Measurement of Gelpoint Temperature and Modulus of Pectin Gels

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ABSTRACT

Methods which permit the measurement of gelpoint (setting) temperature (T_{gel}) and rigidity modulus (G) of pectin gels were improved. Gel development on cooling was determined with an oscillatory pressure testing device capable of detecting a modulus as low as 3 Pa and strain values no greater than 5×10^{-3}. Sample was set in a glass "U" tube during pressure oscillatory assay for T_{gel} determination, and transferred after gelling in the same tube for G modulus determination with a modified Saunders-Ward apparatus. Results confirmed rheological behavior reported for these kinds of gels and compared favorably with small amplitude oscillatory measurements performed with a stress controlled rheometer using cone and plate (4°, dia = 4 cm) geometry at different frequencies (0.5 to 1.5 Hz) and cooling rates (1 to 3°C/min).

Key Words: pectin, gelpoint, rheology, rigidity, modulus

INTRODUCTION

PECTINS HAVE LONG BEEN USED AS GELLING AGENTS (Oakenfull and Scott, 1985) and those with >50% methylation, high methoxyl pectins (HMP) form gels in sugar solutions at concentrations higher than 55% and pH <3.5. The gelation of HMP with sugar is quite complex and several interactions are involved (Oakenfull, 1987). When conditions favorable to gelling are created by cooling a hot solution, a progressive association of long chain galacturonic acid molecules takes place. Large clusters are formed, and critical temperature (T_{gel}) where viscosity tends toward infinite and shear modulus G diverges from zero, is reached. This gel point is also defined as the stage at which the liquid begins to exhibit pseudoplastic properties, and may be conveniently observed from the inflection point on a viscosity time plot.

After adequate elapsed time, a stable gel is reached (Doublier et al., 1992). The rates of gel-structure development and gel strength are affected by type of pectin, pH, solute and temperature. The gel forming ability of pectin is usually determined by the SAG method (IFT, 1959) and commercial pectins are standardized by this method. However, in practice it is important to know at what temperature a gel will set under specified conditions.

There is no widely accepted method for determination of the temperature and time at which pectin gelation occurs. Characterization of G and T_{gel} can be done using a rheometer either with controlled step displacements or with dynamic oscillatory deformations (Lopes da Silva and Goncalves, 1994) and if fracture at the measured surfaces can be prevented, the yield stress also can be determined. There are, however, some limitations regarding size of samples and control of dehydration when commercial rheometers are used. The transition from viscolastic liquid to viscolastic solid is gradual with no discontinuity in rheological behavior. A reliable, practical gelling point determination method should: (i) be non-destructive; (2) deform gels within the linear viscolastic range; and (3) be expressed in fundamental terms. Our objective was to develop a low cost device for obtaining quantitative data on T_{gel} and G of HMP during the sol-gel transition, based on a long-known established method (Saunders and Ward; 1954) and a simplified technique for gelpoint measurement proposed by Dahme (1992).

MATERIALS & METHODS

Pectin sample

The pectin samples were: (1) commercial HMP citrus pectin (CP sample) obtained from Braspectin (Brazil), with anhydrogalacturonic acid content (AGA) 62.0% and degree of methylation (DE) 54.2%; and (2) and apple pectin (AP sample) from Sigma Chem. Co. (AGA = 77.5%). Pectin dispersions were prepared as indicated (IFT, 1959 Method 5-54). Pectin concentration was varied over the range 0.25–0.75%.

Gelpoint measurement: Oscillatory pressure testing device (OPTD)

The basic concept was from the device described by Dahme (1992). The apparatus (Fig. 1) consisted of a modified Teflon piston pump with variable speed (0-100 strokes/min ≃1.33 Hz) and 0.30 mL/stroke [1]; a narrow stainless steel connection tube system (2 mm i.d.) [2]; a solenoid valve [3]; glass "U" tubes 1.23 cm i.d., 30 mL capacity [4]; a Differential Pressure Transducer Modulus T40

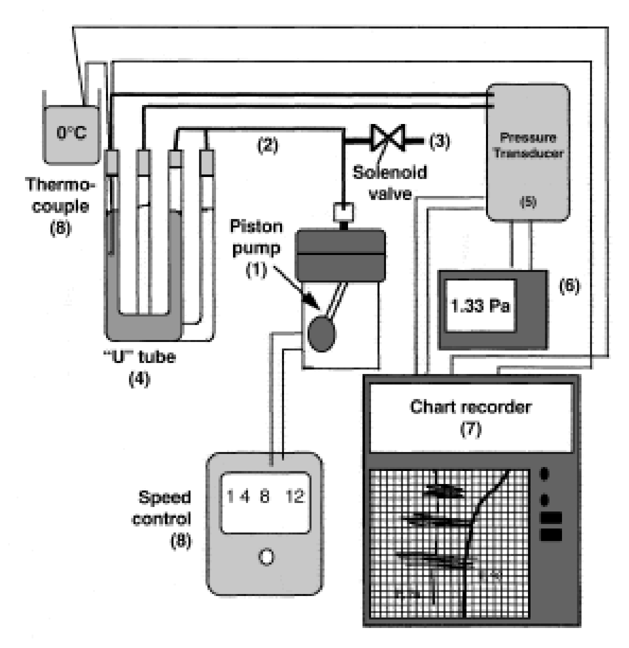

Fig. 1—Oscillatory pressure testing (OPT) device. Teflon piston pump [1]; connection tubes [2]; solenoid valve [3]; glass "U" [4]; a Differential Pressure Transducer[5]; Digital Indicator [6]; potentiometric chart recorder [7]; solenoid valve [8]; thermocouple [9].

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(Modulus Instrument Inc., Northboro, MA) [5]; a Digital Indicator (Cole-Parmer, Model 7350-31) [6]; and a two channel potentiometric chart recorder (Rikadenki, Model DB3; Toshin Electron, Tokyo, Japan) [7]. The principle of operation was: a variable sinusoidal pressure generated by the piston pump displaced the volume of the liquid column in both "U" tubes, one filled with hot pectin/sugar solution at a temperature higher than T_{gel}, and the other filled with water. Tubes were fixed into an isolated box where the rate of cooling was 2.5 °C/min. The imposed variable sinusoidal pressure on one branch of tubes generated a sinusoidal output in the other branch. These output pressure variations were subtracted in the pressure transducer and recorded.

A typical test was conducted as follows: Hot pectin/sugar and water were into two "U" tubes which were connected to the pumping system and the pressure transducer, respectively. The pump was started and periodically a timer closed the solenoid valve [3] (13 sec open/30 sec closed) to allow the pump to displace the liquid column of both "U" tubes. At this point the response the two tubes compensated each other, and the compared pressure signal was near zero. When the temperature of the hot solution reduced to a value near T_{gel} the viscosity and/or the rigidity of the gel reduced the pressure output as compared with the other tube and the output was recordered in appropriate pressure units. The temperature reduction was sensed by a thermocouple [8]. This output value increased with gel formation. In the linear region, no residual differential pressure was measured after pressure release, and this behavior could also be used as elastic linear confirmation. In the linear region, the shear modulus (G) is given by:

$$G = \pi P R^4 / 8VL \qquad (1)$$

where L = length of gel sample; P = acting pressure; R = tube radius; and V= volume displaced. V depended on the stroke volume of the piston pump (Vp) and the output differential pressure (DP), as given by the linear relationship:

$$V = (Vp/2) - b\ \Delta P \qquad (2)$$

where under our experimental conditions, Vp = 0.319 mL; and b = 0.399×10^{-3} $mLPa^{-1}$. Considering this double "U" tube system, the maximum volume deformation in the gel side was Vp/2 (0.159 mL). Consequently, for a gel probe of 1.23 cm dia and 25 cm length, calculated maximum strain results: $\gamma = \Delta L/L = 5 \times 10^{-3}$. Dahme (1985) concluded that weak HM pectin-sugar-water gels showed a linear viscolastic region for $\gamma \leq 0.05$ for elastic deformation and that fracture occurred in the deformation region $0.6 \leq \gamma \leq 0.7$. For rigid gels, Eq(1) did not calculate the modulus value, due to the proximity between P and ΔP. Therefore, this method is only proposed for determination of T_{gel} and G through deformation during the very early stages of gelling. For absolute determinations of shear modulus in more rigid pectin gels, the classical method with the following modifications is proposed.

Modified Saunders-Ward (MSW) method

Saunders and Ward (1954) showed that a sample of gel in a glass "U" tube together with a capillary filled with an indexing fluid could be used to determine the modulus G, calculated from Eq(1). In the case of soft gels, a modification was proposed in the "U" tube construction in which a nearly horizontal capillary containing a drop of colored alcohol was attached. In our work, the capillary [4] was attached vertically and filled with inked ethanol (Fig. 2). The capillary in a vertical position ensured that the movement of the alcohol resulted only from deformation of the gel and not from its slipping along the walls of the tube. Moreover, this modification simplified the volume measurement with a cathetometer (accuracy 0.001 mm) and avoided the use of mercury. The air supply was a compressed cylinder [1]; the flow was controlled by a needle valve [2] and determined by a mass flowmeter [3]. The pressure *P* required in Eq(1) was measured with the same transducer-indicator as shown (Fig. 1). Total recovery of the initial volume was assumed to indicate that the gel was strained in the linear elastic region.

Rheological measurements

Small amplitude oscillatory (SAO) measurements were performed with a Bohlin RVO stress controlled rheometer using cone and plate (4°, dia = 4 cm) geometry. Strain values <5% were selected. Storage moduli G′ and loss moduli G″, the elastic and viscous components of the sample solution respectively, and phase angle δ were measured at three different frequencies (0.5 , 1,0 and 1.5 Hz) and cooling rates of 1, 2 and 3°C/min.

RESULTS & DISCUSSION

DETERMINATION OF THE GELPOINT WAS DERIVED FROM THE recorded sample temperature and differential oscillating pressure vs time plot, respectively (Fig. 3). The sinusoidal nature of output was not observed due to the low speed. A typical curve for different concentrations of HMP (65% w/w of sucrose, pH=3) showing the evolution of ΔP with temperature (T) was plotted (Fig. 4). At temperatures higher than the estimated T_{gel} (1st Region) a moderate and near exponential increase of ΔP with T was observed. By following one of the curves the beginning of the periodical pressure signal indicated the setting temperature (e.g. for 0.35% HMP solution the temperature of gelation was in the range 48-52°C). This is referred to as the "true gel temperature," $T_{gel,r}$. From a practical point of view, a more

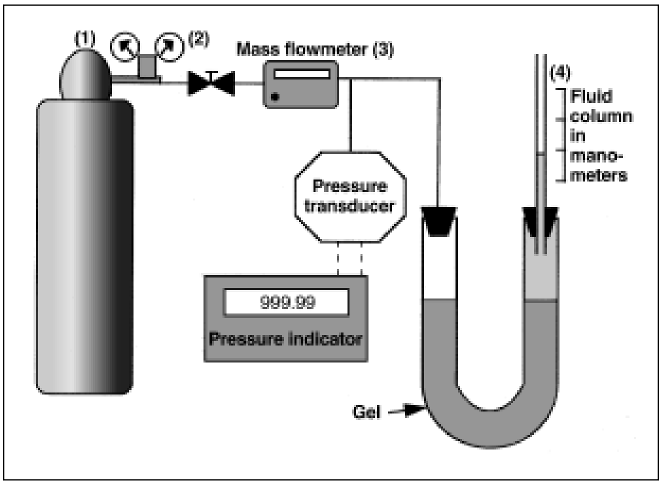

Fig. 2—Modified Saunders-Ward method. Compressed air cylinder [1]; needle valve [2]; mass flowmeter [3]; capillary tube [4].

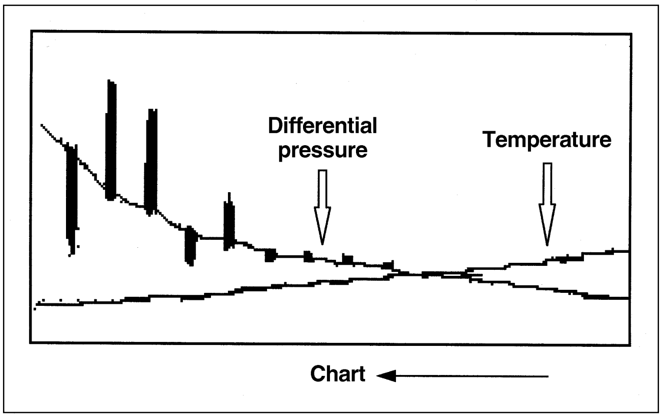

Fig. 3—Typical record of sample temperature and differential pressure variation with time.

Table 1—Gelation temperature($T_{gel,p}$) determined for different pectins and concentrations

Pectin[a]	Conc (%)	True gel temp $T_{gel,r}$ (°C)	Practical gel temp $T_{gel,p}$ (°C)
CP	0.25	46–49	45 (1.3)*
	0.35	48–52	49 (2.1)
	0.50	53–56	54 (2.0)
	0.65	67–72	56 (1.5)
AP	0.25	70–75	64 (2.5)

*Standard error.
[a]CP= citrus pectin; AP= apple pectin.

Table 2—Gelation "true gelling temperature" ($T_{gel,r}$) determined with the rheometer for 0.35% CP pectin solution

Frequency (Hz)	Cooling rate (°C/min)	$T_{gel,r}$(G′= G″) (°C)	$T_{gel,r}$(δ_o/2) (°C)	$T_{gel,r}$ (avg) (°C)
0.5	1.0	64.0 (1.0)*	68.2 (2.8)*	66.1
	2.0	62.0 (7.1)	66.2 (4.1)	64.1
	3.0	68.9 (2.9)	66.7 (2.9)	67.8
1.0	1.0	68.3 (3.1)	65.7 (4.7)	67.0
	2.0	64.5 (4.0)	58.5 (4.5)	59.5
	3.0	51.4 (4.4)	46.7 (0.5)	49.0
1.5	1.0	65.2 (3.9)	60.6 (4.3)	62.9
	2.0	62.0 (2.3)	58.0 (3.1)	60.0
	3.0	41.2 (0.5)	44.0 (0.1)	42.6

*Standard error, %.

easily read value is preferable for routine gel point determination. When temperature was further reduced (Fig. 4, 2nd region) a linear dependence of ΔP with T was shown. Extrapolation of the linear region to the abscissa was considered to be the "practical temperature of gelation" $T_{gel,p}$ ($T_{gel,p}$ = 46°C for 0.35% HMP solution). Values were satisfactorily linear in the applied range of pressure, and a linear elastic behavior was assumed. The gelation temperature was determined for different pectins and concentrations (Table 1). At concentrations >0.7%, results were not very reliable. This was attributed to the high kinetic rates of the gelation process at elevated concentrations, even at low cooling rates. Dependence of T_{gel} on pectin concentration was shown (Fig. 5). Gelpoint increased linearly with concentration and results confirmed those of Barford and Pedersen (1990) for similar pectin gels. Calculated shear modulus (G) during the beginning of gelation was in the range of 2-6 Pa.

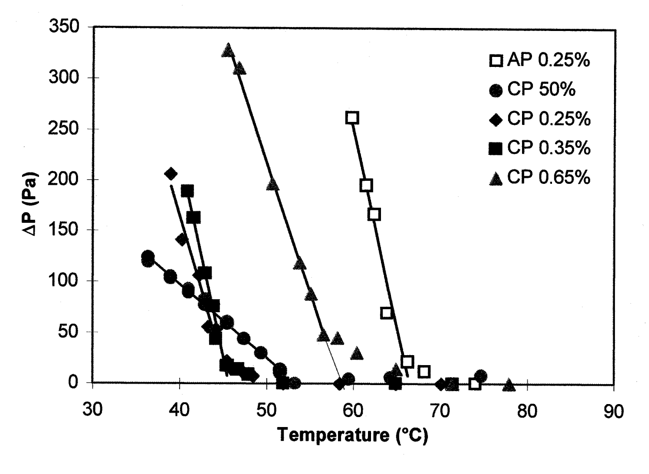

Fig. 4—Increase of ΔP with cooling for different pectin samples. Linear extrapolation to the abscissa indicates T_{pg} value.

Rheology results

Semilogarithmic plot of G′, G″ and δ vs temperature was obtained from small amplitude oscillatory (SAO) measurements (Fig. 6) at constant frequency during controlled cooling. Two dynamic methods have been proposed for testing the setting temperature in these types of gels: (1) the temperature where the total phase angle variation was halved ($\Delta\delta_o/2$) (Barford and Pedersen, 1990) or (2) the temperature were G′= G″. In food gels, G′= G″ at a given frequency can be regarded as reliable criterion to define the gel point, if the chosen frequency is sufficiently low (Doublier et al., 1992). As shown (Fig. 6), G′ also showed two regions, as in the case of OPTD measurements. After an initial unstable period (90-75°C) attributable to low viscosity of samples and the inertia of the cone and plate geometry, G′ rose in a non-linear way (first region) from about 0.1 Pa to 10 Pa (50-72°C), including the crossing point with G″ at a well defined temperature ($T_{gel,r}$). As cooling proceeded, G′ increased linearly with time (second region). The point where the extrapolation of the second region intercepts the tangent in $T_{gel,r}$ nearly coincided with the proposed practical gel point ($T_{gel,p}$). Pectin gels are weak gels and both cooling rate and oscillatory frequency influence measurement of T_{gel}. Values obtained for $T_{gel,r}$ at different cooling speeds were evaluated (Table 2) by the two criteria (G′= G″ and $\Delta\delta_o/2$). Practically no differences were found in the range of frequencies

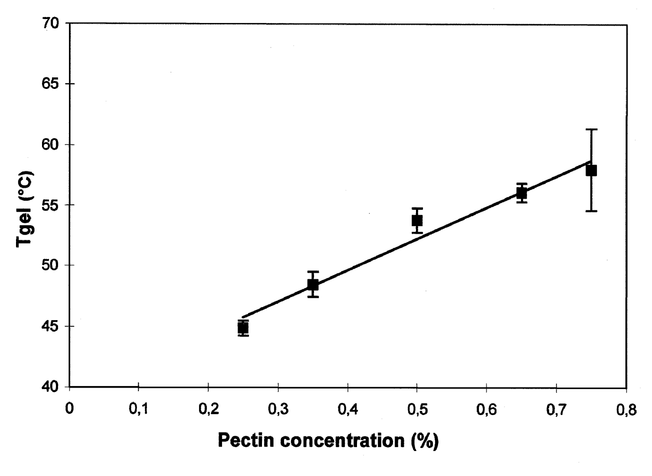

Fig. 5—Variation of T_{pg} with pectin concentration determined with the OPT method.

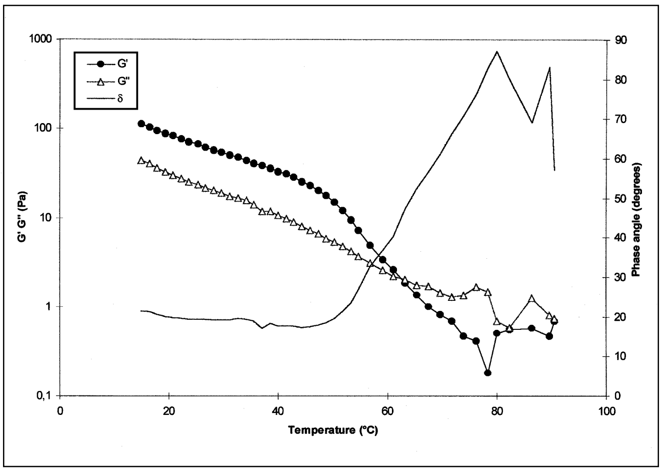

Fig. 6—Semilogarithmic plot of G′, G″ and δ as related to temperature, obtained from small amplitude oscillatory (SAO) measurements at constant frequency (1.5 Hz) during controlled cooling (2.0 °C/min).

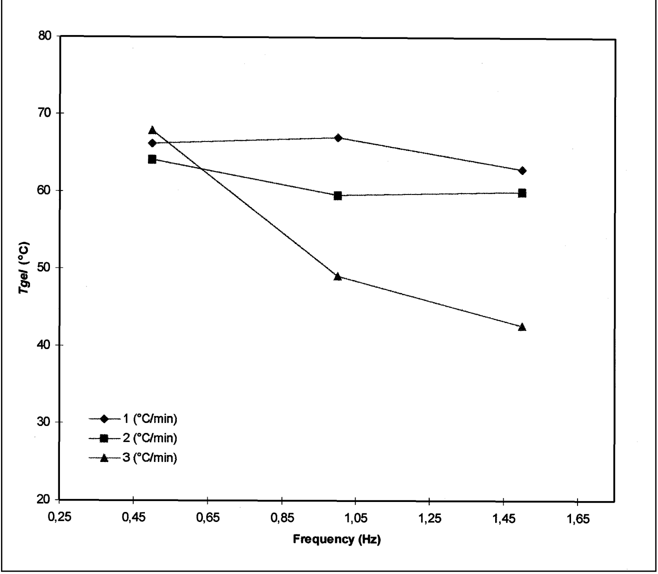

Fig. 7—Influence of frequency of oscillation on T_{rg} (average) at different cooling rates.

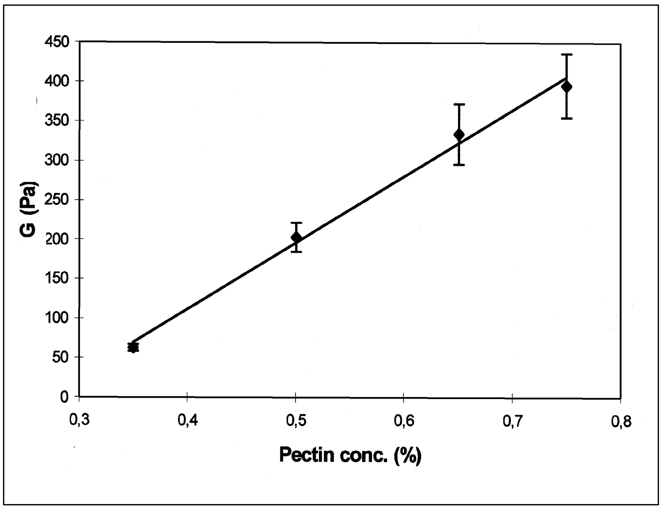

Fig. 8—Variation of modulus G with pectin concentration (citrus pectin) determined with the MSW apparatus.

(0.5 to 1.5 Hz) at cooling rate 2.0°C/min in accordance with the pressure pulse frequency used with the device we described. However, at a cooling rate of 3.0 °C/min, the influence of oscillation frequency was apparent **(**Fig. 7**).** Our results confirmed previous works on weak gels reviewed by Oakenful (1987) and Doublier et al. (1992), among others.

Shear modulus determination of HMP gels

Once aging proceeded and the gel was rigid, the dynamic method was inappropriate and G determinations could be accomplished in the classical modified configuration, after transferring the gel in the "U" tube from the OPT device (Fig. 1) to the MSW apparatus (Fig. 2). The rigidity of citrus HMP gels was found to depend on concentration (Fig. 8). It was difficult to obtain reliable data above 0.75% pectin levels. The concentration of sample by evaporation could be neglected due to the relatively large volume assayed.

CONCLUSION

GELATION TEMPERATURE T_{GEL} DEPENDED ON VARIABLES including type and concentration of pectin, type and content of soluble solids, pH, temperature, rate of cooling, method of preparation and aging of pectin solution regardless of method applied. No method has been widely accepted for the determination of T_{gel}, because pectin gels are complex, multi-variable systems. The methods described here were rapid. The OPT method was sufficiently sensitive and precise to evaluate pectin gels formation from practically the beginning of gelation. However, a more practical $T_{gel,p}$ value was proposed for standardizing and comparison of pectins of the same origin. The true setting temperature measured on the rheometers was ≈3°C higher than that measured by the proposed method. This was probably due to the greater sensitivity of the SAO method.

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