RHEOLOGICAL AND THERMODYNAMIC PROPERTIES OF GLUTEN GEL

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ABSTRACT

When specimens of wheat gluten gel were stretched under constant stress to small extensions ($\epsilon^c<1$), the recovery following release of load was complete and mainly immediate, while the apparent modulus of immediate recovery was low and constant, similar to rubber elasticity. Beyond a certain extension, however, the recovery was no longer complete; the residual deformation was attributed to viscous flow; then, the apparent moduli of immediate and delayed recovery increased with the stress preceding recovery and the coefficient of apparent viscosity decreased with stress. Part of the energy of recovery or the conserved energy (W_{ie}) was dissipated during sustained loading at a time-dependent rate. An increase of loading time from 5 sec to 5 min caused an energy decay at a ratio of 25:1. Since the material changed during the experiment from a linear viscoelastic solid (full recovery) to a nonlinear elasticoviscous liquid (flow and full stress relaxation) it is proposed to call it rheologically unstable. This instability is described by a rheological model based on a modified Kelvin body in series with a Hooke body. The modification consists in a Newton element bridged by a shear pin, in series with the Hookean element of the Kelvin body, the shear pin accounting for the solid-liquid transition beyond a yield point.

In wheat flour dough, the wheat gluten forms an elastic network which largely determines the mechanical behavior of the whole material.

There is a rich literature on wheat-flour dough, but few attempts have been made to describe the mechanical and the thermodynamical behavior of wheat gluten gel and its interpretation in physical parameters.

The mechanical properties of wheat gluten gel were first studied by Schofield and Scott Blair (1) who proved that the gluten determines the mechanical behavior of dough. They obtained gluten from wheat flour dough by washing out the starch and compared its behavior to that of a linear Maxwell body. Hlynka and Cunningham (2) studied the relaxation of washed gluten and described it by a spectrum of relaxation times.

The mechanical properties of gluten were measured in an Instron machine by Barney *et al.* (3) and also be Heaps *et al.* (4). Rinde *et al.* (5) measured the mechanical properties of gluten for large deformations followed by rupture in washed gluten.

Thermodynamic properties such as the adsorption isotherms for gluten and flour were measured by Bushuk and Winkler (6), who calculated the respective heats of adsorption. Based on the statistical theory of rubber elasticity Muller (7) calculated the molecular weight between cross-links of washed gluten gels.

The importance of the gluten proteins for the viscoelastic properties of flour dough and gluten-starch-water mixtures was reported by Bloksma (8).

MATERIAL AND METHODS

Gluten gel of 46% concentration was prepared by mixing commercial Hercules "Vicrum" brand gluten powder (Table I) with distilled water under isothermal conditions (30° C) in a Brabender Farinograph bowl to 600 Brabender units, for 5 min (t_m). The Farinogram parameters of the gluten gel are presented in Table I.

The gel obtained was then extruded through a 6.5-mm diam nozzle under 30 kg/cm^2 pressure and the rubbery extrudate was cut into 100-mm long cylindrical samples. These were floated on a mercury bath.

The method of measurement was creep under constant stress followed by recovery as described in (9). The only difference was that here the samples were stretched at constant true stress by applying the load over a spiral cam; the spiral was designed in such a way that the acting lever (and, therefore, the force acting on the sample) diminished in the same ratio as the cross-sectional area (A_t) of the sample, the volume of the sample being assumed to remain constant (10).

In each experiment a fresh gluten gel sample was prepared and the true stress (σ_{A_t}) was calculated as the acting force (P) per cross-sectional area (A_0); the corresponding deformation ϵ^C was determined as the Cauchy measure: $\Delta l/l_0$.

The extension under constant stress was measured against time; the recovery following unloading (ϵ_{te}) could be resolved into two components: immediate[1] (ϵ_{ie}) and delayed (ϵ_{de}) elastic strain; that portion of the deformation which did not recover represented the viscous flow (ϵ_v) during the load period.

RESULTS

Creep and Recovery Experiments

Figure 1 presents deformation measured in a series of extension and recovery experiments—each one performed under a different specific stress—plotted

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[1] Theoretically "immediate" deformation occurs at acoustical speed, therefore, we speak here of "rapid" elasticity measured after 3-5 sec.

TABLE I
Farinogram Parameters (AACC 54-21 A) of Wheat Gluten Gel Compared with Wheat Flour Dough (A_I).

Parameters	Material Gluten (Hercules)	Flour (A_I)[a]
Consistency "a" (BU)	600	600
Mixing time "b" (min)	5–8	3.5
Stability "d" (min)	30	2
Time to breakdown "f" (min) (AACC 54-21 A)	25	1
Moisture content (%) (AACC 44-19)	3	13.1
Protein Pr (%) (%N_2 × 5.7)	75.9	12.3
Absorption w_B (%) (AACC 54-21 A) (ml water/100 g gluten powder)	107	55.6
Absorption w (%) (ml water/100 g gel)	51.5	35.8
Absorption v_1 (in volume, %) (ml/100 ml gel)	54	
Gluten $v_{2(g)}$ (in volume, %) (AACC 38-10)	46	7
Gluten $v_{2(P_r)}$ (%) (based on protein concentration)	39.2	7
Loaf volume (ml) (Conventional Baking Test)[b]	2400	2200

[a] A_I = Hard red winter wheat flour (Kansas, 1963) (10).
[b] Wheat-flour dough with 4% Hercules Gluten added.

against time.

The immediate or rapid recovery (ϵ_{ie}), delayed recovery (ϵ_{de}), and viscous flow (ϵ_v) obtained after 330-sec loading time were plotted against the true tensile stress (σ_{A_t}) in Fig. 2.

Under the conditions represented in Fig. 1, the deformation proved almost totally recoverable, 74% of it rapidly, and 20% delayed, while only up to 6% constituted viscous flow (11). This high proportion of rapid recovery is characteristic for gluten gels; in flour doughs, by contrast, as much as 90% of the deformation measured after similar loading conditions (stress, time) would be irrecoverable, *i.e.*, constitute viscous flow, no more than 10% being recoverable, *i.e.*, elastic. The apparent moduli of total, rapid, and delayed recovery (E_{te}, E_{ie}, E_{de}) were calculated as quotients between the stress and the respective portion of the recovery. These were plotted in Fig. 3 against the tensile stress (σ_{A_t}). These values are called "apparent" (or "nominal") since they constitute average values derived from the average deformation during the arbitrary load period of 330 sec.

The order of magnitude of the modulus of rapid recovery (E_{ie}) was $35 \cdot 10^3$ dyn/cm^2. The nominal moduli of recovery were constant up to a stress of $20 \cdot 10^3$ dyn/cm^2; beyond this stress, the moduli increased with the acting stress. Since the same stress coincided with the appearance of a significant portion of irrecoverable deformation, we termed this stress "yield stress." Below that value the constancy of modulus signifies essentially linear behavior; above that value the material shows nonlinear performance.

We define a "yield function" as the lowest tensile stress (σ_y) causing irrecoverable deformation in the sample, on acting over the time (t_y) which we

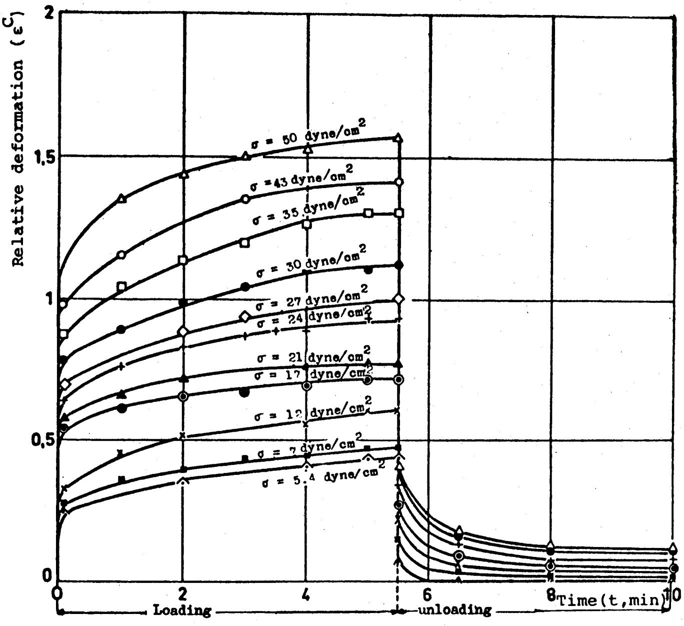

Fig. 1. Relative deformation (ϵ^C) *vs.* time (t) at different constant stresses (σ_{A_t}). Loading time (t_l) = 330 sec; 46% gluten. T = 30°C.

termed yield time (12). The lowest stresses, which under these conditions (σ, t) produced viscous flow detectable on unloading, were plotted against the yield time in Fig. 4. The yield function thus derived divides the stress-time field into a linear (below) and a nonlinear range (above).

The effect of the loading time is shown in Fig. 5 which represents creep measurements during longer loading times up to 90 min, until rupture. The point of change of slope in these curves corresponds to the yield time for each specific yield stress. The compliances were calculated as the ratio of strain:stress (the inverse of modulus) and plotted against the loading time in Fig. 6. The curves thus obtained also present a sharp change of slope, again coinciding with the yield transition. The rapid and delayed recoveries measured after longer loading times—up to 90 min—increased with the loading time (Fig. 7) up to a maximum, which was reached immediately preceding the yield time. Beyond it the curve slowly decreased to a value remaining constant for a long period. As mentioned above, viscous flow appeared at the yield time characteristic for a certain stress. When this loading time was exceeded under that stress (the corresponding yield stress), the irrecoverable portion measured after recovery kept increasing monotonously with the preceding loading time (Fig. 7). The apparent coefficients of viscosity (η), calculated as the ratio of stress (σ) and rate of strain (ϵ) decreased instantaneously with the respective yield time and then asymptotically to a constant value.

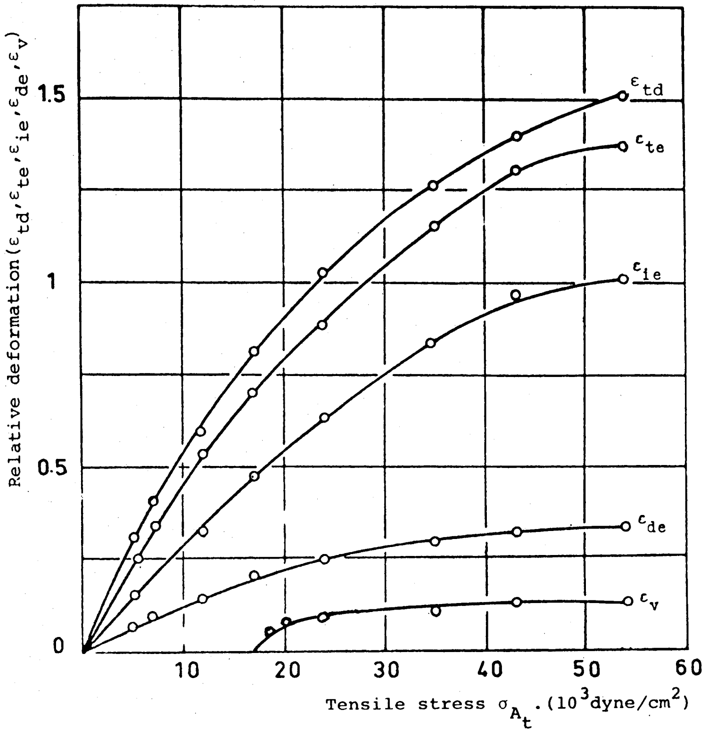

Fig. 2. Recoverable and irrecoverable deformations (ϵ) measured upon unloading, after 330 sec loading time, *vs.* real tensile stress (σ_{A_t}). (See Fig. 1.)

The effect of the loading time is evident from Fig. 8 which represents the rapid recovery (ϵ_{ie}) plotted against the tensile stress (σ_{A_t}) which preceded it, during three different loading times.

The respective apparent moduli calculated for these curves—as the ratio between stress : strain—decrease with the increasing loading time. The area left of the stress-strain curves representing the rapid recovery, or the chief portion of the conserved energy (W_{ie}), is plotted in Fig. 9 as function of loading time. The hyperbolic curve straightened out in double logarithmic coordinates in a manner represented by the empirical power law:

$$W_{ie} \times t_l^{0.55} = 340 \cdot 10^3 \text{ dyn cm sec}^{0.55}/\text{cm}^2$$

$$= 0.008 \text{ cal sec}^{0.55}/\text{cm}^3$$

The dimensional objection can be avoided by rational (dimensionless) formulation (13).

The rapidly recoverable energy (W_{ie}) increases for very small loading times ($\leqslant 5$ sec) and decreases at a ratio of 1:25 as the loading time increases from 5 sec to 5 min.

From Fig. 9 it can be seen that the rapidly recoverable energy decreases with the increase in loading time, while at the same time the viscous flow increased

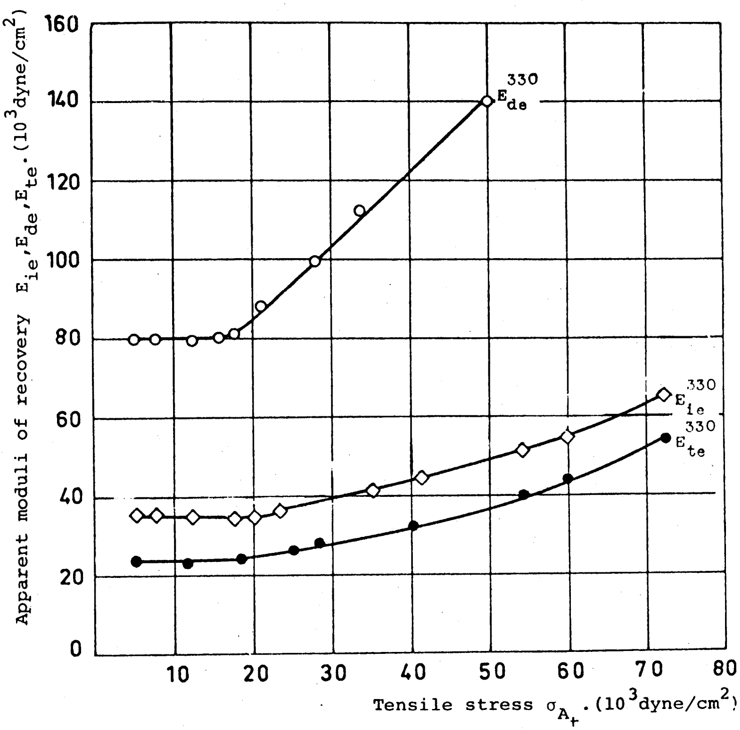

Fig. 3. Apparent moduli of recovery (E_{ie}, E_{de}, E_{te}) after loading time of 330 sec, *vs.* real tensile stress (σ_{At}).

(Fig. 7). The conclusion is that under load, the energy is gradually being transformed from recoverable energy or conserved energy into dissipated energy.

Ultimate Stress Experiments

The influence of the elastic properties on the rupture behavior of the material can be seen also in ultimate stress (σ_{br}) measurements shown in Fig. 10.

The strain preceding rupture (ϵ_{br}) plotted against time to rupture (t_{br}) remained constant even after loading times as long as $5 \cdot 10^4$ sec (Fig. 11), therefore, the strain preceding rupture is a characteristic parameter of the material. This peculiarity suggests comparison with the behavior of a Kelvin body, which is assumed to break when the strength of the elastic elements is exceeded [*cf.* also the Reiner-von Mises criterion of fraction (13)].

Stress Relaxation Experiments

Stress relaxation in gluten gel was measured by stretching the samples quickly to various extensions $0.5 \leqslant \epsilon^C \leqslant 3$ and monitoring the decrease of stress with time, while keeping the strain constant. The functions thus obtained linearized in logarithmic-time scale (Fig. 12) in the range between 1.5 and 10,000 sec. The slopes of these plots decreased with the strain, but appeared to converge on an intercept ($\sigma = 0$) for about 10^4 sec (fluid behavior).

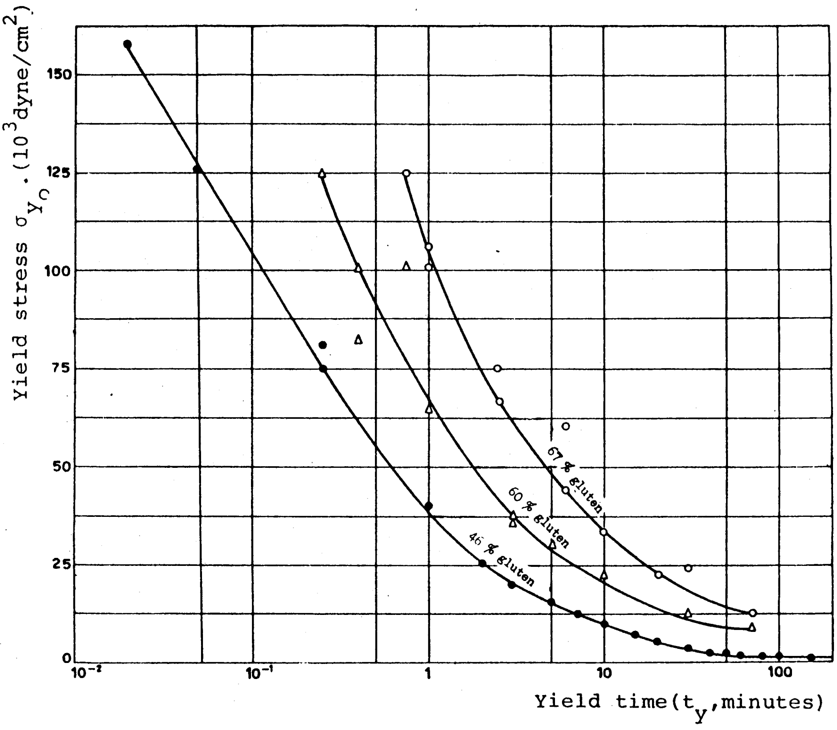

Fig. 4. Nominal yield stress (σ_{yo}) *vs.* yield time (t_y) for different gluten concentrations: 46, 60, 67%. T = 30°C (logarithmic time scale).

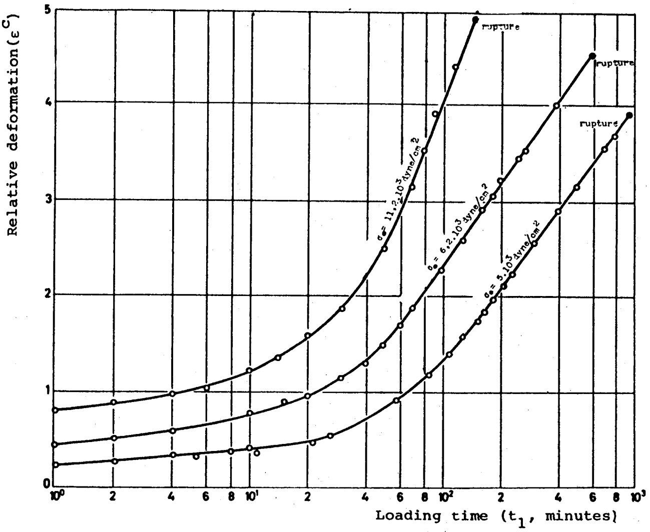

Fig. 5. Creep rupture experiments. Relative deformation (ϵ^C) *vs.* loading time (t_1) under different constant loads: $\sigma_o = 11.2 \times 10^3$ dyn/cm^2; 6.2×10^3 dyn/cm^2; 5×10^3 dyn/cm^2 (logarithmic time scale).

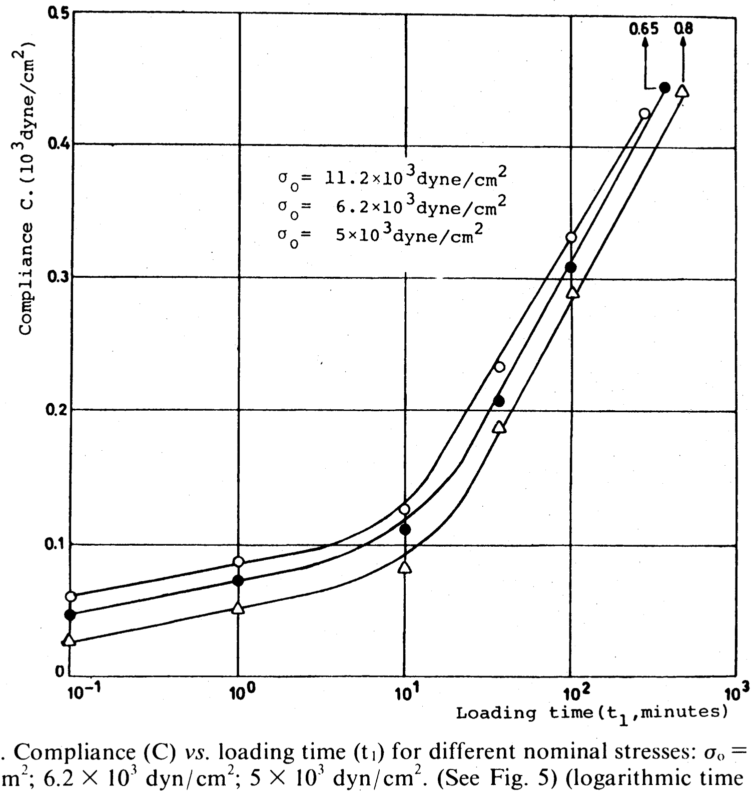

Fig. 6. Compliance (C) *vs.* loading time (t_1) for different nominal stresses: $\sigma_o = 11 \times 10^3$ dyn/cm^2; 6.2×10^3 dyn/cm^2; 5×10^3 dyn/cm^2. (See Fig. 5) (logarithmic time scale).

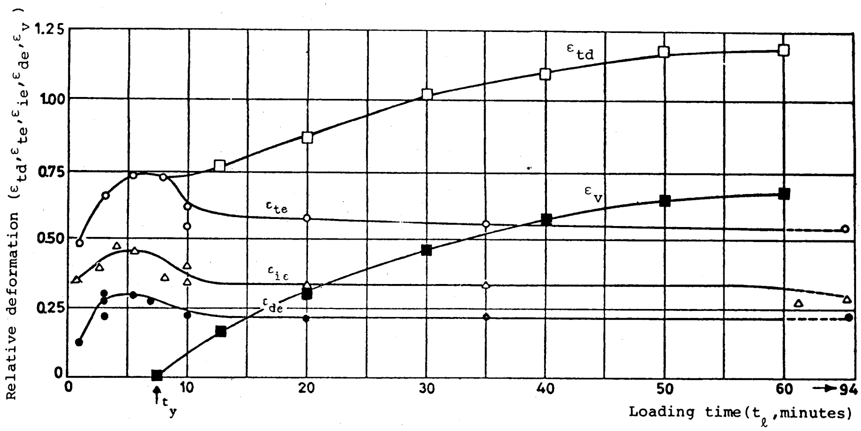

Fig. 7. Total deformation (ϵ_{td}) and its components: total, rapid, and delayed recovery (ϵ_{te}, ϵ_{ie}, ϵ_{de}) and viscous flow (ϵ_v) *vs.* loading time (t_l). Nominal stress $\sigma_o = 10 \times 10^3$ dyn/cm^2; t_y = yield time.

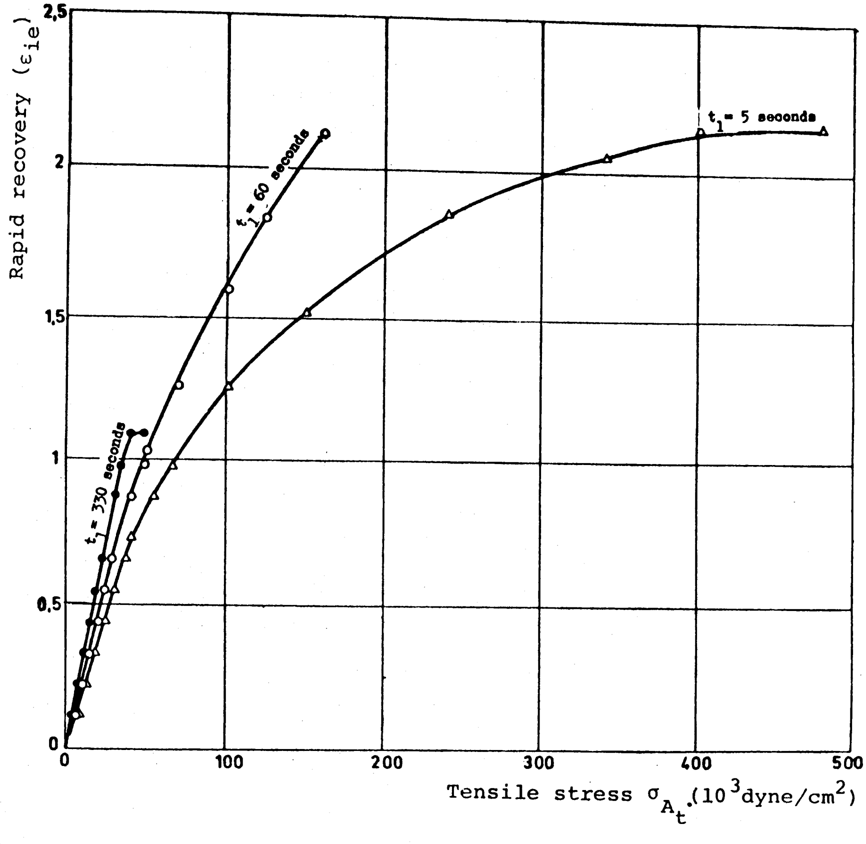

Fig. 8. Rapid recovery (ϵ_{ie}) after various loading times (t_l = 330, 60, 5 sec) *vs.* acting tensile stress (σ_{At}). (See Fig. 1.)

Creep Measurements at Different Temperatures

In this series the gluten gel samples were first rested on the mercury bath for 1 hr between the preparation and the start of the rheological measurement; this rest time served to release the residual stresses in the samples.

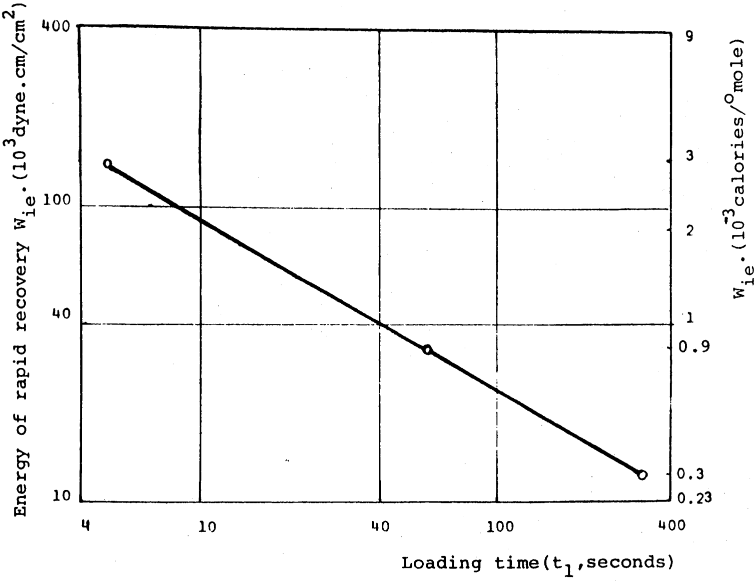

Fig. 9. Energy of rapid recovery (W_{ie}) *vs.* loading time (t_l); (from recovery experiments, Fig. 8); (double logarithmic coordinates).

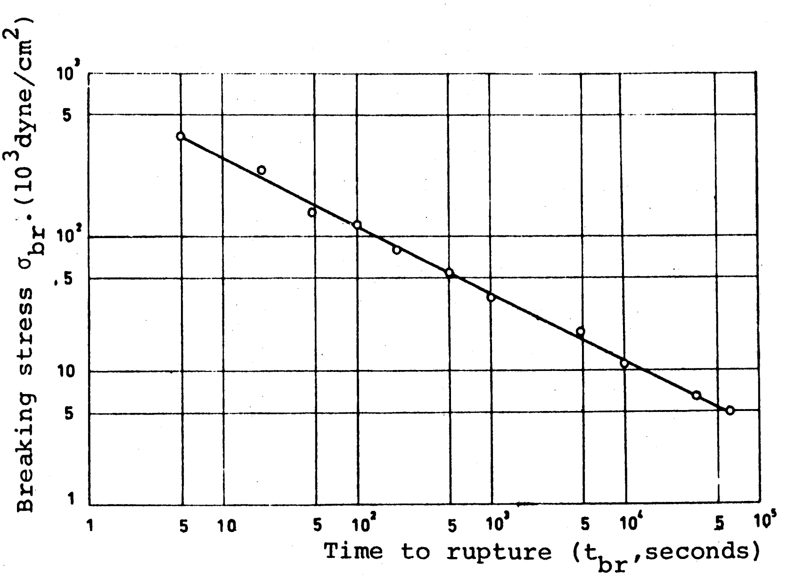

Fig. 10. Breaking stress (σ_{br}) *vs.* time to rupture (t_{br}); (double logarithmic coordinates).

Creep measurements similar to those described above were repeated at temperatures of 293° K, 303° K and 313° K and the deformations $\epsilon_{\sigma,t}$ due to a certain stress σ—measured after the constant loading time $t_1 = 330$ sec—were plotted against the tensile stress (σ_{A_t}) in Fig. 13. This figure shows that the deformation, due to a certain stress acting within that time, decreased with increasing temperature in successive experiments.

In Fig. 14 the same results were plotted in stress-temperature coordinates. The curves, connecting points of equal extension, ascended with temperature; this indicates a behavior similar to that of an ideal rubber (14).

Under conditions of thermodynamic equilibrium, the stress (σ) in a cross-linked rubber can be described by a thermodynamic equation which contains two terms: the first representing the change in internal energy (E) with length (L) and the second the change in entropy (S), at constant external pressure (P) and temperature (T):

$$\sigma = \left(\frac{\partial E}{\partial L}\right)_{P,T} - T\left(\frac{\partial S}{\partial L}\right)_{P,T}$$

The second term is related to the temperature coefficient of tension by the equation:

$$\left(\frac{\partial S}{\partial L}\right)_{T} = -\left(\frac{\partial \sigma}{\partial T}\right)_{L}$$

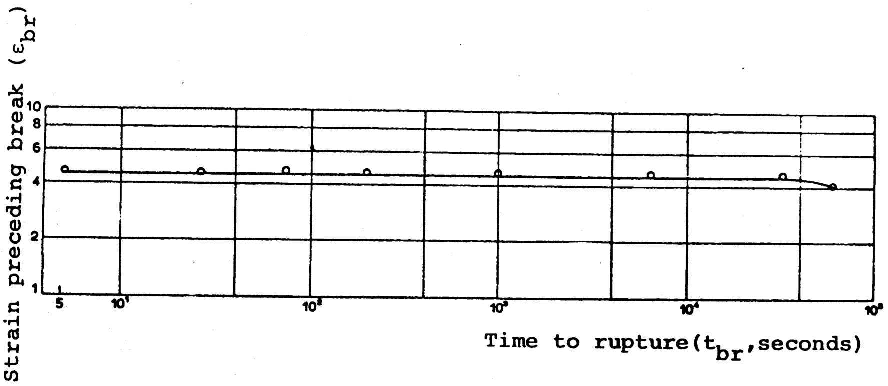

Fig. 11. Strain preceding break (ϵ_{br}) *vs.* time to rupture (t_{br}); (double logarithmic coordinates).

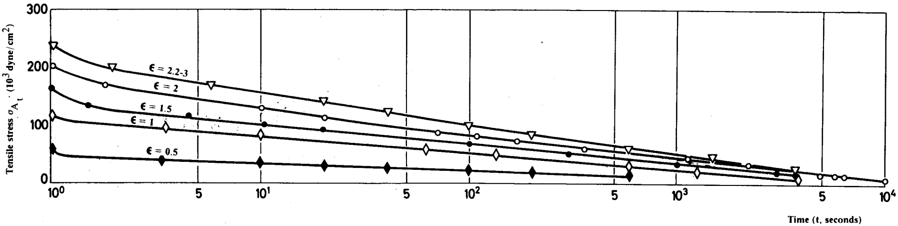

Fig. 12. Stress relaxation experiments. Tensile stress (σ_{A_t}) *vs.* time (t) after loading at constant rate of elongation: $\epsilon = 0.36\ \text{sec}^{-1}$, for different constant strains (ϵ^C); (logarithmic time scale). T = 30° C.

The last equation gives the entropy change per unit extension, in terms of the measurable quantity $(\frac{\partial \sigma}{\partial T})_L$, the temperature coefficient of stress. From the stress-temperature experiments (Fig. 14) the entropy term was calculated. Just as in ideal rubber, so also in gluten gel, the internal energy term is small when the stress is mainly a function of the entropy. The entropy decreases with increasing strain, a behavior similar to rubber.

As long as extensions are small and totally recoverable, *i.e.*, in the range below the yield stress, gluten gels can be supposed to be in thermodynamic equilibrium. In this range of deformations and under otherwise identical conditions (acting stress, loading time) the apparent modulus of rapid recovery and the rapidly recoverable energy increased with the temperature too.

DISCUSSION

Thermodynamic Properties

The most striking fact emerging from the observed effects is that gluten gels are capable of two different types of behavior depending on the experimental conditions.

Below a characteristic combination of stress (or strain) and loading time, the material behaves in good approximation like a soft elastic solid comparable, in many respects, to ideal cross-linked rubbers. Beyond the conditions defined by the characteristic stress-time function (termed "yield function"), the material

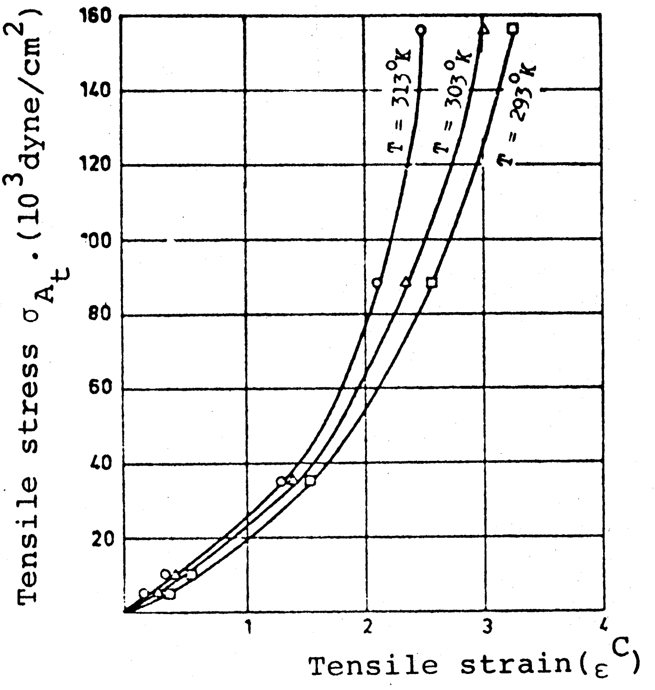

Fig. 13. Tensile stress (σ_{At}) *vs.* tensile strain (ϵ^C) at different constant temperatures (T, °K); (rest time T_{r1} = 1 hr).

assumes the properties of a nonlinear elasticoviscous liquid, comparable in some aspects to certain linear polymers, mostly thermoplastic synthetic polymers above T_g (15).

This transition between two rheologically differing states upon passing characteristic sets of experimental conditions has been termed by us "rheological instability" (12). In particular, the most significant results as reviewed in the light of the above statement are:

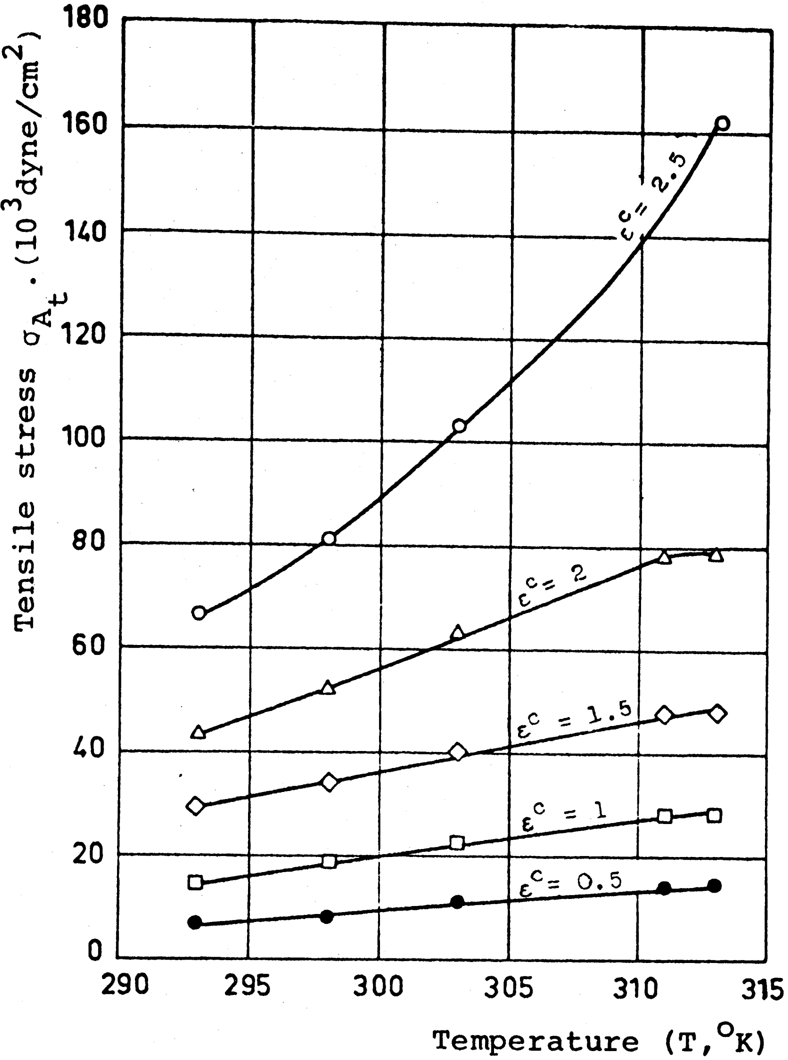

Fig. 14. Tensile stress (σ_{A_t}) *vs.* temperature (T, °K) resulting from different constant strains; (derived from Fig. 13).

1) Observations which, with some reserve, fit the classic theory of rubber elasticity (15)—below the conditions defined by the yield function—:

a) The elastic modulus of gluten gels is very low; indeed in most cases observed, about two orders of magnitude lower than that of most soft rubbers: 10^{5} dyn/cm^{2}, against 10^{7} dyn/cm^{2}.

b) The modulus is constant, *i.e.*, the stress-strain behavior is linear.

c) Virtually the whole deformation is recoverable, almost completely within fractions of a second after load removal.

d) The stress-strain curves obtained for constant sets of deformations and loading time are higher for higher test temperatures.

e) Stress relaxation is slow ($\tau_{relax} > 300$ sec).[2]

f) With increase of external temperature, the gluten gel samples contract.

2) Observations which are at variance with rubber elasticity but which tally with the behavior of certain linear polymers, mostly thermoplastic synthetic polymers, beyond the yield function:

a) Recovery is incomplete (viscous flow component).

b) Stress relaxation is pronounced ($\tau_{relax} < 100$ sec).

c) The apparent modulus of rapid recovery is stress- and time-dependent.

3) The deformability is large ($\geqslant 4.5$) and hence suggests comparison with rubbers, yet only part of it is recoverable—as soon as the very short yield time for large deformations is exceeded—which limits the comparison.

Rheological Model and Underlying Mechanisms

An attempt has been made to represent the unstable behavior described by a rheological model (Fig. 15). In this model, the yield effect is represented by a shear pin (SP), which blocks a Newton element (N_3), as long as it remains intact, making the model act almost like an ideal rubber, represented by Hooke elements of low modulus (H_1 and H_2). The Newton element N_2 serves to illustrate the time dependence of the yield transition which is triggered when the Hooke element H_2 reaches the reaction needed to overcome the resistance of the shear pin (16). As soon as this occurs, the Newton element N_3 is unblocked and transforms the model from that of a viscoelastic solid into an elasticovisous liquid. This model is only a first and qualitative representation. Our observations suggest that a better approximation would probably need several similar models differing quantitatively, in order to represent the spectrum of relaxation times apparently required to account for the nonlinearity observed.

The model described represents essentially a Poynting-Thomson body or Standard Linear Solid body before the transition; the yield mechanism has been added to account for its time- and stress-dependent transformation of the Kelvin component into a Jeffreys body (13).

This model can be represented by the constitutive equation:

$$G = H_1 - \left\{ N_2 \mid [H_2 - (N_3 \mid SP)] \right\}$$

Such a model can, at best, help in formulating the equations describing the mechanical performance of gluten gels in response to various experimental conditions, but it cannot elucidate the physicochemical mechanisms on the molecular level responsible for the observed facts.

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[2] τ_{relax} = nominal relaxation time.

Tentative Analysis of Background

For an analysis of the underlying phenomena we rely tentatively on what is known on the structure of gluten-like proteins. We know that the molecules of such proteins contain a polypeptide chain-like backbone from which the amino acid residues jut out in an unknown sequence; the whole molecule being in a

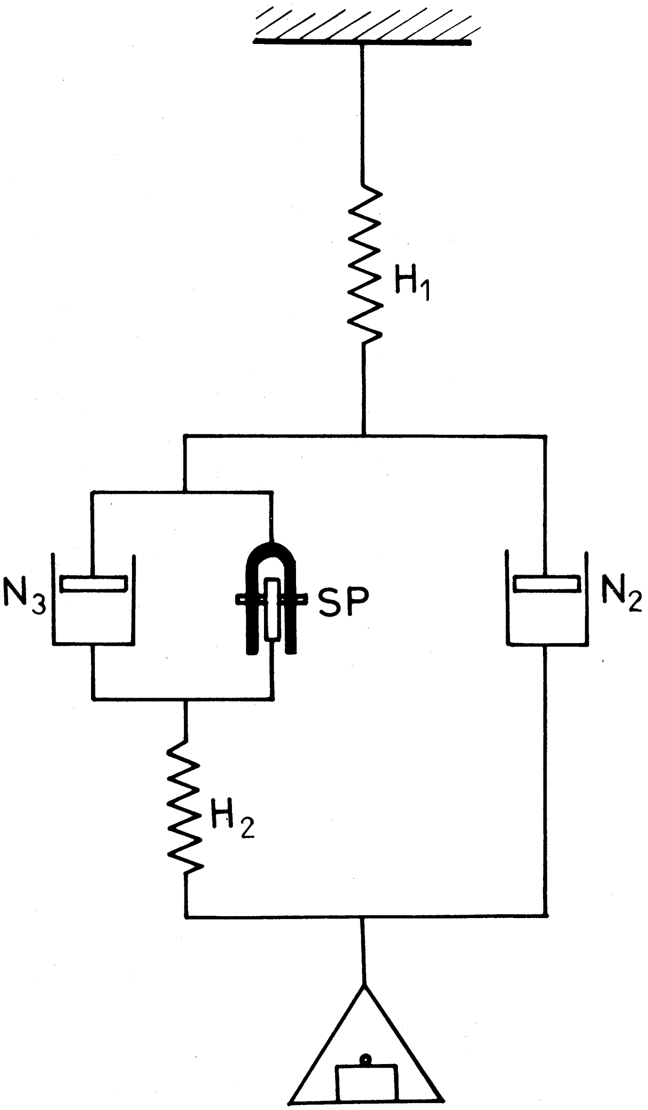

Fig. 15. The simplified rheological model of gluten gel. Below yield, as long as the shear pin remains intact, the lower portion of the model represents a Kelvin body ($H_2|N_2$), the whole model a Standard Linear Solid or Poynting-Thomson body. Upon yield, the element N_3, released from the restraint of the shear pin, transforms the Kelvin component into a Jeffreys liquid (13).

coiled configuration. The free ends of these residues (or side chains) interact in a number of ways, each of which contributes to the macroscopically observed mechanical behavior. These are, arranged roughly in the order of descending energy:

a) True cross-links, provided by S-S bridges connecting cystine, cysteine, and methionine residues, or by aldehyde and similar cross-links.

b) Ionic interactions between anionic and cationic end groups of the side chains.

c) H-bonds which may connect both intermolecular and intramolecular sites, such as nitrogen- and oxygen-containing groups.

d) Hydrophilic (polar) and hydrophobic (mostly apolar) interactions based on the forces acting between hydrophobic groups in a polar medium.

e) Weak interactions such as dipole-dipole interactions, or induced dipole interactions, and London or dispersion forces.

In molecular mechanics it is customary to distinguish between true cross-links representing real chemical bonds between adjoining segments and "entanglements," a term which lumps together all other interactions. Some authors, *e.g.*, Bueche (17), distinguish between intertwined loops of molecular chains on one hand and groups of segments of close proximity and random configuration which "nothing but" entangle each other in a loose way without forming crossed loops on the other. The first would require strong forces capable of breaking the covalent backbone bonds in order to disentangle the chains, comparable to those required to break cross-links, while the latter type obviously yield to lesser forces.

In a cross-linked rubber the cross-links prevent unlimited relative chain displacement as a result of external forces and hence are responsible for the "solid" character of rubbers, warranting complete recovery (15).

In ordinary[3] "thermoplastic" linear polymers nothing but intermolecular forces of the physical type c-e are responsible for cohesion. The external forces to which these interactions yield depend on temperature and on the rate of deformation, the range dividing "solid" from "fluid" behavior being termed the "solid-liquid transition range of temperature."

With this picture in mind, we can tentatively explain the observed facts by comparing the yield transition to the solid-liquid transition temperature. The source of the energy required for the disentanglement, which underlies viscous flow and energy decay is, however, in our case, the external mechanical work supplied by the acting stress, and not the thermal energy usually responsible for the solid-liquid transition. Regarding the time effect, we refer to earlier publications in which the value of the time-energy product (or "action") has been suspected of being the real parameter responsible for similar transitions which occur under isothermal conditions (12,18).

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[3] This excludes polyelectrolytes and ionomers.

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