the number of sign changes is high, which indicates that the calculated curve does not systematically deviate from the experimental points. When the applied strain is smaller (0.2%), the sum of squares increases. In this case, the response signal is more scattered because the limit of resolution of the strain optical encoder is approached (around 0.014% with the geometry used), but the number of sign changes in the residual function is approximately the same: therefore, the response signal can also be considered as sinusoidal. When the strain is higher (20% and 30%), the sum of squares increases strongly, while the number of sign changes in the residual function decreases, which indicates systematic deviations from a sinusoidal function, especially in the second half of the signal, and around its maximum and minimum values, which are flattened (see Fig. 1B).

Therefore, up to a strain of at least 10%, the behaviour can be considered to be linear in a wide sense since the output signal is sinusoidal; in this range, the computer treatment used to calculate G' and G'' is valid. At 20% strain amplitude and beyond, the output signal is distorted and the computation of G' and G'' is no more strictly valid. This change probably occurs gradually, and we have not determined a critical strain where the response becomes non-linear, but clear-cut differences are manifest between 10% and 20% strain amplitudes.

Effects of strain amplitude

Strain sweep tests were carried out at a fixed frequency ($2\pi \, rad \cdot s^{-1}$ in this case), to determine if there is a domain where G^* does not vary with strain. The limit of resolution γ_1 is about 0.014%, and we consider that the

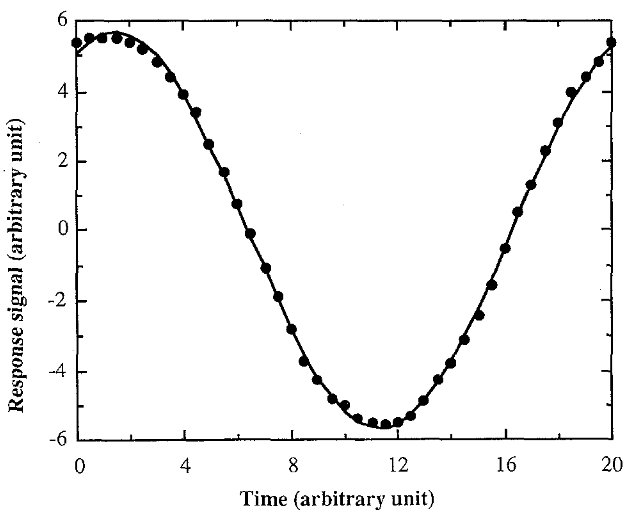

Fig. 1A Fitting of a sinusoidal curve (continuous line) to the experimental points (●). The strain amplitude corresponding to the applied stress is 1% (frequency: $2\pi \, rad \cdot s^{-1}$)

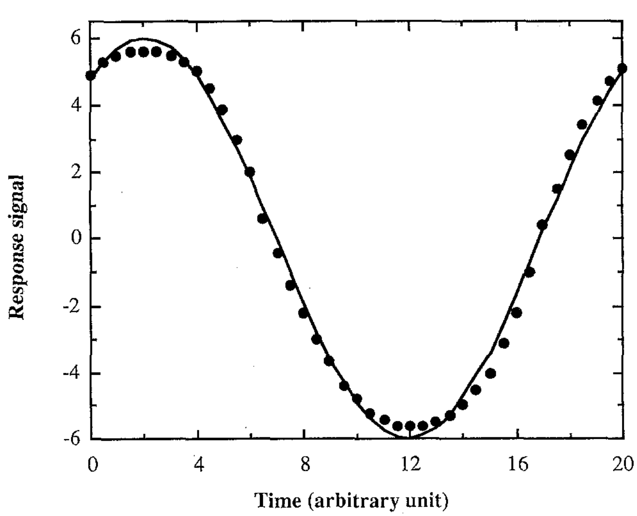

Fig. 1B Fitting of a sinusoidal curve (continuous line) to the experimental points (●). The strain amplitude corresponding to the applied stress is 30% (frequency: $2\pi \, rad \cdot s^{-1}$)

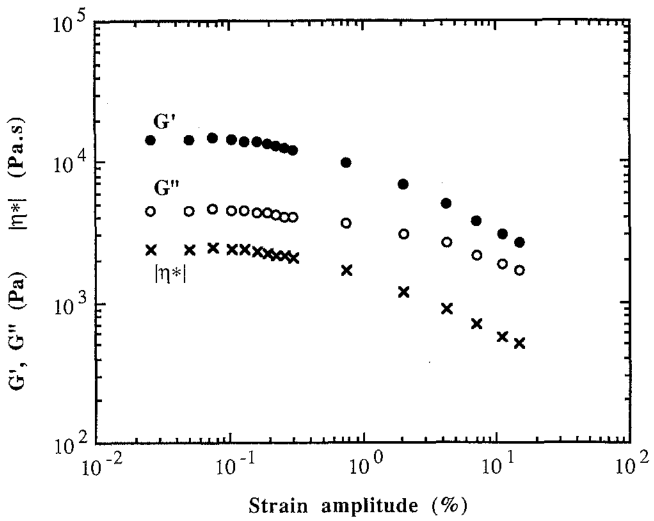

Fig. 2A Strain sweep tests. The values of G' (●), G'' (○) or $|\eta^*|$ (×) are obtained at 2π rad·s^{-1} as a function of increasing strain amplitudes

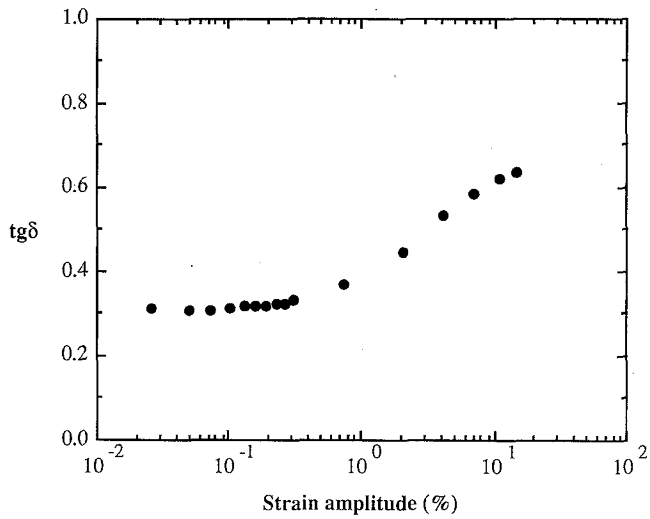

Fig. 2B Strain sweep tests. The values of tgδ (●) are obtained at 2π rad·s^{-1} as a function of increasing strain amplitudes

response signal is still significant until a strain amplitude of $10 \cdot \gamma_1$. However, some exploratory measurements have been done at smaller strain amplitudes (<0.14%). Such measurements are questionable, but we have obtained a very good reproducibility in the range 0.03–0.14% and the corresponding results were in agreement with the values obtained at higher strains.

Figures 2A and B show that wheat flour dough exhibits a quasi-linear behavior for strains up to about 0.2%: the change in rheological parameters is very small when the strain varies between 0.05 and 0.2% (less than 7.5% for G' and $|\eta^*|$, and less than 5% for G'' and tgδ). Beyond 0.2%, G', G'' and $|\eta^*|$ decrease and tgδ increases with strain amplitude, indicating a non-linear behavior. However, up to a strain of at least 10%, the computation of G' and G'' is still valid, and the results indicate that dough presents shear-softening properties in this domain. The same conclusion has been drawn for the value of the elastic modulus G determined from stress relaxation curves (Launay, 1990).

Thixotropic properties

In the strictly linear range, the rheological properties are not modified by the test itself. However, it may not be the case out of this range, and if there are changes in dough structure, they may be reversible or not. Therefore, we made successive measurements of G^* at a frequency of 2π rad·s^{-1} on the same sample. The first test was done at low strain amplitude ($\gamma_0 = 0.2\%$): dough structure is unaffected, and G'_0 and G''_0 are the moduli corresponding to this reference test. Dough was then submitted to a test at an higher strain (1.3 to 21.4%). Further measurements at $\gamma_0 = 0.2\%$ permit to evaluate, in non-destructive conditions and in function of rest time, the effect of the "high" strain previously applied. The moduli obtained under these conditions are called $G'(t)$ and $G''(t)$, $t = 0$ corresponding to a measurement just started after having completed the "high" strain test.

The results (Fig. 3) show that the effect of strain was "immediately" reversible, when the strain amplitude is 1.3% or less. Shear softening seems to be reversible within less than 1 min, for a strain amplitude equal to or lower

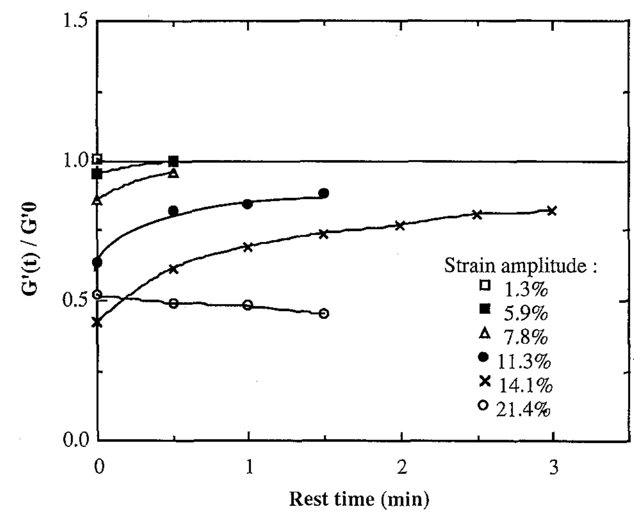

Fig. 3 Thixotropic properties of wheat flour doughs. Dependence of G' measured in the linear domain on the strain amplitude of a previous test and on recovery time (2π rad·s^{-1})

than 7.8%. It is, at least partially, reversible when the strain amplitude is between 11.3 and 14.1%, but it seems to be completely irreversible for $\gamma_0 = 21.4\%$ where, moreover, G' decreases during recovery. This effect may be due to a "spontaneous" change in dough properties during rest, maybe triggered by unrelaxed internal stresses, but it can also be postulated that, following a high shear test (21.4%), the low strain amplitude measurements (0.2%) are no longer non-destructive.

It is worthwhile to mention that the limit values of strain corresponding to a sinusoidal output (10–20%) and to a recoverable change in the viscoelastic properties (14–21%) are close, or may be identical, to each other.

Interrelation between viscoelastic and flow properties

Extended Cox-Merz rule

The flow properties of doughs are also of great relevance for practical applications, and have been studied by several groups. In some instances, flow and viscoelastic properties may be connected. The Cox-Merz rule is the simplest relationship between these properties (Cox and Merz, 1958): log η versus log $\dot\gamma$ and log $|\eta^*|$ versus log ω superimpose for $\dot\gamma = \omega$. It may apply to synthetic polymer or biopolymer solutions as well as to melts.

The Cox-Merz rule was tested in our study. On one hand, frequency sweep tests were performed from 0.2 to 20π rad·s^{-1}, at a strain amplitude of 0.2%. On the other hand, we have carried out creep tests at several stress levels (40–190 Pa), during 4 min, a duration sufficient to attain a permanent flow régime and to calculate the corresponding shear rates and viscosities. Thus, the stress was gradually increased, and a flow curve could be obtained. The flow of wheat flour doughs follows a power law, at least for shear rates varying between 10^{-4} and $6 \cdot 10^{-2}$ s^{-1}, and it is also the case for $|\eta^*|$ (Berland and Launay, 1995).

Results on Fig. 4 show that the Cox-Merz rule did not apply. On the contrary, Dus and Kokini (1990) have claimed that wheat flour doughs obeyed this rule: $\eta(\dot\gamma)$ and $|\eta^*(\omega)|$ were said to converge at high shear rates but the agreement was considered to be unsatisfactory at shear rates or frequencies less than 10 s^{-1}. Despite the fact that, in our results, $\eta(\dot\gamma)$ and $|\eta^*(\omega)|$ do not overlap, both power laws have practically the same slope as shown on Fig. 4 and, therefore, it is unlikely to get a converging value, even in the high shear rate range. However, it is possible to superimpose these straight lines, using on the x-axis a shift factor "a".

$$\eta = K\dot\gamma^{1-n} \tag{3}$$

$$|\eta^*| = K^*\omega^{1-n^*} \tag{4}$$

$n \approx n^*$, and the shift factor is calculated as:

$$a = \frac{\log K - \log K^*}{1-N}\ , \quad \text{with} \quad N = \frac{n+n^*}{2} \tag{5}$$

An "extended" Cox-Merz rule may be used, as shown on Fig. 5:

$$|\eta^*|(\omega) = \eta(\dot\gamma)\ , \quad \text{with} \quad \omega = 10^a \cdot \dot\gamma \tag{6}$$

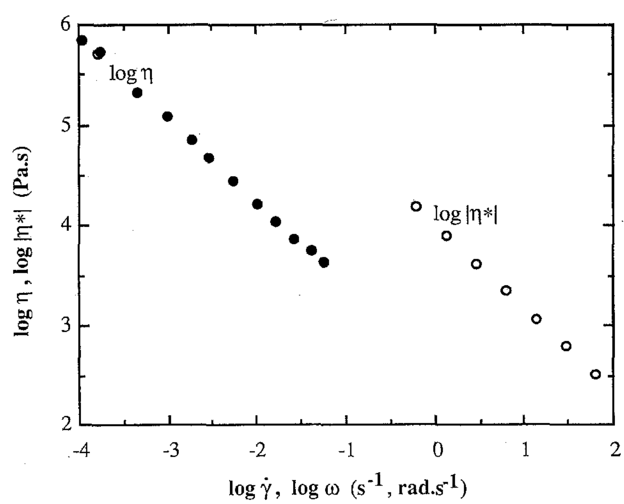

Fig. 4 Test of the Cox-Merz rule: (●) steady state viscosity, (○) modulus of the complex viscosity (strain amplitude: 0.2%)

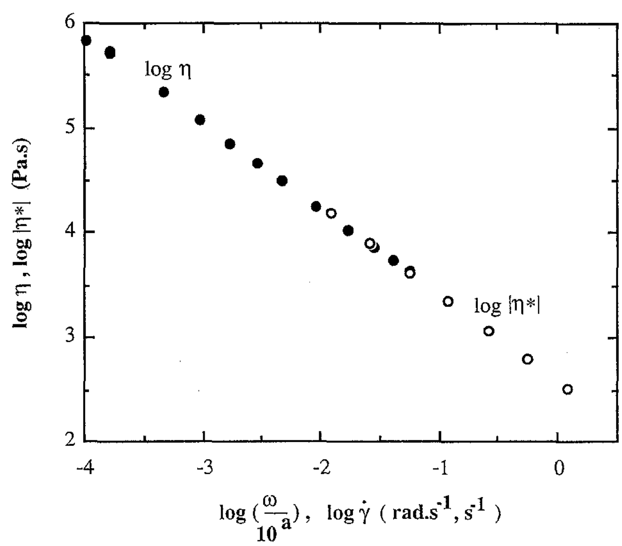

Fig. 5 Results obtained with the extended Cox-Merz rule. *a:* shift factor; (●) steady state viscosity, (○) modulus of the complex viscosity (strain amplitude: 0.2%)

Relationship between the shift factor "a" and strain amplitude γ_0

Frequency sweep tests were realized for strain amplitudes varying between 0.15% and 25%. In all cases, G', G'' and $|\eta^*|$ follow power laws. We have found that the corresponding exponents, in particular n^* (Eq. 4), were practically independent of strain amplitude in the shear-softening domain, allowing the value of the shift factor, as defined by Eq. (5), to be calculated. Figure 6 shows the relationship between the shift factor a and the strain amplitude γ_0: three domains may be observed. The first one (I) is the strictly linear domain where, obviously, the shift factor is constant. In the second one (II), the shift factor decreases with strain amplitude according to a linear relationship in semi-log scales. This is in qualitative agreement with a theoretical model developed by Doraiswamy et al. (1991) for concentrated suspensions and other materials with a yield stress. They have predicted that the Cox-Merz rule may be extended by using an "effective shear rate", simply defined by:

$$\dot{\gamma} = \gamma_0 \cdot \omega \tag{7}$$

According to the results of Fig. 6, the following equation applies in our case:

$$\dot{\gamma} = 0.024 \cdot \left[\frac{\gamma_0}{\gamma_c}\right]^{0.47} \cdot \omega \ , \tag{8}$$

where γ_c ($\approx 0.27\%$) is a critical strain corresponding to the outset of the shear-softening domain (see Fig. 6). By extrapolation, Eq. (8) shows that a strain amplitude γ_0 of about 750% should be applied to get $a = 0$, emphasizing that considerable shear softening has to occur before a steady flow régime may be attained. In fact, this value of γ_0 is overestimated: from $\gamma_0 \approx 10\%$, a third domain (III) is reached where Eq. (8) is no longer valid.

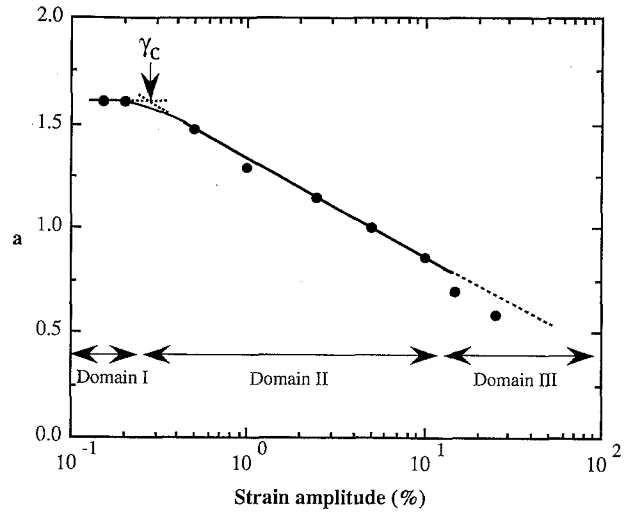

Fig. 6 Dependence of "a" on strain amplitude

Discussion

This work confirms that, in practice, it is possible to carry out measurements on wheat flour doughs at strain amplitudes lower than a critical value ($\approx 0.2\%$) to get strictly linear viscoelastic properties (domain I). In this domain, the Cox-Merz rule did not apply: a large shift factor has to be used to superimpose $|\eta^*|(\omega)$ and $\eta(\dot{\gamma})$. Beyond the critical strain, domain II is entered. As seen from the response to a sinusoidal stress input, the behaviour is still linear in the wide sense, but G', G'', $|\eta^*|$ and, accordingly, the shift factor, decrease with the strain amplitude. In addition, dough tends to quickly recover its pre-sheared properties during a rest period, the higher γ_0, the longer the time required. Therefore, dough exhibits strain softening and thixotropic properties in domain II. At values of γ_0 higher than about 10%, G', G'' and $|\eta^*|$ become more strain-sensitive but, as γ_0 increases, the resulting signal is distorted and the strain softening effects become progressively irreversible. In this domain, it may be hypothesized that some ruptures have occurred in the protein fibrils constituting the elastic network in doughs. The reversible changes observed in domain II could be more likely attributed to starch-protein interactions (Hibberd and Parker, 1975 a), starch granules acting as a filler dispersed in the insoluble protein matrix. It is well known that mechanical treatments and rest periods play a decisive role in wheat flour dough properties during its processing: the methods presented in this work could be useful to study strain softening and recovery effects that are implied in such treatments.

Rheologica Acta, Vol. 34, No. 6 (1995)

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