



FROM RESEARCH  
& DEVELOPMENT



**Rheological Methods  
to Characterize Pectins  
in Solutions and Gels**

## Introduction

The development of new rheological measuring devices has given us a wide range of possibilities to characterize pectins in solutions and gels. This may give us important data for

- the layout of technological processes
- the quality control of raw materials, and standardized products or
- the determination of material specific data in research and development.

This treatise wants to give a short but not necessarily complete overview of the standard rheological equipment of a modern progressive laboratory in the food industry, starting off with purely empirical rheometers like the Ridgelimeter, the Pectinometer of Herbstreith & Fox, and penetrometers, passing over to more sophisticated instruments, capable to give fundamental data.

## The Ridgelimeter

The ridgelimeter is the most commonly used device to standardize highly methoxyl pectins for commercial use (Cox and Higby 1944). This empirical Sag-test is a one-point, non-destructive measurement.

In spite of the excellent reproducibility and easy handling this method has the disadvantage, that it takes in only the elastic properties of the gels. But Mitchell (1980) pointed out, that the breaking strength of a gel may not be related to the gel's elastic modulus, and therefore measurements based on breaking strength will not rank a series of gels in the same order as the Sag test.

The reason for this behaviour is due to the molecular weight. The elastic modulus will remain constant when reaching a certain molecular weight, while the breaking strength will further increase.

Sag measurements are therefore not a sufficient quality criterion.

## The Herbstreith Pectinometer

The original method was developed by Lüers and Lochmüller in 1927 using a beam balance. The results of this method correlate well with the firmness and the sensory impression of the gels of confectionery articles, and jams, jellies, and marmalades. The development of the Herbstreith-Pectinometer is based on this method. The breaking strength of the gel is now measured with a wire strain gauge. The breaking strength obtained is the maximum value derived from the force variation during the entire measurement, according to the tension needed to pull the standardized shear insert out of the gel filled into a standardized test cup. With a new software program it is possible to measure the "Texture Constant" of pectins. This "Texture Constant" K is calculated by the ratio of the maximum force during the time interval of the measurement and the measured area below the force-time curve. The resulting "constants" K correlate well with the dynamic Weissenberg number of oscillating measurements carried through with the same pectin gels.

An elastic brittle gel will give a relatively high "Texture Constant". Compared to elastic brittle gels, elastic viscous gels with the same maximal breaking strength resist the gliding of the shear insert to a greater extent. For this a greater force during the time is needed and therefore the area below the force-time curve is larger, and the "Texture Constant" small. The sensory examination of gels formed from pectins of different raw materials, confirms the test results. The sensory examination reveals, that gels made from apple pectin, with their small values for the "Texture Constant" K, need a lower rupture strength than gels made from citrus or citrus/apple pectin to be regarded as equally firm (Kratz, 1994).

#### **Penetrometers**

Penetrometers are easy to use and giving good results and correlating well with the sensory assessment of gels etc. Nevertheless these instruments yield purely empirical methods working on the principal of linear compression, penetration or back extrusion.

At the penetrometers the form and the weight of the probe are preselected depending on the test material. The penetration speed or the penetration depth can not be preselected. The penetration measurements are based on the gravitational force applied by the probe.

#### **The Texture-Analysers**

The texture analysers have been specifically designed to examine the texture of foodstuffs. They are multifunctional, giving values for the gel strength and penetration as well as penetration curves. The probe is pressed on or into the tested sample with a preselected speed and distance. The starting point of the measurement

is reached, when the plunger touches the surface of the sample with a certain minimum load. The breaking strength of gels can be determined via the force-distance-curves.

#### **Advanced Rheometers**

The flow behaviour of a material is described by the relationship between the force acting on the sample of a material, and the effect of this force. The effect may be elastic deformation or viscous flow. For technological and historical reasons, the standard measuring technique has been to force the sample to undergo a predetermined shear rate and measure the force required.

The measuring modes of rotation rheometers can be divided in the following manner:

##### **1. Controlled shear rate flow mode**

The measurements are carried out at preselected shear rates. The results are plotted in form of flow-curves  $\tau(D)$  or viscosity-curves  $\eta(D)$  and give information about the viscosity of a substance at certain shear rates and about their rheological character dividing the substances in Newtonian and Non-Newtonian fluids.

##### **2. Controlled stress mode**

This method applies a constant force to the sample. The resulting strain (deformation) is measured and monitored as a function of time. This test is called the creep test which gives information about the elastic and viscous properties of substances.

### 3. Controlled stress flow mode

In this test the applied force is increased and the resulting shear rate is measured. The results are plotted on a flow-curve. This is a test to attain the yield point of pseudoplastic material.

#### The Controlled Shear Rate Method

#### Investigation of Aqueous Pectin Solutions

Pectins are longchain macromolecules. In aqueous solutions they form more or less stiff rods or coils depending on their degree of branching and linking as well as their molecular weight. In addition interparticular or intermolecular physical-chemical interactions like Van-der-Waals forces, ionic interactions or hydrogen bonds influence the active volume of the molecule, their stiffness, and the viscosity. Pectins in aqueous solutions show pseudoplastic non-thixotropic behaviour, independent of their degree of methoxylation.

The pseudoplastic behaviour, i.e. the decrease of the viscosity with an increasing shear rate, becomes more important when the polymer concentration and molecular weight increase. For low hydrocolloid concentrations the viscosity is nearly independent of the shear rate. Figure 1 shows the viscosity curve of a 2.5% pectin solution, sheared with the preselected shear rate-time function. The viscosity curves for the increasing and decreasing shear rate are superimposed.

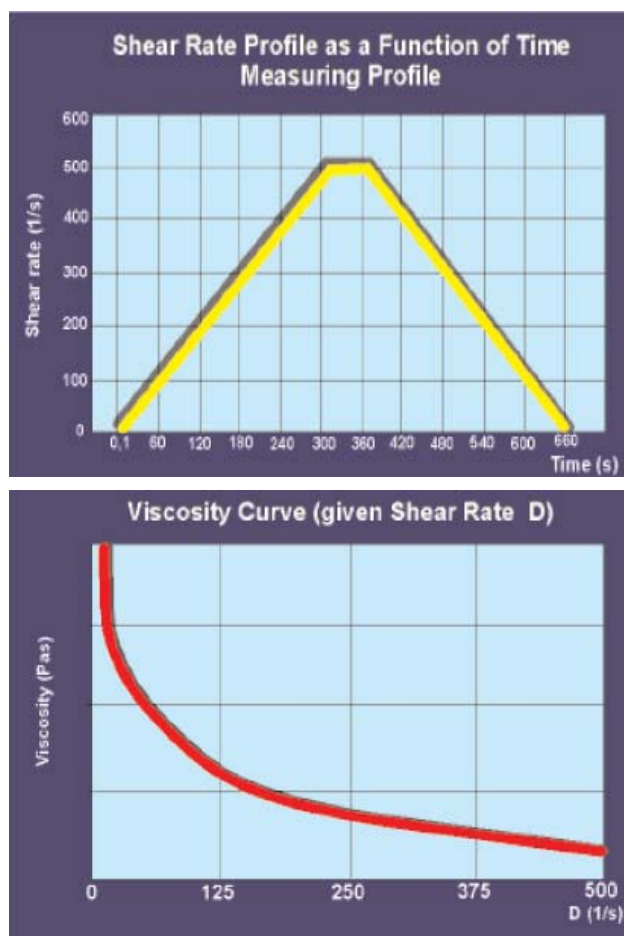


Fig. 1: Viscosity curve of a 2.5% pectin solution

Most pectin solutions behave like Newtonian liquids, below a pectin concentration of about 1% (w/w). Onogi (1966) derived the critical concentration of polymer solutions from plotting the double logarithmic curves of viscosity ( $\eta$ ) against concentration at constant shear rates.

Each curve consists of two straight lines intersecting at the critical concentration. At higher concentrations than given by this point, the solutions have pseudoplastic flow.

This behaviour is thought to be due to the formation of a network structure caused by entanglement of the longchain molecules in solution. With the data of viscosity measurements of pectin solutions of different concentrations the same behaviour can be attained, confirming Onogi's observation, with a critical pectin concentration of about 1% (w/w).

The value of critical concentration depends strongly on the pectin being used. Figure 2 gives the viscosity curves of two different pectins at the same concentration of 2.5% (w/w). The different production parameters, that have been used for these pectins, have strongly influenced their flow behaviour.

The enzymatic reduction of the molecular weight down to approx. 50.000 dalton<sup>1)</sup> has produced a pectin of very low viscosity and nearly ideal Newtonian flow, even at this higher pectin concentration. In comparison to this pectin, the plot also shows the viscosity curve of a pectin produced under regular parameters. Its unchanged high molecular weight of approx. 100.000 dalton<sup>1)</sup> leads to a much higher viscosity and pseudoplastic flow.

Commonly, the application of rheological data from aqueous pectin solutions is limited to a narrow field in the food industry. The direct transfer to other properties is limited, since the rheological behaviour of pectins show very complex dependencies on other additives like sugars, acids, salts and many more. Pectins standardized to a defined viscosity are applied in beverages and as soluble dietary fibres.

<sup>1)</sup> intrinsic viscosity measurement using the constants of Owens et al. (1946).

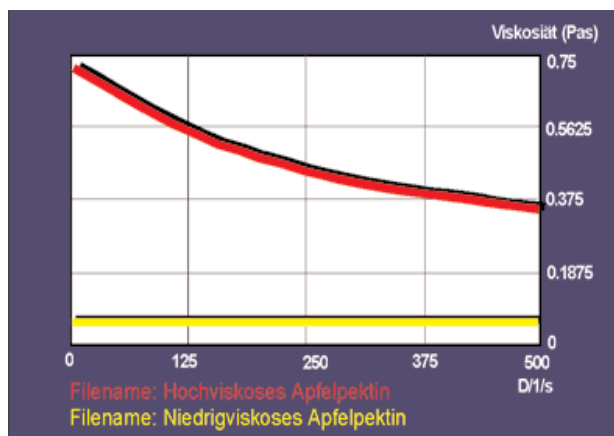


Fig. 2: Pectins with Different Viscosity Behaviour due to Different Production Processes – Viscosity curves of pectins with different molecular weight (2.5% sol.)

### The Term Thixotropy

In thixotropic substances shear thinning depends mainly on the particle or molecular orientation or alignment in the direction of flow. This orientation is changing with a changing shear rate and is dependent of the time of shearing. Additionally many dispersions show this potential for particle or molecule interactions, this leads to bonds creating a three-dimensional network structure.

They are often build-up from relatively weak hydrogen or ionic bonds. When the network is disturbed by shearing, bondings break easily and the viscosity drops asymptotically reaching a minimum viscosity after a certain time. This minimum describes the so-called "sol"-status of a dispersion. The viscosity of a thixotropic substance decreases in dependence of the time to a certain value. But this thixotropic substance is able to regenerate its structure within a certain time when the shear rate is decreased or set to "0".

The viscosity time curve of thixotropic substances marks the two phases of transformation:

- a) from gel to sol, when a defined shear rate is given
- b) from sol to gel, when removing the shear rate.

Thixotropic behaviour of pectins can be observed with the drop of their degree of esterification, and with the onset of a distinct reactivity towards divalent cations. The common measuring principle is pictured in figure 3.

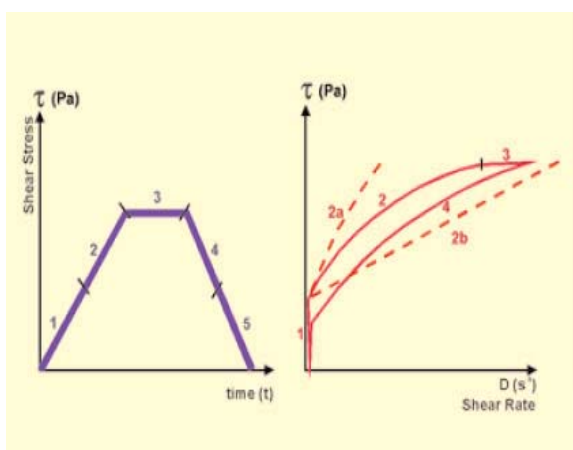


Fig. 3: Measuring Profile for Determination of the Yield Point and Thixotropy of fruit preparations

The shear stress time profile is divided in three sections:

- the up-curve, the increasing shear stress destroys the structure in dependence of the time,
- the plateau, the constant shear stress destroys the structure in dependence of the time,
- the down-curve, the decreasing shear stress leads to the partial regeneration of the structure of the material, like a fruit preparation.

The area of the hysteresis loop is a measure of the thixotropy of the tested system. These measurements are easy to carry out and give a quick overview of the thixotropic properties of different pectins in specific preparations. Yet, the results obtained are only a relative measure and depend strongly on the preliminary treatment of the sample.

### Rheometry of Fruit Preparations

Fruit preparations for yoghurt are a typical example, how the influence of pectin in these preparations can be characterized with the help of rheological characterization (Kratz and Dengler, 1995), using

- the yield point determination,
- the determination of the thixotropic behaviour
- and the viscosity.

For best results, the measurements are carried out in the controlled stress mode. The samples are subjected to a preselected defined stress profile, leading to comparable results.

Figure 3 gives an example of a typical shear stress profile. The shear stress is increased and reaches the point – at the end of the first part of the force profile – where the pectin preparations start to flow. The so-called yield point is reached. The further increase of the shear stress leads to the continuous destruction of the internal structure and the proceeding shear thinning.

The applied shear stress in part 3 of the shear stress profile destroys the structure of the fruit preparations completely. Now the shear stress is reduced linearly, see part 4 and 5, down to zero stress. The resulting flow curves 2, 3 and 4 and the enclosed calculated area from the hysteresis loop give important evidence about the time-dependent decrease of viscosity and is a relative measure of its thixotropy.

The rheologically expected complete regeneration of the viscosity after the shearing experiment is not common for these fruit preparations. The reason for this loss of viscosity must be searched for in the destruction of those parts of texture being caused from a gelation process. A yield point is necessary to guarantee a homogeneous distribution of fruits in the big containers where fruit preparations are transported. The shear thinning of the preparations is an important aspect for their pumping and mixing properties. The loss of viscosity due to the shearing should be large enough to render a product, that can be easily pumped with no negative effect for the pieces of fruit, and can be easily mixed with the yoghurt, but afterwards will regenerate enough to produce a pleasant creamy texture in the final product.

The yield points measured at the beginning (1. section) and at the end of the measurement (5. section) can be thought of as a criterion for texture. A big difference of the two yield points is a sign of a higher degree of gelation and a higher tendency for syneresis.

**The advantages of pectins in fruit preparations are quite obvious:**

1. Plastic flow: pectins build up a yield point without giving the product a slimy characteristic.
2. The thixotropic texture has the advantage, that the viscosity of the pectin preparations will decrease with increasing shear stress and regenerate quickly to a great extent when shear stress decreases.
3. The yield point regenerates within short time.
4. Pectins show great stability towards shearing.

The very special demands on the pectins used in yoghurt fruit preparations show the usefulness of rheological measurements. Figure 4 and 5 explain the difference in rheological behaviour of fruit preparations made from

- two low methoxyl apple pectins (Classic AY 901 and Classic AY 905)
- two amidated pectins (Amid AY 015-A and Amid AF 015-A) and
- the amidated pectin (Amid AF 015-A) also in combination with locust bean gum (LBG).

The yield points before and after shearing the yoghurt fruit preparations were measured at 20°C and different contents of soluble solids of 35 and 50%.

The ratios of the two yield points before and after shearing depend on the content of soluble solids. The apple pectin Classic AY 905 has before shearing the highest yield point of all at a content of soluble solids of 35 %, but as one can see from the regenerated yield point (after shearing), this high value must be mainly due to gelation (see figure 4).

For the apple pectin Classic AY 901 this ratio is much smaller, and its texture has less gel characteristics.

Fruit preparations with the amidated pectins, with or without locust bean gum, do not have at 35% SS yield points high enough to prevent floating.

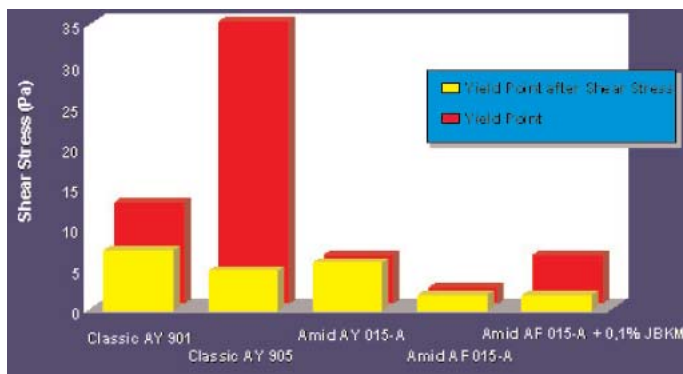


Fig. 4: Comparison of Yield Points and after Shear Stress of Different Yoghurt Fruit Preparations with 35% SS at 20°C.

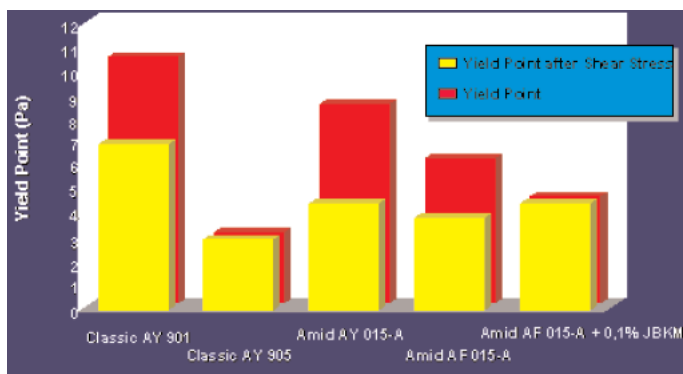


Fig. 5: Comparison of Yield Points and after Shear Stress of Different Yoghurt Fruit Preparations with 50% SS at 20°C.

With a content of 50 % soluble solids the amidated pectins have yield points before and after the shearing process, which are sufficient to prevent floating.

For more details of the sensory properties of the pectin preparations with a soluble solids content of 35 % additional sizes such as thixotropy and viscosity have to be referred to (see figure 6). Fruit preparations with apple pectin Classic AY 901 have a relatively high yield point after shearing, a small thixotropic area, and a relatively high viscosity. This supports the statement, that their texture is weakly elastic and highly reversible.

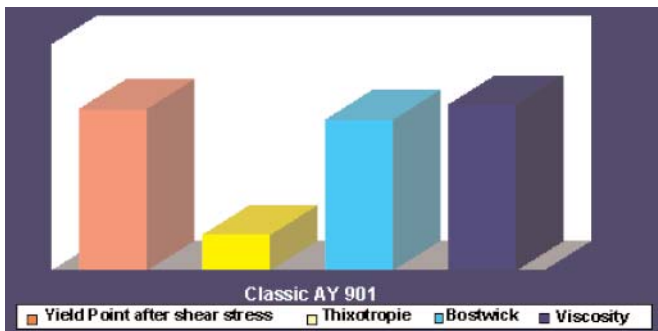
The apple pectin Classic AY 905 gives products with a sufficiently high yield point at 35% soluble solids and a pronounced area of thixotropy. The elastic components of the texture are destroyed and only partially regenerated in the course of the measurement as can be seen in the large difference of the yield points. The viscosity being reached is sufficient for the product.

The texture of the amidated pectin preparations shows little elasticity as indicated by the yield point differences. Nevertheless the thixotropic area is rather large due to time dependent shear thinning and the low viscosities leave a watery mouthfeel.

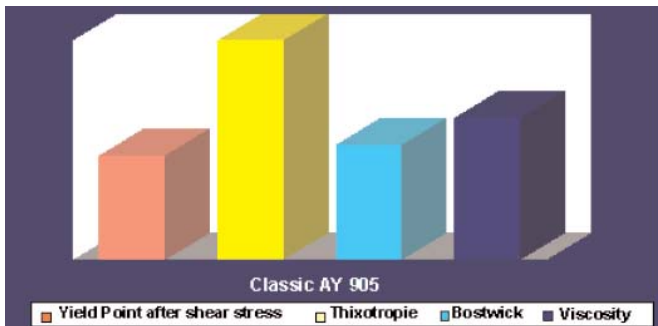
The locust bean gum increases the viscosities remarkably, but does not result in a yield point (after shearing) large enough to prevent floating.

### The Oscillating Mode – a Further Rheometric Technique

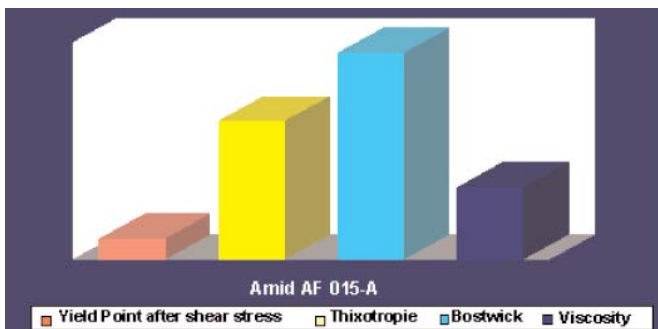
Viscoelastic substances like pectin gels, behave as well like elastic solids as viscous liquids, and can only be clearly characterized by means of an oscillation test. In these tests the substance of interest is subjected to a harmonically oscillating shear deformation. This deformation  $g$  is given by a sine-function,  $[g = g_0 \sin(\omega t)]$  by  $g_0$  the deformation amplitude, and  $\omega$  the angular velocity. The response of the system is an oscillating shear stress  $t$  with the same angular velocity  $\omega$ .



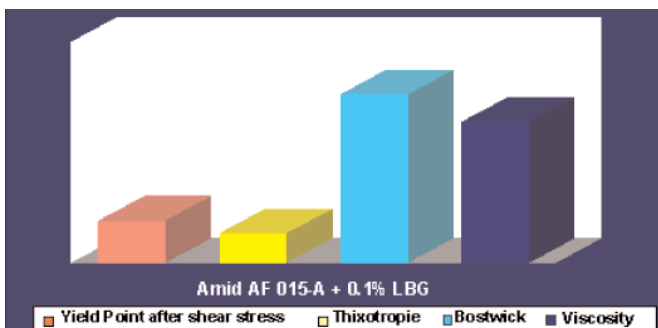
Comparison of Measured Values of Classic AY 901 (35% TSS)



Comparison of Measured Values of Classic AY 905 (35% TSS)



Comparison of Measured Values of Amid AF 015-A (35% TSS)



Comparison of Measured Values of Amid AF 015-A + 0.1% LBG (35% TSS)

Fig. 6: Comparison of Measured Values at 35% TSS

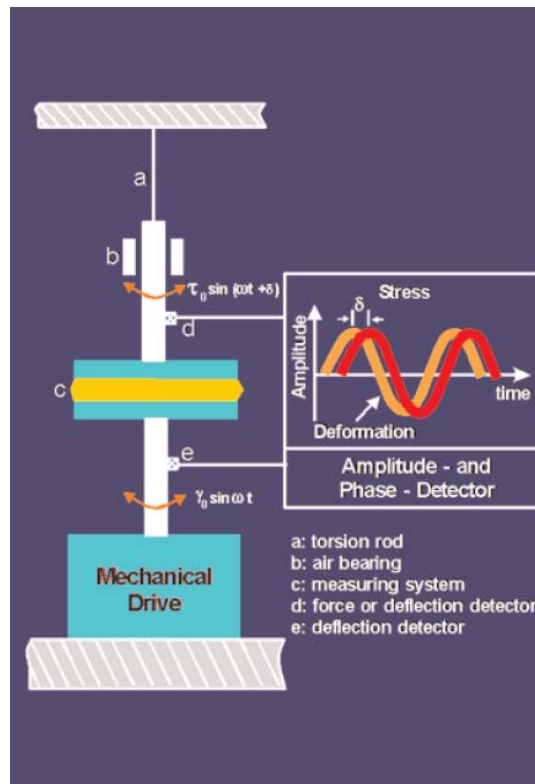


Fig. 7: Schematic Construction of an Oscillation-Rheometer

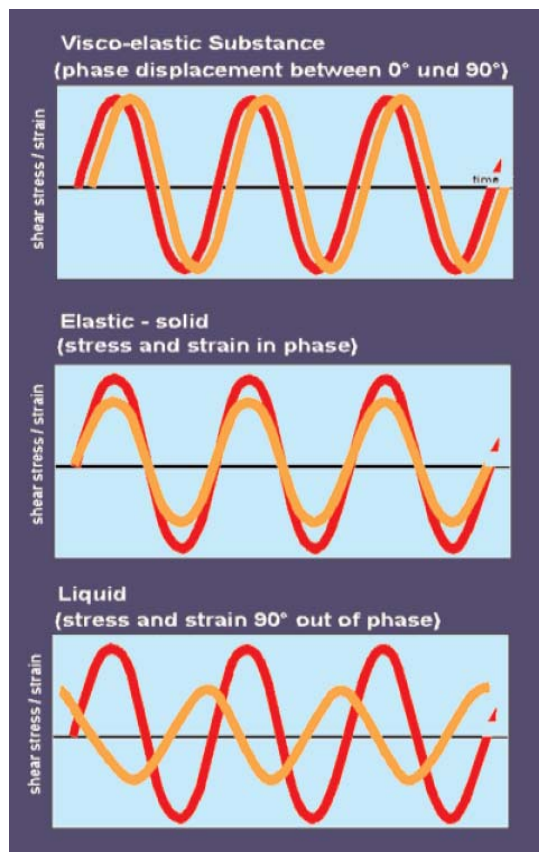


Fig. 8: Phase Displacement between Stress and Strain

The mathematical dependence can only be applied in the linear visco-elastic region. In this region the sample can be deformed up to a maximum deformation ( $g_0, \max$ ) without destroying the structure of the sample.

A purely elastic substance (model: spring) is linearly connected with the deformation via Hooke's Law producing a phase displacement  $d$  of  $0^\circ$  (see figure 8). The deformation of the spring is caused by energy, this energy is stored and completely gained back when the applied force is removed. Ideal viscous substances can be described with the shock absorber model of Newton. The energy applied to the viscous body is completely transformed in energy of deformation or dissipated in the form of heat.

The mathematical description of this problem shows that the shear stress and shear rate curves are in phase compared to the deformation curve  $[g(t)]$  this is equivalent to a phase displacement of  $d$  of  $90^\circ$  (see figure 8).

Visco-elastic substances can be described with the spring/shock-absorber model of Kelvin and Voigt, and have phase displacements of  $0^\circ$  to  $90^\circ$ . In analogy to other time dependent processes in physics, the oscillation tests are evaluated with complex arithmetics. Obtained are the complex quantities:

- the complex viscosity ( $h^*$ )
- the complex Young modulus ( $G^*$ )
- the storage modulus ( $G'$ ), as a measure for the reversibly stored energy (this is the elastic share of the complex Young modulus)
- the loss modulus, representing the irreversibly stored energy (this is the viscous share of the complex Young modulus)
- the loss factor  $\tan d$  giving the ratio of the viscous and elastic share ( $G''/G'$ ).

#### Different Tests and their Application

##### Strain amplitude sweep

The deformation amplitude is varied  $[g(t) = g_0 \sin(\omega t)]$  at a constant angular velocity. The resulting elastic modulus ( $G'$ ) is plotted versus the strain.

The test can be used

- to determine the stability of a system
- to determine the linear visco-elastic range, important for further measurements.

The linear visco-elastic range ends when the elastic modulus  $G'$  starts to fall off with the further increase of the strain amplitude. This deformation is called the critical amplitude  $\gamma_c$ . This is the maximum amplitude that can be used for non-destructive dynamic oscillation measurements.

Figure 9 gives the visco-elastic ranges of gels prepared with three different pectins with the same degree of esterification. The gels are prepared and measured under equal conditions. The gels based on citrus pectin have the highest storage modulus of the three pectins and the shortest linear visco-elastic range. In general citrus pectins form highly elastic, brittle gels. They are not well spreadable and show high tendency to syneresis. The lowest storage modulus is shown by the gels based on apple pectin. They have a wide linear visco-elastic range correlating well with the sensory evaluation of an excellent spreadability and low tendency to syneresis, highly estimated in jams, jellies and marmalades and in household gelling agents.

### Strain frequency sweep

The strain frequency sweep measurement can give answers on questions concerning the stability or the structure of visco-elastic material. The measurement is conducted at a pre-set strain amplitude, increasing the oscillation frequency in dependence of time. The resulting double-logarithmic plot of the storage modulus  $G'$  versus the angular velocity  $\omega$  shows characteristic spectra depending on the measured substances. Figure 10 gives the four types of spectra:

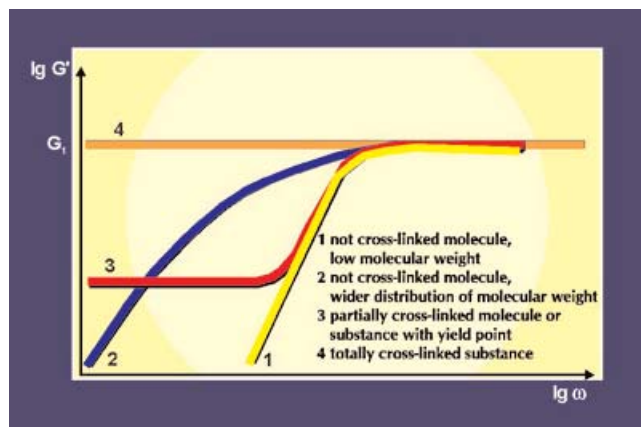


Fig. 10: Storage modulus versus angular velocity diagrams from strain

- curve 1: substance with low molecular weight, no network
- curve 2: substance with wide molecular weight distribution no network
- curve 3: substance with partial network or yield point
- curve 4: substance with complete network

Short chain linear molecules which cannot form a network change directly from the flow zone to the glassy zone. A plateau zone always indicates a network structure, its width depends on the molecular weight. In the transition zones the mobility of the chain molecules decreases,

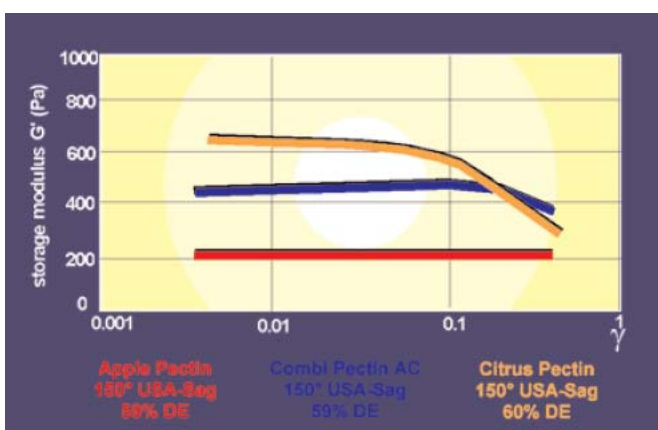


Fig. 9: Visco-elastic Range of Pectin Gels made of Pectins from Different Raw Materials

the chain segments can no longer relax completely. At even higher oscillation frequencies the chain segments can move no longer, this is called the glassy zone (G1).

The spectra of pectin gels recorded follow the general rule for polysaccharide gels, being characterized by a flat dependency of the storage modulus ( $G'$ ) over the wide range of frequencies studied. This behaviour reflects the existence of a three-dimensional network. The values for  $G'$  depend on the parameters in the gels.

The dynamic Weissenberg number  $W'$  can be calculated from data obtained by the strain frequency sweep measurement. It's the ratio of the elastic to the viscous shares in the measured gel and leads to an objective description of the sensoric properties of the gel (Windhab, 1990), representing the basis for the standardisation of pectins.

The elastic properties and resulting from this the dynamic Weissenberg number of pectin gels are influenced by the raw material used for pectin extraction, the production process and by the degree of esterification of the applied pectin. With a decreasing degree of esterification of HV-pectins the elastic properties of the gels are decreasing and therefore the dynamic Weissenberg number also decreases.

The ratio of elastic to viscous shares in a visco-elastic gel influences the texture as follows: Very large elastic and very small viscous shares resulting in a high dynamic Weissenberg number give a gel which is very brittle and has a high breaking strength. The gel is sensible to mechanical treatment and shows a high tendency to syneresis.

Gels with a low dynamic Weissenberg number that means with large elastic and increasing viscous shares are soft and show better spreadability. They are more stable against mechanical treatment and have less syneresis.

There is a good correlation to sensory properties:

Gels made from citrus pectin have a small linear visco-elastic range. To puncture the gels takes a big but only short time effort. The gel breaks into small lumps immediately.

In the mouth the gel feels rough and crumbly, the gels have little body. Gels with higher dynamic Weissenberg number need higher breaking strength values, here expressed in Herbstreith-Pectinometer units (HPU) to be judged sensorically equally firm as gels with a smaller dynamic Weissenberg number.

Gels made from apple pectin have a wide linear visco-elastic range. Therefore a big effort is necessary to puncture the gel. On spreading the gel it remains joined, does not break into small lumps and shows a smooth and shiny surface. In the mouth the gel feels clear and smooth when squashing it between palate and tongue, the sweet fruity taste remains for a long time. The gels have "body".

#### **Strain Temperature Sweep**

The temperature sweep measurement is conducted with a preselected constant deformation ( $g$ ) and a constant frequency ( $f$ ). The changing parameter is the temperature  $T$ , which is given in a temperature-time profile [ $T = T(t)$ ]. This test method serves to illuminate the structural build-up, the softening, the melting and the gelation of pectins influenced when the temperature changes.

The gelling temperature is an important factor for the characterization and application of pectins. The pectin consumer wants a pectin fulfilling his special requirements, this can mean either working with or without pregelation. Pregelation, the weakening of gel structure, occurs when pectin preparations are stressed below their gelation temperature so that the mechanical treatment leads to an irreversible destruction of the three-dimensional network.

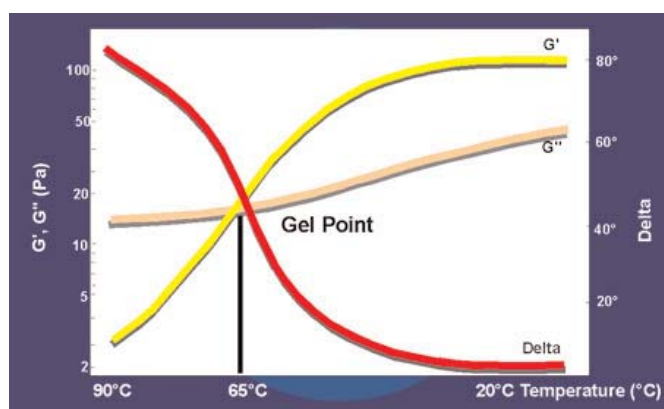


Fig. 11: Strain temperature sweep measurement

The pectin sol is prepared and filled into the measuring system at elevated temperature higher than its gelling temperature.

The system is cooled at the given rate and the gelation threshold is defined, when the loss modulus  $G''$  and the storage modulus  $G'$  are equal – this means when the elastic and the viscous shares in the gel are equal – and the phase displacement  $d$  is  $45^\circ$  (see figure 11). At this point the gelling temperature is read.

The gelling temperature is an important criterion for the production of jelly fruits and in jam production and must be chosen suitably for the desired packaging size.

### The Temperature Sweep

Figure 12 demonstrates the different gelling behaviour of three samples of apple pectin with different degrees of esterification. The gel is produced from pectin, water, sugar, acid and fruit concentrate. The gelling temperatures at the phase displacement of  $45^\circ$  were compared with the sensory evaluation. The sample with the highest degree of esterification showed the highest gelling temperature (sample 1, ca.  $72^\circ\text{C}$ ), the shortest setting time and a very brittle texture. Sample 3 shows a lower gelling temperature and a more viscous texture. The behaviour of sample 2 lies between sample 1 and sample 3.

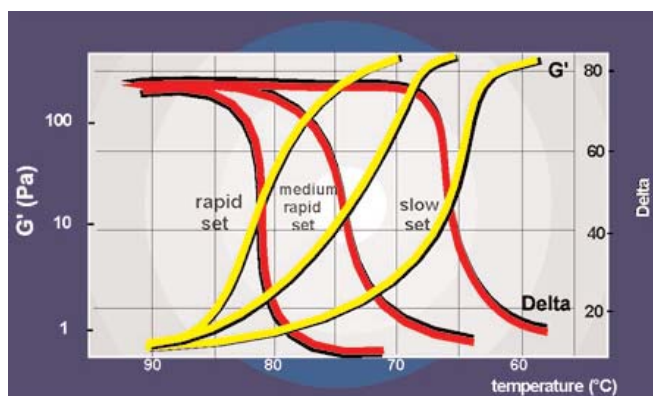


Fig. 12: Determination of setting temperature of pectin gels

The gelling processes are not solely temperature dependent but also time dependent. The determination of the setting temperature is therefore dependent on the temperature profile being used. Results can only be compared, when the pectin preparations are pretreated and measured with exactly the same parameters.

### Strain Time Sweep

This test is based on a preselected constant deformation ( $\gamma$ ) at a constant frequency ( $f$ ) and a constant temperature ( $T$ ). The method can be applied to test the stability of substances with temporary physical changes of structure or the course of chemical reactions like gelling at a given temperature. Again the pectin sols are filled into the measuring system at temperatures higher than their setting temperatures and afterwards immediately cooled down to the wanted measuring temperature. The criterion for gelation is also a phase displacement of  $45^\circ$ .

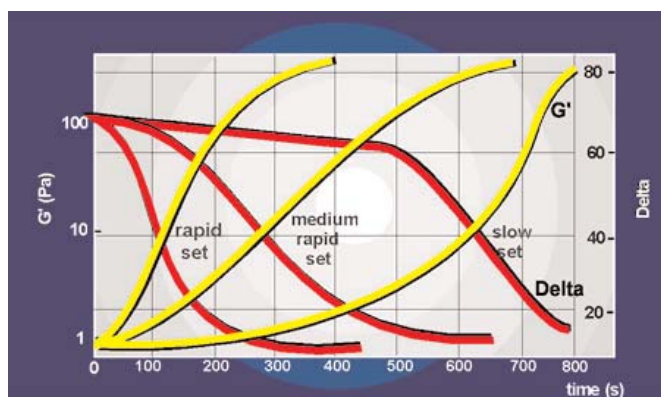


Fig. 13: Determination of setting time of pectin gels

A typical graph is plotted in fig. 13, showing the storage modulus and the phase displacements for the previously mentioned pectin samples. Sample 1 with the highest setting temperature builds up its network structure in a relatively short time compared to sample 3. Therefore the setting time of sample 1 is shorter than the setting time of sample 3. The setting time of sample 2 lies between sample 1 and sample 3. With the determination of the setting time it is possible to classify HM-pectins as rapid set, medium rapid set and slow set. Resulting from this the pectins can be chosen for each specific application. In manufacturing, exact setting times have

the advantage that the products reach their final gel structure at the predetermined setting time resulting in a constant production process.

### Conclusion

Using these rheological methods laboratories for quality control and research and development have good tools to characterize pectins in gels and solutions. The most important points are the reproducible handling, pretreatment, and measurement of the samples and the knowledge which information can be derived from the measured data regarding the texture, the production parameters, and the sensory evaluation of the product.

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