zwischen der Kurvenform der Strömung plastischer disperser Systeme und der Kurve der Strömung besteht, die beim Strömen der Polymerschmelzen während des Übergangs von innerer zur äußeren Reibung erhalten wird.

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Dynamic Viscoelastic Behaviour of Wheat Flour Doughs

Part 1: Linear Aspects

By G. E. Hibberd and W. J. Wallace

With 6 figures in 11 details

(Received April 1, 1966)

Introduction

The underlying processes involved in modern baking techniques such as high speed mixing, mechanical dough development, continuous processes etc., and the reaction mechanism of chemical improvers can only be fully determined from a detailed knowledge of the rheological phenomena involved and from a thorough understanding of the viscoelastic behaviour of wheat flour dough in terms of its physical and chemical structure.

For the macroscopic rheological phenomena to be described at the molecular level the strains imposed must be of an appropriate order of magnitude. Hitherto only the gross macroscopic behaviour of dough has been studied and interpretation in terms of the molecular architecture is extremely difficult. Moreover, the majority of instruments that have been employed are empirical in principle and usually measure a complex interaction of several factors. Ill-defined sample geometry and loading patterns and the fact that the test procedures significantly change the material properties have rendered the results obtained incapable of interpretation in basic physical terms.

For a complete description of the rheological behaviour of a viscoelastic substance, a study must cover a wide time scale. In principle, this information may be obtained from static measurements such as creep and stress relaxation or from dynamic measurements. In dough rheology the static approach has been used almost exclusively (2–5, 7, 8, 11, 13–16). These techniques are important for studying effects at times greater than about five seconds but at shorter times their value is limited by inertial effects and by instrument response. To cover this latter time scale, dynamic methods are preferable (5).

In this study, the dynamic mechanical properties of wheat flour doughs have been determined for a wide range of flours milled from known wheat varieties. It is believed that from this approach further insight into the rheological behaviour of wheat flour dough will be gained, leading to a better understanding of the performance of a dough under the transient stresses imposed during the various processes encountered in the modern commercial bakery.

Experimental

The rheometer used to measure the dynamic mechanical properties of wheat flour doughs has been described in a previous paper (10). In this instrument, a sample is sinusoidally sheared in the axial direction in the annular spacing between two concentric cylinders. The components of the complex shear modulus ($G^* = G' + i\,G''$) are obtained by following the applied force and resultant displacement of the inner cylinder as functions of time.

To adequately cover the range of material properties exhibited by wheat flour doughs, a cell system with inner cylinder of radius 0.505 cm., outer cylinder of radius 0.864 cm. and length 14.1 cm. was used. For this system, calculations indicated that there was no significant distortion, due to inertia, of the displacement field in the annulus for the range of frequencies examined (9).

This instrument satisfies the basic rheological requirements and avoids the pitfalls associated with previously used methods. Constant sample geometry is maintained so that, for all equivalent points in the material stress and strain are homogeneous and, for the small strains involved, the deformation approximates pure shear. In view of the consistency of dough complicated end effects are avoided by having the cell system open at both ends. The exposure of only a small surface area limits skin formation due to evaporation and facilitates temperature control.

Doughs were prepared to a stage of optimum development in a 50 g. Farinograph bowl at 25 °C using laboratory milled flours obtained from a number of Australian wheat varieties of widely differing characteristics. After loading the rheometer, doughs were allowed to rest for three hours before measurements were taken (10).

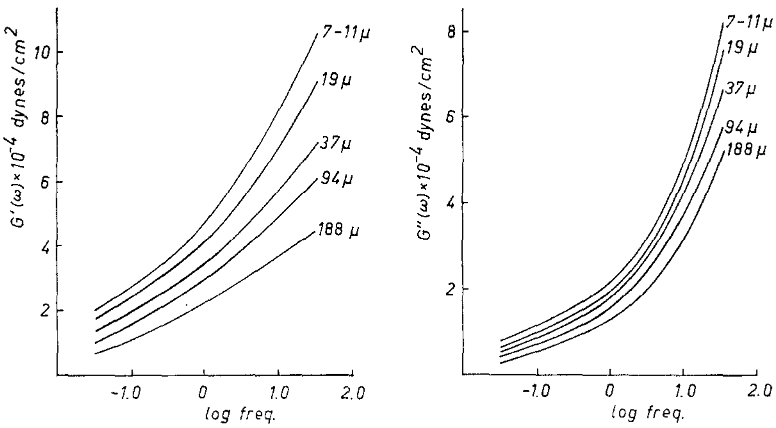

Fig. 1. Variation of dynamic stress relaxation moduli, $G'(\omega)$ and $G''(\omega)$, with frequency for various p. p. displacements of inner rod

Results and Discussion

The aim of this paper is to present rheological behaviour of wheat flour doughs in general, therefore results are presented for only one of the wheat varieties examined. The variety chosen is Mendos which is a hard wheat of good strength and baking quality.

a) Effect of strain on the dynamic moduli

In the majority of studies on dough rheology, linear viscoelastic theory has been assumed (2, 4, 5, 7, 8, 11, 13–17). In all cases this assumption is of doubtful validity in view of the magnitude of the strains involved and no attempt has been made to establish the range of deformation over which dough exhibits linear viscoelastic behaviour. To this end, the dynamic mechanical properties of wheat flour doughs were determined for peak-to-peak (p. p.) displacements of the inner rod ranging from 7 to 188 μ. From the results shown in fig. 1, it is apparent that the behaviour is linear only for displacements less than about 12 μ p. p. which corresponds to a maximum strain of 4.4×10^{-3} at the rod. For higher displacements pronounced non-linearity as a result of strain softening is evident.

A plausible explanation of the strain softening at larger strains may be obtained by considering the chain segments formed by the interaction of the protein chains with adjacent starch granules. There will be a distribution of the lengths of chain segments so that some of these chains will be highly elongated, while others will be very loosely coiled. This condition is illustrated in fig. 2. If the dough is now deformed in the X-direction, the starch granules will almost certainly separate in proportion to the overall deformation. Obviously, chain A must break away at a relatively small deformation. At low strains, below the breaking point, it and similar chains will hold a high proportion of the load and will give rise to a high modulus. At larger strains, however, these chains, having broken away, will not be holding any substantial load and consequently the modulus will be lower. On removal of this load, the dough will no longer possess the same high modulus at low strains although a partial recovery may be observed. These strain softening effects may also be interpreted by considering the chain segments to result from loose entanglement coupling of the bulky side chains of the protein molecules.

To illustrate these strain softening and recovery effects, doughs were studied over a period of time at constant frequency and the response to changes in the amplitude of the driving rod was observed (fig. 3). Continued operation at a peak-to-peak displacement of 7 μ induced no significant change after 20 minutes. This provides direct evidence that, while operating at this amplitude, no appreciable work is done on the dough and that the material properties of the sample are not influenced by the test procedure. However, an increase in the peak-to-peak amplitude to 188 μ resulted in an immediate softening effect which continued at a much slower rate until the amplitude was again returned to 7 μ p. p. An immediate partial recovery was then observed which was still incomplete after a further 60 minutes. The time dependence of the softening process may be interpreted in terms of a time dependent stress-biased diffusion process (1). The labile protein-starch interactions could be broken and, under the influence of the deforming stresses, the protein chains may alter their relative positions before interacting at new sites, thus giving a more equitable distribution of the load. A similar explanation could be given to account for the time dependent recovery process. The incomplete recovery after the first loading and the reversibility of subsequent loading and recovery cycles,

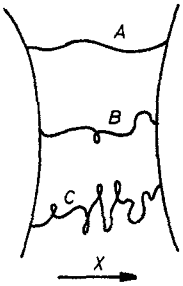

Fig. 2. Interaction of protein chains with starch granules – proposed explanation for strain softening effect

are consistent with the proposed mechanism involving a redistribution of chain segment lengths.

It should be noted that these rheological parameters have been calculated from equations that pertain only to the linear

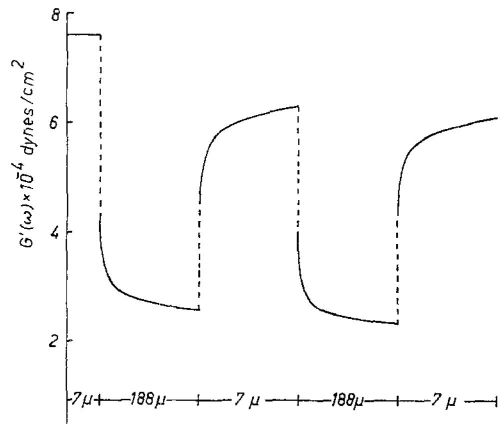

Fig. 3. Effect of strain softening on $G'(\omega)$ over a period of time

region. Any extension to larger displacements is invalid since $G'(\omega)$ and $G''(\omega)$ only have a physical meaning in the linear region[1]). These results clearly reveal the

[1]) However, there is experimental evidence to suggest that, over the range of these measurements, the stresses in the dough may still be characterized by $G'(\omega)$ and $G''(\omega)$ together with a non-linear function of strain which is independent of frequency.

inadequacy of linear theory to describe the behaviour observed with rheometers that impose larger strains on the sample.

b) Effect of temperature on the dynamic moduli

The influence of temperature on the linear dynamic properties are shown in figs. 4a and 4b for the range 5° to 30 °C. As found by *Shimizu* and *Ichiba* (17), both $G'(\omega)$ and $G''(\omega)$ decreased with increase in temperature. The applicability of the frequency-temperature superposition principle (6) was also established over this temperature range and with this principle, the dynamic moduli $G'(\omega)$ and $G''(\omega)$ were obtained over an extended frequency range of 0.018–160 Hz for a reference temperature of 30 °C (fig. 4c). The stress relaxation moduli derived from the composite curve obtained by temperature superposition are shown in figs. 5a and 5b.

These calculations demonstrate the suitability of dynamic methods for exploring the time scale region below about 5 seconds which is inaccessible to transient techniques. At the beginning of a transient stress relaxation test, measurements are unreliable, for the assumption of negligible inertia is certainly not valid and moreover it is not possible, for the same reason, to impose a sudden and homogeneous finite strain on a finite mass of material. Such concepts as 'instantaneous elasticity' (7, 8) should be approached with caution since it is difficult to separate instrumental artifact from true dough behaviour under these conditions.

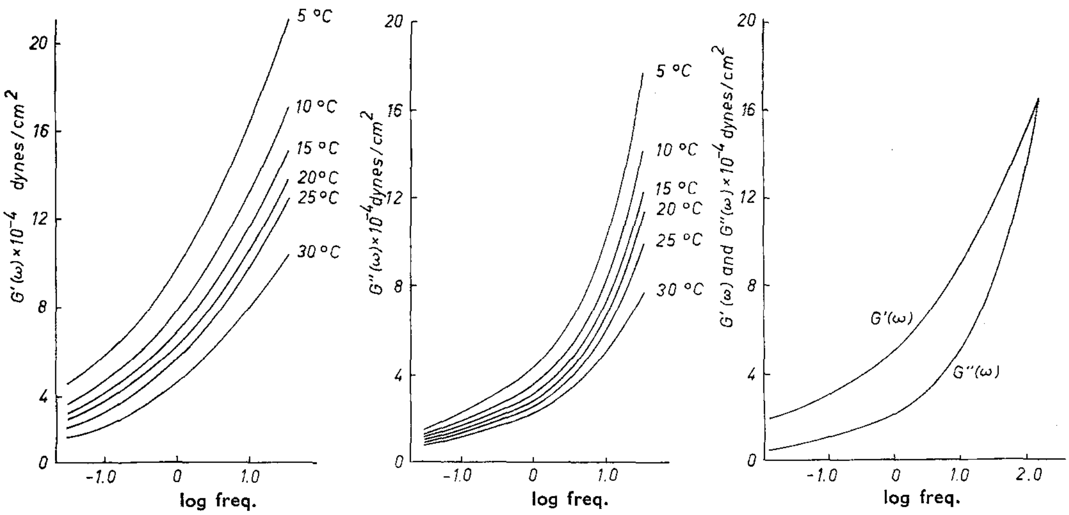

Fig. 4. a) and b) Temperature influence on dynamic stress relaxation moduli and (c), the extended frequency range obtained by temperature-frequency superposition principle

c) Transient stress relaxation modulus

From the dynamic data obtained for the linear region, the transient stress relaxation function $G(t)$ was calculated by the method of *Ninomiya* and *Ferry* (12) using the equation,

$$G(t) = G'(\omega) - 0.40\,G''(0.40\,\omega) + 0.014\,G''(10\omega)_{\omega=1/t}.$$

It was found that, for the range of frequencies examined, the last term on the right hand side could be neglected so that the stress relaxation function $G(t)$ could be calculated for times as short as 0.02 seconds from dynamic data for frequencies up to only 32 Hz.

The stress relaxation moduli derived from the dynamic moduli obtained at various temperatures in the range 5° to 30 °C and the stress relaxation modulus at 30 °C derived from the composite curve obtained by temperature superposition are shown in figs. 5a and 5b.

d) Effect of water absorption on the dynamic moduli

As expected, $G'(\omega)$ and $G''(\omega)$ decreased with increasing water absorption (figs. 6a and 6b). It appears that a water absorption-frequency superposition principle can also be applied to extend the frequency range, giving good agreement with the results obtained with temperature-frequency superposition. This principle would enable measurements on doughs from different types of flour to be referred to equivalent water absorptions. The parameter necessary to bring curves measured at different levels of water into co-incidence could very well prove to be a valuable parameter in the characterization of a given flour sample.

As demonstrated above, the relationship between applied strains and resultant stresses in the dough is linear for only very small strains. The classical linear theory of viscoelasticity should be used to describe the dough's behaviour only in this region and is inadequate for higher values of strain. The indications are however, that provided the strains are not too great, the non-linearity may be treated as a perturbation on the linear case and current work is proceeding according to this approach.

Acknowledgements

The authors wish to acknowledge that this research has been financed in part by a grant made by the United States Department of Agriculture, Agricultural Research Service. The authors also wish to thank Mr. *B. V. Lew* for experimental assistance.

Summary

The general dynamic mechanical properties of wheat flour doughs have been investigated for a range of strains over a frequency spectrum of 0.032–32 Hz. An approximately linear stress-strain relationship was found to hold at the lower range of strains imposed. Departures from the linear response of the dough are explained in terms of a protein chain-starch granule interaction and the accompanying time dependence in terms of a stress-biased diffusion process. The influence of water and temperature on the dynamic moduli are shown, indicating that a frequency-temperature and a water absorption-frequency superposition principle is applicable. The transient stress relaxation modulus is calculated from the dynamic moduli to demonstrate the ability of dynamic methods to investigate the time scale inaccessible to transient techniques.

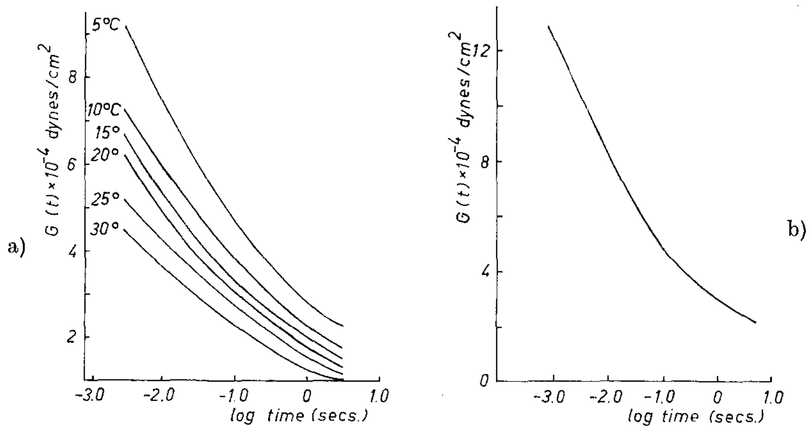

Fig. 5. a) Transient stress relaxation modulus, $G(t)$, for a temperature range 5–30 °C. and (b), the extended time range of $G(t)$ obtained by temperature superposition principle

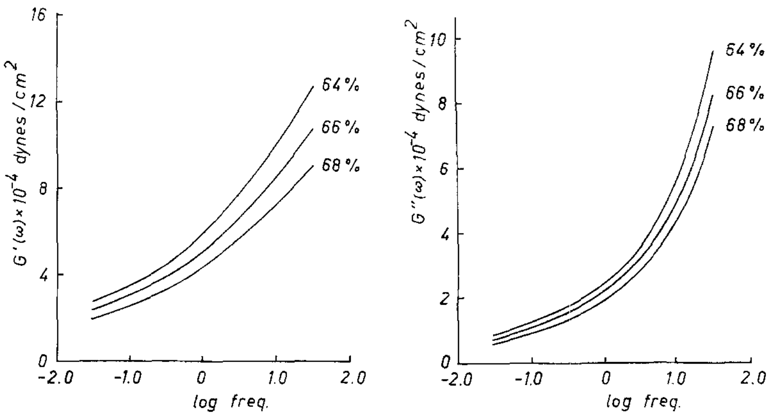

Fig. 6. Influence of water absorption on dynamic stress relaxation moduli

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Kriechen bei gleichzeitigem Schwinden des Zementsteins

Von Folker Wittmann

Mit 12 Abbildungen

(Eingegangen am 19. Februar 1966)

1. Einleitung

Im Zusammenhang mit dem Bau einer Talsperre machte *R. E. Davis* erstmals ausgedehnte Versuche, um das zeitabhängige Verhalten des Betons unter Last zu studieren (1). Obwohl in der Zwischenzeit eine große Zahl von Arbeiten zu diesem Problem erschienen ist, besteht bis heute keine Übereinstimmung darüber, was unter dem Begriff „Kriechen des Betons" genau zu verstehen ist (2, 3). Besonders kompliziert werden die Verhältnisse, wenn der Beton unter Last ausgetrocknet wird. Dann überlagern sich nämlich Kriechen und Schwinden.

Fast alle Autoren haben zur Ermittlung des Kriechens unter gleichzeitiger Austrocknung folgende Methode angewandt: An einer unbelasteten Probe, deren Wassergehalt definiert vermindert wird, mißt man das reine Schwinden als Funktion der Zeit (Abb. 1). Eine unter gleichen Bedingungen austrocknende Probe belastet man nun zusätzlich noch mit einer konstanten Last. Von der so gemessenen Gesamtverformung zieht man für alle Zeiten t die entsprechende Schwindverformung der unbelasteten Probe ab und erhält damit die gewünschte Kriechverformung (3). Diese Methode zur Bestimmung des Kriechens einer unter Last austrocknenden Probe ist nur dann brauchbar, wenn man annehmen darf, daß sich Schwinden und Kriechen gegenseitig nicht beeinflussen. Mehrere Autoren haben bereits darauf hingewiesen, daß eine Korrelation zwischen Schwinden und Kriechen wahrscheinlich ist (2, 4).

Auf Grund von Desorptions- und Adsorptionsmessungen kam *T. C. Powers* zu eigenen Vorstellungen über den Kriechmechanismus (5). Indem er die Eigenschaften der adsorbierten Wasserschichten mit Hilfe der Thermodynamik zu beschreiben versuchte, kam er zu dem Ergebnis, daß Schwinden und Kriechen nur zwei verschiedene Namen für mechanische Verformungen, die auf verschiedene Weise zustande gebracht werden, darstellen.

Im folgenden soll gezeigt werden, daß gleichzeitiges Kriechen und Schwinden dann quantitativ erklärt werden können, wenn man annimmt, daß sich die Schwindspannung und die außen angelegte Spannung additiv zur Gesamtspannung, die die Verformung verursacht, zusammensetzen. Die Verformung, die die Summe der beiden Spannungen hervorruft, soll im folgenden Kriechen genannt werden.

Im Beton ist hauptsächlich der Zementstein für die Kriecheigenschaften verantwortlich (2, 4). Die hier verwendeten Messungen wurden deshalb an reinem Zementstein durchgeführt. Sie sind in Form von Tabellen zusammengefaßt und an anderer Stelle veröffentlicht (6).

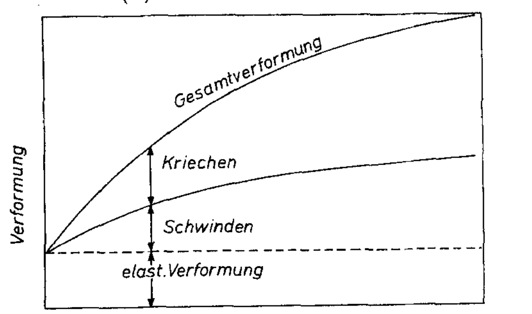

Abb. 1. Skizze zur herkömmlichen Ermittlung des Kriechens aus der Gesamtverformung bei gleichzeitigem Austrocknen