Characterization of Dynamic Viscoelastic Behavior of Wheat Flour Doughs at Different Moisture Contents

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ABSTRACT

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Three different flours were examined to study the influence of moisture content on the dynamic viscoelastic behavior of wheat flour dough. Doughs with moisture contents varying from 43 to 58% were submitted to dynamic testing using a mechanical spectrometer operating in frequency sweep mode, obtaining information about rheological response in the linear viscoelastic range. To characterize the influence of moisture content on the dynamic viscoelastic behavior of wheat flour dough, some hypotheses regarding the functional role of the water molecules were verified by applying reduction procedures of the rheological curves. By shifting the rheological curves along the vertical axis, it was possible to verify that varying the moisture content of the doughs not only changed dynamic properties but also modified viscoelastic response. By applying a reduction procedure similar to that used to estimate the constants of the Williams, Landel, and Ferry equation, we demonstrated that not only did the viscoelastic response of doughs vary, but that water molecules interfere with the dynamic by which relaxation phenomena take place. Finally, we proved that the rheological behavior of flour dough is similar to that of concentrated polymer solutions, and that it can be characterized by using a double reduction procedure, shifting the rheological curves along the vertical and horizontal axes, and obtaining a master curve that can be considered inherently characteristic of viscoelastic behavior.

Wheat flour doughs are viscoelastic materials; they possess, at the same time, the characteristics of viscous liquids and elastic solids. When flour and water are mixed and kneaded, mechanical denaturation of gluten proteins occurs. Noncovalent bonds among functional constituents form with the active participation of water molecules (Laszitity 1984). Basically, one can imagine that when the dough is submitted to external forces, the physical entanglements and the weak bridges that hold the dough constituents together can break and reform, allowing the dough to relax, partially or completely, under applied stresses. This peculiar behavior makes flour doughs very similar to synthetic polymeric materials. It is not surprising that many processes used in polymer technology (extrusion, blowing, calendering, molding) are commonly used to process doughs.

The similarity existing among synthetic polymers and doughs is not limited to technological aspects but applies to research as well. In the last decade, an increasing number of food scientists have borrowed analytical techniques and theories from polymer science to characterize and explain the physicochemical behavior of foods (Slade and Levine 1991, 1994). In particular, dynamic moduli measurements of a sample of regular geometry submitted to small amplitude shearing proved to be a suitable technique to gain information about dough systems for characterizing the influence of temperature on rheological response and water-dough structure interaction (Hoseney et al 1986, Masi 1989, Cavella et al 1990, Masi et al 1990). Dynamic measurements at various temperatures demonstrated that dough viscoelastic behavior is governed by dynamic properties. The temperature at which the glass-rubber transition occurs (T_g) can provide information on processability, quality, and stability of dough and dough-based foods. The influence of T_g on the dynamic viscoelastic behavior of gluten proteins can be described using the Williams, Landel, and Ferry (WLF) equation with constants that are only slightly different from those found for synthetic polymers (Cocero and Kokini 1991). Water plays a central role as a ubiquitous plasticizer lowering T_g in doughs. Madeka and Kokini (1993) demonstrated that when the moisture content of glutenins was raised from 4 to 14%, the T_g fell from 130°C to room temperature. However, this is not the only interpretative approach to explain the change of the dynamic response in the dough as a result of water-structure interaction. One hypothesis was advanced (Hibberd and Wallace 1966, Hibberd 1970) that water molecules in high moisture content doughs behave as an inert fillers. Both $\log G'$ and $\log G''$ were functions of frequency but independent of water content. Loss tangent was also independent of water content. Thus, the effect of frequency and water content may be separated. Both $\log G'$ and $\log G''$ differ proportionally, but are independent of frequency (macromolecular mobility).

The study attempted to verify which of these hypotheses is more convenient for characterizing the dynamic behavior exhibited by wheat flour dough at room temperature with various moisture contents.

MATERIALS AND METHODS

Flours were supplied by Mulini di Vigevano (Vigevano, Italy) (Table I). The material used to prepare all the samples belonged to the same lot.

Samples were prepared before each test by mixing the flour with distilled water in a farinograph for 15 min (Brabender, Duisburg, Germany). Water content of the dough was measured by determining the weight loss of samples kept under vacuum at 105°C for 24 hr. Tests were duplicated using a new sample from the same batch for each test. Before rheological analysis, the dough rested for 30 min in an environmentally controlled room (22°C, 95% rh).

Rheological analyses were performed using a dynamic mechanical spectrometer (RSF2, Rheometrics, Piscataway, NJ) equipped with parallel plates (5 cm diameter) and an environmental chamber (±0.1°C). Sample thickness was 2 mm. To avoid rapid drying during the test, the exposed edges of the samples were covered with a thin layer of petroleum jelly. The benefits of this procedure and the data reproducibility were discussed in a previous work (Sepe 1994).

TABLE I
Flour Composition[a]

Flour	Gluten Wet Basis	Gluten Dry Basis	Moisture	Ash
A	31.8	10.2	14.1	0.55
B	20.7	6.8	13.3	0.60
C	30.7	9.7	13.5	0.58

[a] %, w/w. $n = 3$.

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Dynamic tests were run in frequency sweep mode using a strain amplitude of 0.05%. Preliminary tests performed in strain sweep mode were made by varying the strain amplitude from 0.05 to 100%, which indicated that, for all the doughs, the range of strain in which the viscoelastic response is independent of strain amplitude is quite small, but it is quite well defined below strain at 0.07%. Test were repeated three times using a new sample from the same batch for each test. Data reproduction is within the range of ±2%.

Dough viscoelastic behavior has been described in terms of dynamic properties (Ferry 1980). Accordingly, G' is representative of the energy stored in the sample at any cycle and G'' is a measure of the energy lost at any cycle. The G''/G' ratio is representative of the relative viscous and elastic contribution to the complex modulus G^*, expressed numerically by the tangent of the phase lag angle (δ) between stress and strain waves.

RESULTS AND DISCUSSION

The change in frequency for doughs prepared from flour A with moisture contents of 43.5–58.24% is illustrated in Fig. 1. The behaviors of dough from flours B and C are quite similar. Increasing the frequency from 0.1 to 100 rad/sec, increases both G' and G'', while the tan δ decreases approaching an asymptotic value. In the frequency range explored, the elastic contribution to the complex modulus is always larger than the viscous one. Moisture exerts a strong influence on the dynamic viscoelastic behavior of doughs, considering that the dynamic modulus decreases more than 20 times when the water content of doughs increases from 43 to 58%. Correspondingly, the tan δ reduces to half.

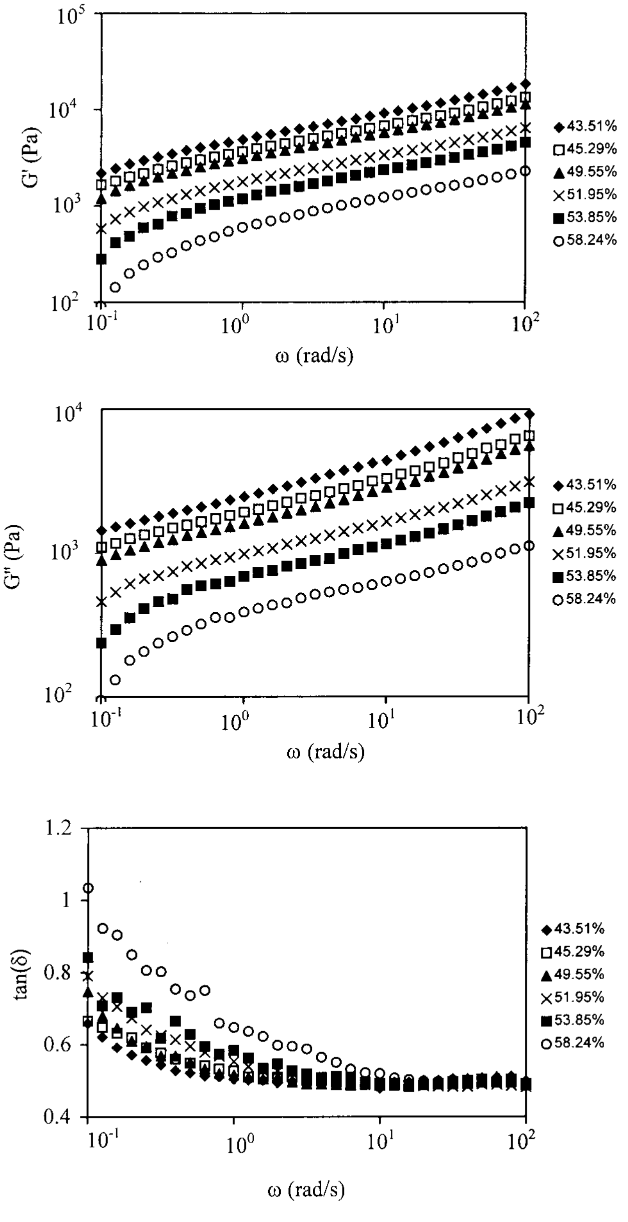

Fig. 1. Storage modulus (G'), loss modulus, (G''), and tan δ of doughs made with flour A at different moisture contents (43.5–58.24%) vs. frequency ω(rad/sec).

The influence of water on the dynamic viscoelastic behavior of flour doughs has been interpreted in two different ways. It has been advanced that water above a given limiting value does not interfere with dough structure but acts as a simple inert filler. Consequently, varying moisture content of the dough proportionally changes dynamic properties, but relaxation behavior is independent. On the other hand, it has been suggested that water molecules act as a plasticizer lowering the T_g of the doughs. In this case, increasing the moisture content of doughs changes dynamic response because the relaxation dynamic accelerates in a manner similar to that of amorphous synthetic polymers when the temperature rises.

If the hypothesis is valid that dynamic properties of dough change proportionally with moisture variation, while viscoelastic behavior is independent of moisture variation then, according to Hibberd (1970), shifting the dynamic curves along the vertical axis relative to dough with different moisture contents should superimpose them, generating a master curve. The results of such an attempt using a reference curve corresponding to dough with 43% moisture is shown in Fig. 2. The data produced by multiplying G' by the shift factor a_M do not produce a single composite curve. Only those corresponding to frequencies >5 rad/sec describe the same curve. Others follow individual curves that are well defined in the low frequency region. Clearly, the hypothesis that water does not interfere with the relaxation behavior of dough structure is not completely valid. The same conclusion could be drawn by considering the curves of tan δ with varying frequency and water content (Fig. 1), which show that tan δ is not independent of water content over the entire range of frequency explored.

The influence of moisture content on the mobility of the functional constituents of dough can be illustrated by comparing the moisture content of the slope of the derivative of logG' with respect to log frequency (Fig. 3). According to Ferry (1980), when the slope of logG' vs. logω had a value approaching 0, the material behaves like a rubbery material, while a liquid flow material had a slope approaching 2. The curve of the dough with the highest moisture content has a slope ≈2 at low frequencies. It reduces very rapidly with increasing frequency, becoming almost constant at ω > 5 rad/sec. By lowering the moisture content of the dough, one

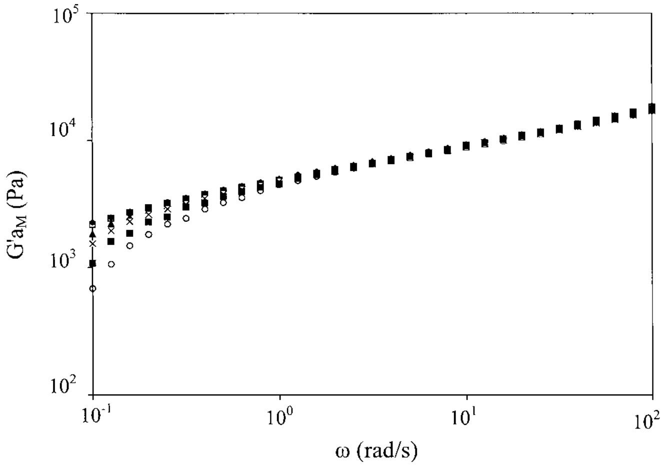

Fig. 2. Reduced storage modulus $G'a_M$ vs. frequency ω(rad/sec). Moisture contents as shown in Fig. 1.

observes a large reduction in the slope at low frequency. The lower the moisture content, the smaller the slope, and all the curves approach the same constant value at high frequency.

The behavior of the curves shown in Fig. 3 clearly indicates that the moisture content of the flour interferes with the mobility of structural components in the dough. Data suggest that water molecules enhance relaxation behavior of mobile units which evolve in less time than the experimental period, and the dough behaves as a liquid flow material. By lowering the moisture content, the relaxation dynamic slows down and the percentage of mobile units increases. They become cooperatively immobilized during the experimental period. The same occurs by reducing the experimental period and increasing the frequency. At high enough frequency values, the system will reach a steady state. The amount of mobile units that have enough time to relax compared to those that appear immobilized remains constant. Once this situation occurs, water and frequency effects can be separated, and the principle of corresponding water content as proposed by Hibberd applies.

To show the applicability of this correspondence principle, the shift factor a_M required to reduce G', in the region of frequency where $\log G'$ with respect to log frequency is constant, has been plotted against the difference between the moisture content of the dough and the moisture content of the reference sample ($M - M_R$) (Fig. 4). For the three different flours, the a_M value changes almost linearly with increasing excess moisture content in the dough, suggesting that, in principle, it is possible to further reduce the dynamic curve by introducing varietal factors. This is accomplished by arbitrarily assigning the value unity to a given variety and attributing a relative value to other varieties (Hibberd 1970).

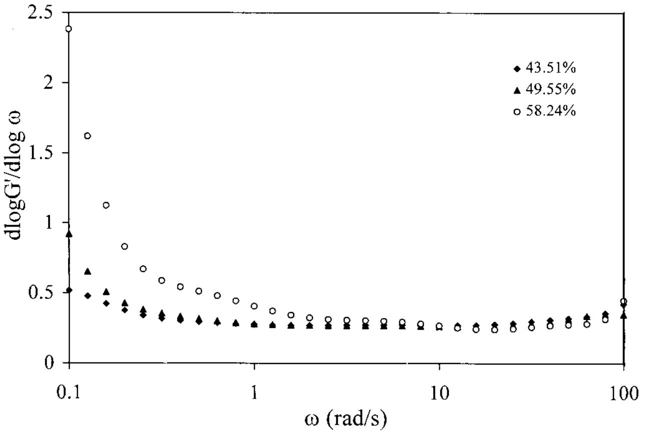

Fig. 3. Change of the slope of log storage modulus with log frequency of doughs (dlogG'/dlogω) at three different moisture contents vs. frequency ω(rad/sec).

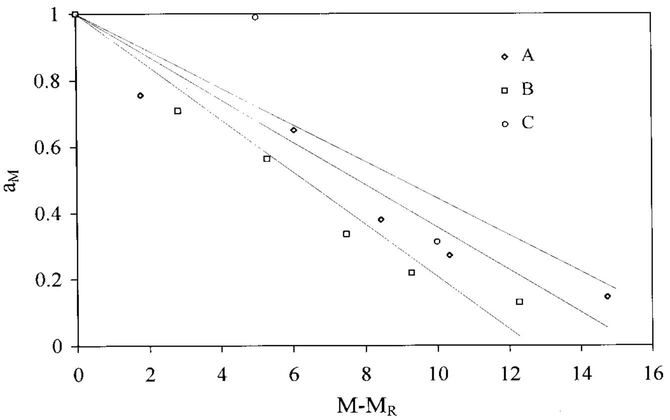

Fig. 4. Relationship between shift factor a_M and excess moisture content of doughs ($M - M_R$) from three flour samples.

Data so far discussed suggest that the role of water as plasticizer cannot be neglected in characterizing the dynamic viscoelastic response of flour doughs. When a dough is diluted, the local friction of its structural components drops, reducing all relaxation times. This situation is very similar to what occurrs when the temperature of an amorphous synthetic polymer is increased (the principle of corresponding states applies). Accordingly, G' measured at frequency ω and temperature T is equivalent to G' measured at frequency ωa_T and temperature T_0. The effect of the temperature on viscoelastic properties is described by the function a_T given by the WLF equation:

$$a_T = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \tag{1}$$

where T_g is assumed as the reference temperature, and C_1 and C_2 are constants determined from displacements of the viscoelastic curves along the logarithmic time or frequency axis. Tentatively,

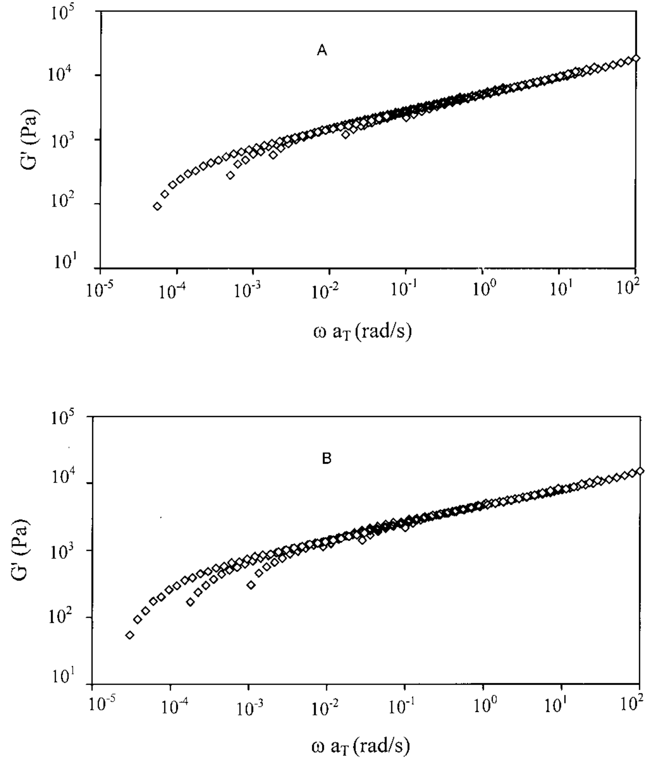

Fig. 5. Storage modulus (G') vs. reduced frequency ωa_T(rad/sec) for flour types A and B.

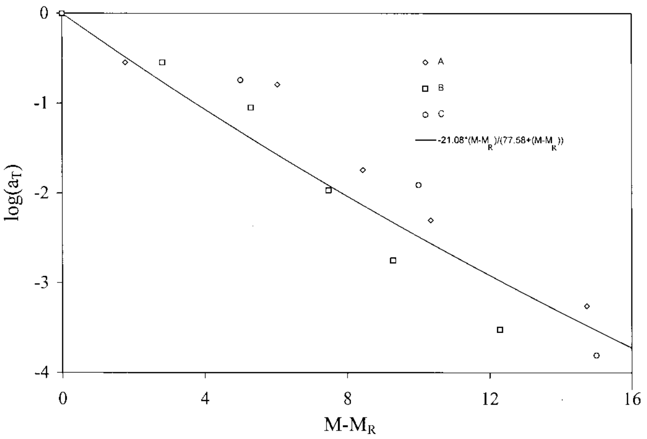

Fig. 6. Relationship between the shift factor log(a_T) and excess moisture content of doughs ($M - M_R$) from three flour samples. Solid line represents best fit of experimental data.

one can assume that there is an analogy between the effect of the temperature on the viscoelastic response of polymers and the effect of moisture on the viscoelastic response of flour doughs. Therefore, one could use the WLF procedure to determine the function a_T which should describe the effect of moisture content on the viscoelastic behavior of the dough. Figure 5 shows the composite curve obtained from this procedure. The attempt to generate a single composite curve by shifting the G' curves along the frequency axis does not succeed: the curves shift well in the apparent plateau region, but not in the terminal region of the viscoelastic curves.

The influence of excess moisture content in the dough ($M - M_R$) on the logarithm of a_T is illustrated in Fig. 6. The function a_T was determined by shifting each curve obtained from dynamic mechanical analysis along the frequency axis so as to superimpose it to the one corresponding to the dough with the lowest moisture content in the apparent plateau region. Data are scattered however. The behavior follows that predicted by WLF equation where $M - M_R$ has been used in place of $T - T_g$. Note that the coefficients estimated by the best fit of the experimental data differ slightly from those characterizing temperature dependence of shear viscosity data for water-plasticized glutenin above T_g (H. Madeka and J. L. Kokini, *unpublished data*).

Both attempts to reduce experimental data by shifting them along the vertical or the horizontal axis resulted in master curves with poor agreement in the terminal region of the viscoelastic curves. This situation is quite similar to that which occurs when attempting to develop suitable shift routines for rheological data of semidilute and concentrated polymer solutions. As extensively discussed by Ferry (1980), the use of reduced variables to combine viscoelastic data measured at different concentrations for these materials has to be considered separately for the plateau and the terminal zones. This is done by shifting the curves measured at each concentration with different concentration dependence in both regimes and then to create a master curve. Thus, by looking at the flour dough as concentrated polymer suspensions, it should be possible to use a double reduction procedure to construct a single master curve from G' curves measured at different moisture contents. With the dough with the lowest moisture content chosen as the reference, and then by using the procedure for construction of master curves, each G' curve was shifted along the vertical and the horizontal axes so as to superimpose it on the reference curve. Figure 7 shows the composite curves obtained by this procedure for flours A–C. The G' measured at frequency ω and moisture content M is equivalent to $G'_R a_D$ measured at frequency ωa_C and moisture content M_R. The function a_D describes the influence of dilution on the dough viscoelastic properties and the function a_C describes the influence of moisture on relaxation times. All the experimental data relative to a given flour belong to the master curve that covers four orders of magnitude of reduced frequency (ωa_C) and four orders of magnitude of reduced storage modulus ($G'_R a_D$). Data obtained from the dough with the highest moisture content describe the portion of the curve that corresponds to the lowest reduced frequencies. Data corresponding to doughs with low moisture content contribute to a larger extent to the definition of the shape of the curve at fast reduced frequencies. As the curve has been derived using data corresponding to doughs with various moisture contents, they can be assumed, together with those that describe the relationship existing between the shift factors a_D (Fig. 8) and a_C (Fig. 9) and the excess moisture content of the dough ($M - M_R$), to

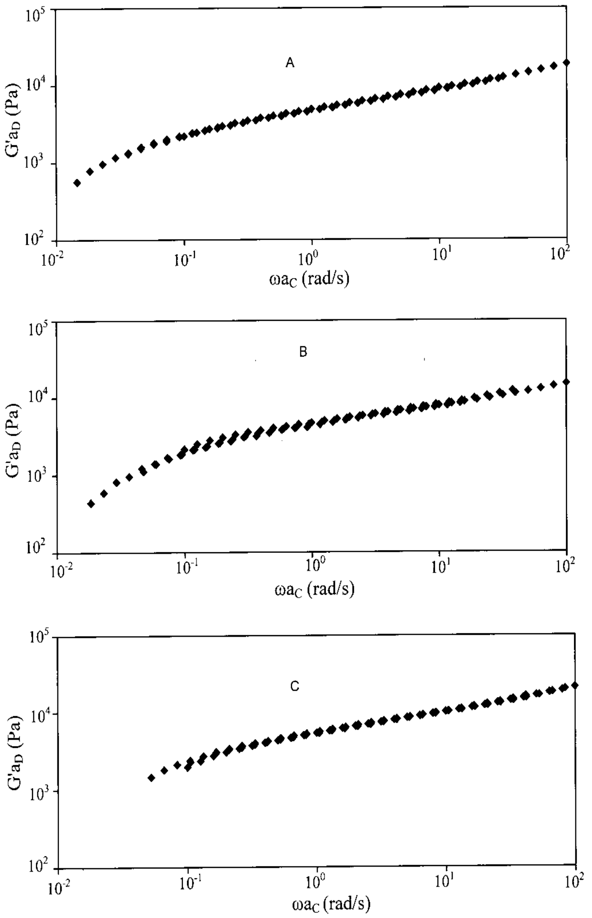

Fig. 7. Reduced storage modulus ($G'a_D$) master curve vs. reduced frequency ωa_C(rad/sec).

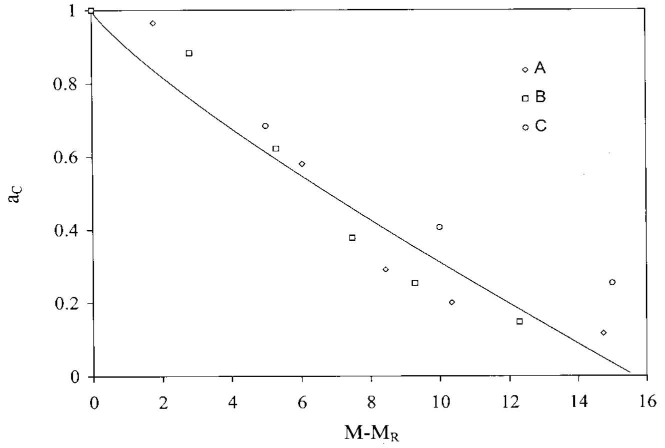

Fig. 8. Relationship between shift factor a_C and excess moisture content of doughs ($M - M_R$). Solid line represents best fit of experimental data.

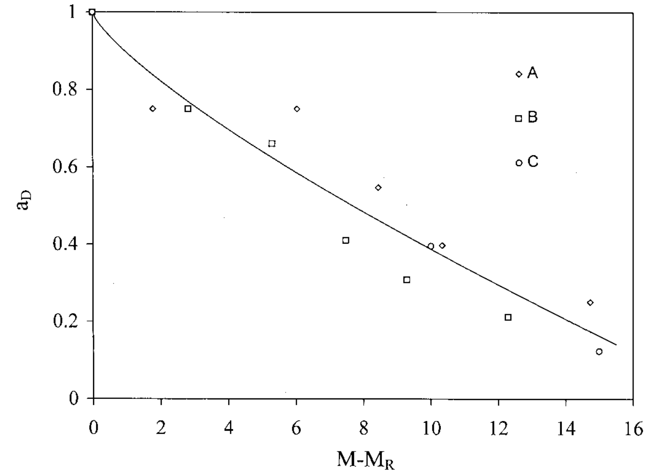

Fig. 9. Relationship between shift factor a_C and excess moisture content of three doughs ($M - M_R$). Solid line represents best fit of experimental data.

be representative of the influence of moisture content on the dynamic viscoelastic behavior of doughs.

At this stage, it is risky to try to explain the dependence of function a_D and function a_C on moisture content and flour varieties because only three flour varieties were considered and only a limited range of moisture contents were explored. However, it is worth noting that both the function a_D and the function a_C can be described by the simple equation:

$$a_D, a_C = 1 - a(M - M_R)^b \qquad (2)$$

where a and b are constants that differ for each function and all data relative to the different flours examined seem to describe the same curves.

CONCLUSIONS

The dynamic viscoelastic behavior of flour doughs with varying moisture contents cannot be characterized without taking into account the dual role of nonfunctional water. Water can act as an inert filler, causing the dynamic properties to reduce proportionally to moisture content or water can behave as a lubricant enhancing the relaxation phenomena.

From a practical point of view, flour dough behaves in a manner similar to that of concentrated polymer solutions. A double reduction procedure consisting of shifting the dynamic curves along the vertical and the horizontal axes so as to superimpose them on a reference curve generates master curves. These curves can be considered inherently characteristic of a material's viscoelastic response. Moreover, this scheme for constructing the master curve provides a way to separate the dilution effect of water from the lubrication effect, each of which is described by the relationship between shift factor and moisture content.

Although the results presented here involve only three flour varieties, the fact that each reducing factor can be described by a unique equation whose constants are independent of flour varieties is very interesting and deserves further investigation.

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