

## Dynamic Rheology of Modified Starches\*

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### Introduction

Most of the food uses and industrial applications of starch involve the mechanical properties of pastes made by heating aqueous dispersions of the granules; in many cases the granules have been modified by acid, oxidants, or crosslinking agents before pasting. In recognition of this fact, the corn wet-milling industry has made extensive use of viscometers and gel testers in characterizing pastes, generally with results that are recognized as providing only tentative answers; reproducibility has been poor and interpretation of the information has not been particularly revealing of the fundamental chemistry of starch.

The characterization of starch pastes by viscometry has been unsuccessful because the measurement is destructive of the system being measured and because viscometry reveals only part of the information needed for a reasonable characterization of any paste which possesses structure. Similar objections can be leveled at measurements of gel strength.

This paper describes the development of a non-destructive means for determining the mechanical properties of starch pastes and the application of the method to the study of two series of chemically modified starches.

### Viscoelasticity

The alternative to viscometry in monitoring a starch modification, and in predicting the performance of the modified starch produced therefrom, is a dynamic study of the elastic and viscous parameters governing its mechanical behavior. Basically, one must evaluate not only the viscosity and elasticity but also determine how these two

parameters are interrelated. If the paste is rigid, its properties are those of a *viscoelastic* substance; if no structure exists, the paste is *elasticoviscous*. This study covers the borderline region in which are found extremely fragile structures.

The type of dynamic measurement which best reveals gross structural features of this nature is the application of low-frequency shear waves to the paste. This measurement was performed on a series of acid-modified corn starches and on a series of phosphate-crosslinked white milo (waxy sorghum) starches, using a rotational viscometer<sup>1</sup> modified so as to reciprocate at frequencies ranging from 0.1-40 cycles/sec. and at an oscillation amplitude of 1.5 to 3°. Results were converted into dynamic viscosity  $\eta$  and rigidity  $G$  with sufficient precision to permit comparisons within a given series of modified starches.<sup>2</sup> Both  $\eta$  and  $G$  (often called the modulus of shear elasticity, contrary to the usage employed in the starch industry) are frequency dependent, and this behavior requires an arbitrary selection of conditions.

### Experimental

#### *Instrumentation*

A mechanical oscillator was constructed along lines similar to a resonance elastometer,<sup>3-5</sup> wherein a cup containing the material under study is driven harmonically at a given amplitude, and a coaxial bob suspended in the material responds by oscillating at an amplitude which depends on the frequency with which the cup (and therefore the bob) is driven. At a given frequency the bob achieves its maximum amplitude and the system is said to be in resonance. The theory and operation of this type of instrument have been developed by Markowitz<sup>6</sup> and Oldroyd.<sup>7</sup>

The instrument employed in this study was constructed from a rotational viscometer<sup>1</sup> employing a ring immersed in an annular-shaped cup (Fig. 1). The advantages of this instrument are

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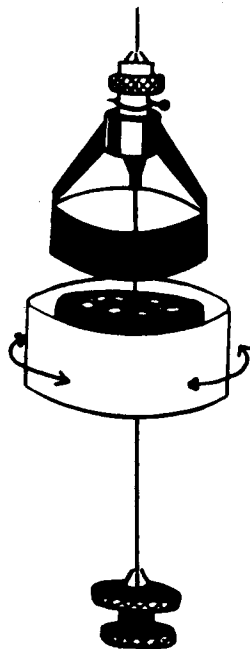


Fig. 1. Dynamic viscometer consists of oscillating cup containing the paste and ring immersed in the paste. Amplitude of ring oscillation depends on cup oscillation frequency. Adapted from *SPE Journal* by permission.

its large torque and shear area, the frictionless suspension of the ring, and the consequent high sensitivity to changes in the mechanical properties of the material under study. The viscometer was converted into a reciprocating instrument by means of a variable speed cam drive. Deflection of the ring was measured optically.

#### Measurements

The dynamic viscometer was operated by choosing a wire with a torque constant low enough so that the instrument resonant frequency lay far below the resonant frequency  $f_0$  of the sample. Observations were made of the relative amplitude  $m$  as a function of frequency  $f$  (when  $m$  exceeds 1, the ring oscillates with a larger amplitude than the cup). The low-frequency limiting value of  $m$  was 1;  $m$  increased to a maximum governed by the sample viscosity at a frequency governed by the geometrically dependent sample rigidity  $k$  and by the moment of inertia  $I$  of the ring. The relation between  $k$  and  $I$  is given by

$$k = I\omega_0^2 \quad (1)$$

where  $\omega_0 = 2\pi f_0$ . In short, the qualitative statement may be made that rigidity is related to the square of the resonant frequency.

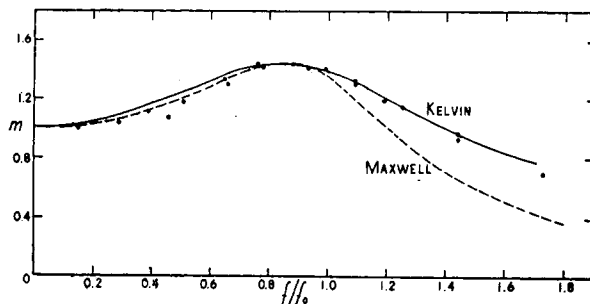


Fig. 2. Phosphated white milo starch (sample *E*) produced an amplitude curve which was approximated by a Kelvin model (solid line) with  $G = 71$ ,  $\eta = 2.1$ . Best fit by Maxwell model is shown by dashed line. Ordinate  $m$  is ratio of ring amplitude to cup amplitude;  $f$  is the observed frequency and  $f_0$  is the frequency without viscous damping ( $f/f_0 = \psi$ ).

If the material is highly "elastic," then the sample rigidity  $G$  may be calculated from the relation

$$G = k/a \quad (2)$$

where  $a$  is a geometrical factor containing the cup clearances and radii. The factor  $a$  is evaluated from viscosity measurements of Newtonian materials, and is 4020 cm.<sup>3</sup> for the ring and cup used in this work.

Equation (1) shows that some control may be exercised over the resonant frequency by varying  $I$ , thereby extending the useful range of measurement by the addition of weights to the ring.

In order to obtain  $\eta$  as well as  $G$ , either a second measurement must be made, such as the determination of phase angle between cup and ring, or else a viscoelastic model must be assumed to represent the mechanical behavior of the material. The former alternative is the more elegant method, but the latter produces an analog which serves as an excellent means of communication. In these preliminary experiments the model technique was employed. As a first approximation, two 2-parameter models were assumed as representative of a viscoelastic and elasticoviscous system: the Kelvin model<sup>8</sup> with a spring and dashpot in parallel for a (viscoelastic) gel, and the Maxwell model with the units in series for the (elasticoviscous) sol. Then parameters were selected which produced the best fit of the experimental data.

In most cases the Kelvin model produced the most satisfactory fit of the data. A typical match is shown in Figure 2. Values for  $\eta$  and  $G$  were 2.1 poises and 71 dynes/cm.<sup>2</sup>, respectively. In this instance a Maxwell model could be constructed to

fit the data, but only by using an unreasonably high value for  $\eta$ .

### Calculations

It is instructive to develop the equations which express the dependence of ring amplitude on frequency in the case of a Kelvin solid. For the present instrument, the following differential equation

$$I \frac{d^2\theta}{dt^2} + a\eta \left[ \frac{d\theta}{dt} - \frac{d\Omega}{dt} \right] + g\theta + aG[\theta - \Omega] = 0 \quad (3)$$

resolves the forces present in the case of a Kelvin body, if inertial forces in the liquid are neglected. The first term expresses the inertial force on the ring; the second term accounts for the viscous damping by the paste, which depends on the shear rate denoted by the bracketed term; the third term expresses the restoring torque of the torsion wire; and the fourth term accounts for rigidity of the starch paste,  $\theta$  is the angular displacement of the ring and  $\Omega$  is the angular displacement of the cup;  $g$  is the wire torsion constant and is made much smaller than  $aG$ . Then, if the cup is given the steady oscillation  $\Omega = \Omega_c e^{i\omega t}$ , the relative amplitude  $m$  turns out to be

$$m = \frac{\theta_r}{\Omega_c} = \left[ \frac{d^2 + \frac{1}{\psi^2}}{d^2 + \left(\psi - \frac{1}{\psi}\right)^2} \right]^{1/2} \quad (4)$$

where  $\theta_r$  is the oscillation amplitude of the ring and  $\Omega_c$  is the oscillation amplitude of the cup at any given frequency. Here  $\psi$  is the dimensionless frequency variable  $f/f_0$ , and  $d$  is the damping coefficient of eq. (3) divided by the undamped resonant frequency:

$$d = \frac{a\eta}{I\omega_0} = \frac{a\eta}{2\pi I f_0} \quad (5)$$

The frequency at which maximum amplitude is observed does not correspond to the resonant frequency  $f_0$  of the undamped system. If eq. (3) is solved for the undamped situation (involving only the first and last terms)  $\omega_0$  results, for in undamped systems with small  $g$  the equation

$$\frac{d^2\theta}{dt^2} + \frac{aG}{I} (\theta - \Omega) = 0 \quad \text{or} \quad \frac{d^2\theta}{dt^2} + \omega_0^2 (\theta - \Omega) = 0 \quad (3a,b)$$

applies. Instead, the oscillation peaks occur at  $\omega_1$ , which lies somewhat lower in damped systems. Therefore, it is necessary to distinguish between the natural, undamped, resonant frequency  $f_0$  and the observed resonant frequency  $f_1$  (otherwise, calculations of  $G$  would not provide the true shear modulus of elasticity). To exploit  $f_1$ , eq. (4) is differentiated and  $dm/d\psi$  is equated to zero. For the Kelvin solid the damping coefficient  $d$  can then be found in terms of  $\psi_1$  (the ratio of  $f_1$  to  $f_0$ ):

$$d = \left[ \frac{2(1 - \psi_1^2)}{\psi_1^4} \right]^{1/2} \quad (6)$$

When eq. (6) is substituted into eq. (4) at  $m = m_1$ ,  $\psi_1$  is obtained from the relation involving only the measured peak amplitude:

$$\psi_1^2 = \left[ 1 - \frac{1}{m_1^2} \right]^{1/2}; \quad \psi_1^4 = \frac{m_1^2 - 1}{m_1^2} \quad (7)$$

Maximum amplitude  $m_1$  is used directly to evaluate both  $\psi_1$  and  $d$ . The rigidity  $G$  is obtained by rewriting eqs. (1) and (2) in terms of the observed resonance frequency (using the identity,  $\psi_1 = f_1/f_0$ ):

$$G = \frac{I}{a} \omega_0^2 = \frac{4\pi^2 f_1^2 I}{a\psi_1^2} \quad (8)$$

This equation permits one to calculate  $G$  directly from the measured values of  $f_1$  and  $m_1$ .

The value of  $\eta$  is obtained by rewriting eq. (5) as

$$\eta = \frac{2\pi f_1 I d}{a\psi_1} \quad (9)$$

where  $I$ , the moment of inertia, is 323 g.-cm.<sup>2</sup> and  $a$  is the instrumental constant of eq. (2).

A typical calculation is made as follows: the measured values are  $f_1 = 9.4 \text{ sec.}^{-1}$  and  $m_1 = 5.0$  (relative to 1 when the ring is locked to the cup). The first quantity to be calculated is

$$\psi_1^4 = \frac{m_1^2 - 1}{m_1^2} = \frac{24}{25} = 0.960 \quad (7a)$$

$$\psi_1^2 = 0.978; \quad \psi_1 = 0.988$$

Then

$$d = \left[ \frac{2(1 - 0.978)}{0.960} \right]^{1/2} = 0.214 \quad (6a)$$

And, from these values, knowing  $I$  and  $a$ ,

$$\eta = \frac{6.28 \times 9.4 \times 323 \times 0.214}{4020 \times 0.988} = 1.03 \text{ poises} \quad (9a)$$

$$G = \frac{39.9 \times 88.5 \times 323}{4020 \times 0.978} = 290 \text{ dynes/cm.}^2 \quad (8a)$$

### Materials

White milo starch was crosslinked at the laboratories of the Corn Products Co. by treatment of aqueous slurries with sodium trimetaphosphate.<sup>9</sup> Table I gives the identities of five samples investigated. Sample *A* is a random production batch of white milo starch; samples *B*, *C*, and *D* are random selections from production batches of crosslinked material; and sample *E* is an experimental phosphated starch made by an alteration in the process which produces significantly higher phosphate content. The samples constitute a series in that they are listed in order of decreasing viscosities of the hot pastes (Hot Scott viscosities).

TABLE I  
Characteristics of Phosphated White Milo Starch

Sample	Consistency	Phosphorus, % (dry basis)	
		Soluble	Combined
<i>A</i>	Long-stringy	0.0004	0.0038
<i>B</i>	Short-cohesive	0.0073	0.0067
<i>C</i>	Medium-long	0.0011	0.0060
<i>D</i>	Thin-watery	0.0017	0.0059
<i>E</i>		0.87	0.44

Each sample was prepared for the experiment by the following cooking procedure. Ten grams of the white milo starches containing roughly 10% water was placed in enough distilled water to make 200 g. total weight. The slurry was immersed in boiling water, stirred for 5 min., covered, and cooked 10 min. longer. Water was added to keep the total weight at 200 g. Gelatinization usually began about 2.5 to 3 min. after placing in the boiling water bath at temperatures ranging from 65 to 80°C. depending upon the sample.

The second series investigated consisted of samplings of an acid modification of cornstarch at increasing times of modification, and is listed in Table II. The acid was 0.2*M* HCl on a slurry basis. Alkali fluidity<sup>10</sup> numbers (which reflect the amount of molecular degradation) are given, along with intrinsic viscosities determined by repeated dilution of 2% alkaline solutions of the starch.

The control sample was removed from the slurry before addition of acid; samples withdrawn from the acid slurry were neutralized immediately to pH 4.5-5, filtered on a Buchner funnel, and

TABLE II  
Characteristics of Acid-Modified Cornstarch\*

Sample	Modification time, min.	Alkali fluidity number	Intrinsic viscosity $[\eta]$ , ml./g.
<i>F</i>	0	2.0	190
<i>G</i>	10	5.0	180
<i>H</i>	18	13.5	165
<i>I</i>	23	19.0	150
<i>J</i>	28	27.5	135
<i>K</i>	33	35.5	116
<i>L</i>	48	53.5	95
<i>M</i>	68	64.0	80
<i>N</i>	78	68.0	75
<i>O</i>	138	76.0	55

\* Modification and fluidity determinations were performed by Corn Products Co.

washed with a volume of distilled water equal to the original volume. The samples were then air-dried and ground in a Wiley mill.<sup>10</sup>

The cornstarch samples were prepared for the experimental run by the same procedure as used for the white milo starches, except that a 15-min. cooking time at 91° was employed and starch weights were corrected at the outset for their moisture content. Because the dry starch had to be slurried in cold water before pasting, 91° is only a nominal temperature which prevailed over the last half of the pasting step. Starch concentration was 5%, dry basis, in the acid-modified series.

Dynamic studies were performed at 25°C. 2 hr. after the samples were placed in the viscometer. The properties of the white milo series had become constant by this time; the magnitudes of both  $\eta$  and  $G$  for the cornstarch series were still rising, but the changes during the 15 min. required for the dynamic measurement were imperceptible.

## Results

### Phosphated White Milo Starch

Figure 3 gives the amplitude curves of the 5% pastes (wet basis) of the five starches listed in Table I. Table III lists the essential parameters which were used in calculating  $\eta$  and  $G$  from the curves according to eqs. (8) and (9).

An increase in temperature from 25°C. (the standard temperature) to 60°C. changed  $\eta$  to a lesser extent than  $G$ . This behavior of  $\eta$  is in sharp contrast to its large temperature dependence when determined viscometrically and may result from the drop in  $f_1$  with an increase in temperature. In a separate experiment not detailed here, the

TABLE III  
Dynamic Properties of Phosphate-Treated White Milo Starches

Sample	$T, ^\circ\text{C.}$	$m_1$	$f_1$	$\psi_1$	$d$	$\eta$ , poises	$G$ , dynes/cm. <sup>2</sup>
A	25	2.07	5.5	0.93	0.59	1.8	110
	42	2.09	5.1	0.93	0.59	1.6	94
	61	2.12	4.6	0.94	0.56	1.4	76
B	24	3.04	15.5	0.97	0.37	3.0	810
	40	2.77	14.5	0.96	0.40	3.0	710
	57	2.57	13.7	0.96	0.44	3.1	645
C Maxwell	22	1.64	10.9	0.89	1.56	9.6	475
	40	1.60	10.0	0.88	1.51	8.7	405
	60	1.55	8.7	0.87	1.45	7.3	314
D Maxwell	25.5	1.55	10.3	0.87	1.45	8.7	440
	44.5	1.48	9.9	0.86	1.39	8.1	420
	64.5	1.36	9.5	0.82	1.26	7.4	420
E	27.5	1.54	4.3	0.87	0.91	2.6	77
	46	1.43	3.7	0.84	1.08	2.8	61
	62	1.43	3.2	0.84	1.08	2.4	46

concentration  $c$  dependences of  $\eta$  and  $G$  were somewhat unexpected:  $\eta$  increased linearly with  $c$ , whereas  $G$  increased as  $c^2$ .

#### Acid-Modified Cornstarch

The family of resonance curves shown in Figure 4 was obtained with the series of acid-modified cornstarches. The steady trend toward lower resonant frequencies is immediate qualitative evidence of drastic steady decreases in  $G$  as the time in contact with acid was increased.

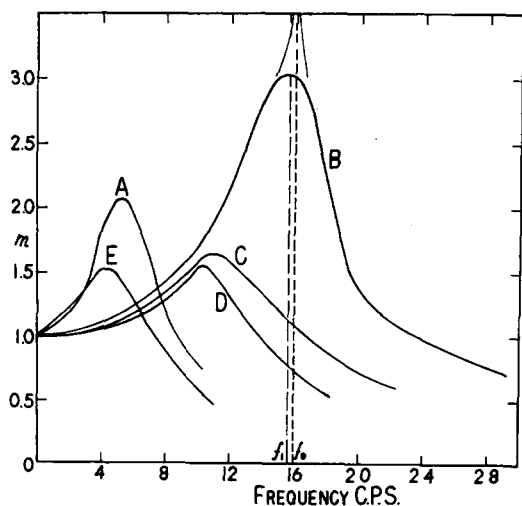


Fig. 3. Dynamic response of the crosslinked white milo starches of Table III. The amplitude curves vary in position and height of peak, as well as in breadth.  $G$  is proportional to  $f^2$ ;  $\eta$  is roughly proportional to the breadth.

Table IV lists the parameters used in evaluating  $\eta$  and  $G$  from eqs. (8) and (9) and indicates that the decrease in  $G$  far outpaces the decrease in  $\eta$  as the severity of acid treatment increases; however, part of this decrease is an artifact, as pointed out in the discussion. Current methods used by the industry measure  $\eta$ , which is the less sensitive of the two parameters available for monitoring the extent of modification.

Not only did the unmodified cornstarch have the expected characteristics of a gel but also this property was apparent to the fullest extent of modification when the pastes had been allowed to sit for 2 hr.

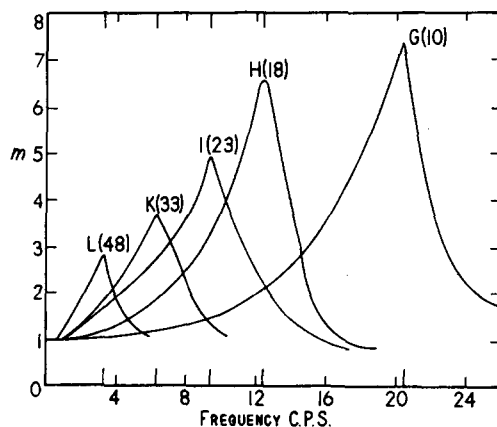


Fig. 4. Dynamic response of acid-modified cornstarches listed in Tables II and IV. Numbers in parentheses indicate the time of modification of the starch.

### Discussion

The properties and their trends that are revealed by dynamic viscometry are real, but in this early stage of their application their relation to preparation variables is strictly empirical. Any change in preparation conditions which effects a change in mechanical properties will net a change in the measured dynamic properties.

Viscosities of 5% pastes were so inclined to cluster around the interval 0.3 to 5 poises for both corn and white milo starches that little interesting information can be added to that already discussed. Rigidities provide a different story. Whereas one

crease in  $f_0$  invariably nets a decrease in  $\eta$  and may effect an increase in  $G$ .

Apparently, the additional phosphating of sample *E* results in the formation of ester groups without extensive intermolecular coupling. This type of behavior is in accord with the chelation possibilities of the phosphate group. It is also apparent that crosslinks which formed early in the reaction (or at low phosphate concentrations) were broken when additional ester groups were formed. Degradation of the starch molecule is not indicated although intrinsic viscosities in nonhydrolyzing media may provide better criteria of the reduction in molecular size.

TABLE IV  
Dynamic Properties of Acid-Modified Cornstarches

Code	$m_1$	$f_1$	$\psi_1$	$d$	$\eta$ , poises	$G$ , dynes/cm. <sup>2</sup>
<i>F</i>	8.32	18.0*	0.9965	0.119	2.81	2636
<i>G</i>	7.35	20.7	0.9953	0.139	1.46	1375
<i>H</i>	6.55	12.5	0.994	0.150	0.95	501
<i>I</i>	5.00	9.40	0.988	0.214	1.03	290
<i>J</i>	4.05	8.25	0.985	0.257	1.09	223
<i>K</i>	3.67	6.35	0.982	0.286	0.85	133
<i>L</i>	2.84	3.25	0.968	0.382	0.64	36
<i>M</i>	1.70	1.85	0.899	0.765	0.73	13
<i>N</i>	1.67	1.10	0.895	0.787	0.49	4.8
<i>O</i>	2.65	1.60	0.962	0.417	0.35	8.8

\* Here  $I = 843$  g.-cm.<sup>2</sup> for this sample;  $I = 323$  in all other cases.

is inclined to attribute the snapback of white milo starches to a high degree of elasticity, many workers confuse elasticity with the reciprocal of rigidity. In this connection, the relative magnitudes of  $G$  for unmodified milo and corn (samples *A* and *G*, respectively) may be compared. Cornstarch has much higher rigidity ( $f_1$  is five times as large) than does white milo starch, and yet the trade considers the latter to be more elastic than the former.

A pertinent observation about the effects of phosphating is that the elasticity is highly sensitive to the method of treatment, and therefore that the degree of crosslinking varies widely. Rigidity was a maximum at sample *B*; viscosity, at *C* and *D*. It is believed that these variations reflect differences in the ratio of monostarch phosphate to distarch phosphate.<sup>11</sup> It is clear, nevertheless, that variations in the amount of phosphate crosslinking altered the rigidity of white milo starch tenfold, but merely doubled the viscosity. Both  $\eta$  and  $G$  are frequency dependent, however, with the result that the in-

The excellent replication of results with the white milo starches, alluded to earlier, is not often found in starch rheology, and hence led to an intensive study of other series in which far greater latitude in physical properties of the pastes was permitted. Early in the investigation a series of four white milo samples had been provided<sup>12</sup> in paste form in order to learn if resonance elastometry could differentiate among the widely different consistency types. Peak locations and peak widths varied so widely that the raw data could be used directly in assigning numerical values to variations in consistency, without an intervening calculation of  $\eta$  and  $G$  and without the assumption of a model. Even more startling was the fact that, over a year later when the dry samples were again made into pastes and tested immediately, nearly identical results were obtained.

Many of the consistency terms used not only in the starch industry but also in other fields can be expressed on a quantitative basis by the use of dynamic data. For example, the milo starch

samples described as long and stringy had viscosities around eight poises and rigidities below 1000; short, cohesive structures of the type found in unmodified cornstarch exhibited  $G$ 's higher than for any of the other members of the two series described here, yet  $\eta$  was only two poises.

Turning now to the acid-modified cornstarch series, one realizes at once that dynamic studies reveal that the degradation mechanism proceeds by scission of natural linkages found in the native starch. The acid fluidizing reduces  $G$  at a much faster pace than the reduction of  $\eta$ : a 300-fold decrease in  $G$  occurred in the same conversion range as an eightfold decrease in  $\eta$ , according to Table IV, but again it must be recalled that the trend in  $G$  has been amplified by the peculiar nature of resonance-type experiments.

Reproducibility was not as good in the cornstarch samples as in the white milo starches, but here the quantity of information far overwhelms any reversals in  $\eta$  and  $G$  trends that may have appeared in error. There can be no question about the trends in  $G$  except to doubt the reversal at the high fluidity end of the series where the precision of the instrument was poorest. This problem resulted from the selection of a single starch concentration for the entire series in order to show the trends in Figures 3 and 4. The concentration had to be selected so as to be too high at the beginning of the series and too low at the end, thereby showing the middle of the series to best advantage.

### Conclusions

1. Quantitative and simultaneous evaluation of rigidity and viscosity has been provided for two series of starch pastes of widely different mechanical properties.

2. When white milo starches are treated with metaphosphate, both  $\eta$  and  $G$  reflect the degree of crosslinking. The peak in  $G$  occurs under different reaction conditions than the peak in  $\eta$ , thereby indicating that the intermolecular ester crosslinks compete with intramolecularly combined (chelated) esters.

3. When cornstarch is acid modified, both  $\eta$  and  $G$  drop. The decrease in  $G$  is considerably more rapid than the decrease in  $\eta$ .

4. Both series of starch pastes produced gels at 5% concentration. The mathematical expressions for rigid (Kelvin) bodies applied to the dynamic data reported in this study.

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### Synopsis

Viscosities  $\eta$  and rigidities  $G$  were determined for 5% pastes of phosphate-linked white milo starches and acid-modified cornstarches, using a resonance elastometer operating in the frequency range 0.1 to 40 cycles/sec. Most of the starches behaved as ideal Kelvin solids under these conditions, thereby permitting  $\eta$  and  $G$  to be evaluated from the height and location of the resonance peak. Sample calculations of  $\eta$  and  $G$  are given, followed by a discussion of the trends displayed by these values as the severity of treatment is increased.

### Résumé

Les viscosités  $\eta$  et les rigidités  $G$  ont été déterminées pour des pâtes à 5% d'amidon de milo blanc pontés au phosphate et d'amidons de froment modifiés aux acides à l'aide d'un élastomère à résonance opérant dans une gamme de fréquences allant de 0.1 à 40 cycles/sec. La plupart des amidons se comportent comme des solides Kelvin idéaux dans ces conditions, permettant ainsi l'évaluation de  $\eta$  et de  $G$  aux dépens de la hauteur et de la localisation du pic de résonance. Des exemples de calculs de  $\eta$  et de  $G$  sont donnés et sont suivis d'une discussion des tendances qui résultent de ces valeurs si on exigeait une augmentation de la sévérité du test.

**Zusammenfassung**

An 5% Pasten aus Phosphat-gebundener weisser Milostärke und säurebehandelter Maisstärke wurde mit einem Resonanzelastometer im Frequenzbereich von 0,1 bis 40 Hertz Viskosität  $\eta$  und Starrheit  $G$  bestimmt. Die meisten Stärkeproben verhielten sich unter diesen Bedingungen als ideale Kelvin-Festkörper und daher war die Ermittlung

von  $\eta$  und  $G$  aus der Höhe und Lage des Resonanzmaximums möglich. Beispiele für die Berechnung von  $\eta$  und  $G$  werden gegeben und eine Diskussion des Ganges der Richtung, in der sich diese Werte bei grösserer Strenge der Behandlung verschieben, wird durchgeführt.

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