



A RHEOLOGICAL STUDY OF STARCH GELATINISATION UNDER STRONG ALKALI CONDITIONS

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ABSTRACT

The rheological properties of a starch solution with a water-starch ratio of 2.0w/w were studied during gelatinisation under strong alkali conditions, in a co-axial cylinder viscometer for 17g/dm³ - 23g/dm³ concentrations of NaOH solution. The viscosities and fluidities of the sample were measured at intervals of ten seconds and plotted. Equilibrium viscosities and fluidities were obtained and sample calculations used to determine which of the two physical quantities is appropriate for starch gelatinisation study and its relation to a degree of gelatinisation.

The fluidity-time curve gave a good fit to a three-parameter exponential model, for all concentrations of NaOH studied and was used to obtain the equilibrium fluidity. The equilibrium viscosity was obtained as the inverse of the equilibrium fluidity and the degree of gelatinisation was defined in terms of viscosity.

This technique gave accurate insight into starch gelatinisation under strong alkali conditions and is recommended for further studies in this area.

Key words: starch, gelatinisation, viscosity, fluidity, equilibrium

1 INTRODUCTION

Starch is one of the most common substances existing in nature and is the major basic constituent of the average diet. Starch is a carbohydrate polymer occurring in granular form in the organs of certain plant species, notably cereals, tubers and pulses such as corn, wheat, rice, tapioca, potato and pea (Austin, 1985;www.cerestar.com, 2004).

The most important practical property of starch is its ability to undergo hydration, irreversible swelling, crystallite melting, loss of birefringence and solubilisation under the influence of heat and/or certain chemical in an aqueous medium to give starch paste. This process is called gelatinisation.

The chemical gelatinisation of starch-under strong alkali conditions-is the basic industrial reaction in the conversion of starch to adhesives (Leach, 1965;Halley & Sopade, 2004;www.cerestar.com, 2004).

Starch adhesives or glues were first used in large-scale industrial application approximately in the 1910's. Their chief advantages over animal glues are that they may be applied cold and do not have the undesirable characteristic odour or taste of some animal glues, though most of them have the disadvantage of less strength and lower water resistance than animal glues. They are also less costly than synthetic resin-adhesives.

Starch adhesives are often used where water resistance is not important. With incorporation of 5-15% resin, such as urea formaldehyde, it can be used where

water resistance is important. it is also a base for many liquid adhesives (Austin, 1985).

This demand for starch base glues notwithstanding, much less is known about alkali gelatinisation-compared to thermal gelatinisation-and especially no kinetic approach has appeared in open literature (Yamamoto et al, 2005).

In order to develop the simple kinetics of starch gelatinisation using the rheological approach, one must properly define a physical (measurable) quantity that is related to a degree of gelatinisation and must measure its time dependence under isothermal conditions. The choice of an adequate physical quantity and its relation with a degree of gelatinisation are not trivial. The following approaches are available from literature:

1.1 Based on Fluid consistency index

Some researchers conducted a study of the time dependence of fluid consistency index for the gelatinisation of rice and potato starches using a capillary viscometer. The starch paste was gelatinised for a fixed time under isothermal conditions. The degree of gelatinisation was defined as a ratio of the fluid consistency index, for computation of the reaction rate constant:

$$x = \frac{K - K_o}{K_e - K_o} \quad (1)$$





Where K , K_0 and K_e are fluid consistency indices of sample at any time, at the initial time and at equilibrium gelatinisation respectively (Kubota et al, 1979).

1.2 Based on Viscosity of sample

Another group of researchers extended the definition of the degree of gelatinisation by applying an additive mixing rule of viscosity with respect to the ungelatinised and gelatinised fractions, to obtain the degree of gelatinisation in terms of viscosity, thus;

$$X = \frac{\mu - \mu_0}{\mu_e - \mu_0} \quad (2)$$

Where μ , μ_0 and μ_e are viscosities of the sample at any time, at the initial time and at equilibrium gelatinisation respectively (Kubota et al, 1979; Yamamoto et al, 2005).

1.3 Based on fluidity of sample

In the kinetic treatment of starch gelatinisation under strong alkali conditions, the degree of gelatinisation can also be defined in terms of the fluidity of the sample.

$$X = \frac{F - F_0}{F_e - F_0} \quad (3)$$

Where F , F_0 and F_e are fluidity of the sample at any time, at the initial time and at equilibrium gelatinisation respectively (Yamamoto et al, 2005).

All previous works focus on gelatinising for a fixed time and cooling to 0°C to terminate the reaction before measuring the sample viscosity. Such processes will be subject to error depending on how fast the sample can be cooled, the validity of the assumption that cooling to that temperature will stop chemical gelatinisation of starch and the possibility that cooling would influence the rheology of the sample.

This work presents a technique that uses the Co-axial cylinder viscometer to measure sample viscosity progressively during gelatinisation under strong alkali conditions.

2 MATERIALS AND METHODS

Raw Materials: Distilled water, Cassava starch and Sodium hydroxide (NaOH).

Equipments and Apparatus: Glass beakers (250 cm³), Measuring cylinders, Conical flask, Temperature sensors, Electronic-weighing balance, Glass rod stirrer, Sieve cloth, Knife, Grating device, Co-axial cylinder viscometer, Water bath and Stopwatch.

2.1 Cassava Starch Preparation

(i) Freshly harvested cassava tubers were washed and skinned. The tubers were rewashed after skinning to ensure cleanliness and mashed using a grating device.

(ii) Water was used as a solvent in the leaching process to extract starch from the mashed cassava tubers. This

was achieved by partially immersing the mashed cassava tubers in water in a bath, and sifting – while separating the mash and water with a semi – permeable membrane (sieve cloth).

(iii) The extract was allowed to settle over-night into three layers. The top layer was basically water, almost colourless. The middle layer was a thin brown liquid, likely to be cell wall components (Stickle et al, 2004). The bottom layer was a dense white solid (the starch cake).

(iv) The top and middle layers were decanted, leaving behind the starch cake.

(v) The starch cake was allowed to dry under the sun for about 48 hours, and then it was pulverized and sifted using a cloth sieve.

2.2 Starch Gelatinisation Study

(i) 50grams of the dry starch powder was weighed out and dispersed in 100 cm³ of distilled water, to obtain dispersion with a water to starch ratio of 2:1 (Freitas et al, 2002).

(ii) 100 cm³ of starch dispersion prepared in (i) above was measured into a metallic cylindrical vessel – originally a component of the coaxial cylinder viscometer – and 100 cm³ of sodium hydroxide solution was added to it. The metallic cylindrical vessel served as the reactor.

(iii) The metallic cylindrical vessel (laboratory reactor) was then incorporated into the coaxial cylinder viscometer set up. The coaxial cylinder viscometer was set at a specified agitation rate of 1 rpm (shear rate of 5s⁻¹) and switched on.

(iv) The corresponding shear stress was read off the dial of the viscometer at intervals of ten seconds, with the rate of agitation kept constant throughout the experiment and in subsequent experiments.

(v) The dial reading (shear stress) was converted to standard viscosity units using factors provided by the manufacturers of the coaxial cylinder viscometer (Nelson, 1990; Chandler et al, 2004).

Thus, viscosity = $F \cdot$ (Dial reading). The inverse of the viscosity was recorded as the fluidity.

(vi) The experimental procedure was repeated for all sodium hydroxide concentrations.

3 RESULTS AND DISCUSSION

Initial Dial Reading for starch solution:	0.5degrees
Initial Viscosity of starch solution:	0.15Pa.s
Initial Fluidity of starch solution:	6.6667(Pa.s) ⁻¹
Rate of agitation (Shear Rate):	1rpm (5s ⁻¹)

All the analysis was done using MATLAB Curve fitting Toolbox. The first kinetic parameter we require is the equilibrium viscosity (μ_e). Fitting the fluidity-time data to a decaying exponential model ($F = F_e \exp(Kt^n)$; $n < 0$) and finding its limiting value as time (t) tends to infinity, gave the equilibrium fluidity, which on inversion gave the equilibrium viscosity.

Equation (2) was used to compute the degree of gelatinisation, which is equivalent to conversion.



4 DISCUSSION

Starch solutions gelatinise at room temperature, in the presence of sodium hydroxide, to produce viscous pastes that have adhesive properties and can readily bond papers. These pastes are mostly milky in colour.

There exists a lag or delay time between the contacting of reactants and any observable reaction (change in sample viscosity). This delay time decreases with increase in sodium hydroxide concentration.

The rate of change of viscosity reduces as the reaction progresses with the viscosity tending towards an equilibrium value.

A study of the viscosity-time curves of Figure 1 revealed the following:

The profile of the viscosity-time curves for starch gelatinisation under strong alkali conditions is inconsistent, based on this inconsistency, no single parametric model gave a good fit for all concentrations of sodium hydroxide studied. Extrapolation revealed that models that will fit the data for most cases would tend to give viscosity predictions that are in discord with experimental observation.

A study of the fluidity-time curves of Figure 2 revealed the following:

There is a consistency in the profile of the fluidity-time curves for all concentrations of sodium hydroxide studied during the experiment. This makes it possible for a single (general) model to fit all profiles no matter the concentration of sodium hydroxide used.

The nature of the fluidity-time curves was in agreement with experimental observation. The fluidity decreases with time and tends to an equilibrium value (equilibrium fluidity) at the end of the reaction, for all concentrations of sodium hydroxide studied.

Based on these observations, from the viscosity-time and fluidity-time curves, the fluidity-time curve was chosen to obtain the equilibrium fluidity, which on inversion gave the equilibrium viscosity.

The challenge, though, with using fluidity-time curve to evaluate the equilibrium viscosity is that minute errors in the fit are enlarged on inversion.

On the other hand, viscosity was chosen as the rheological property for computation of the degree of gelatinisation (x) because fluidity always gave unreliable values that indicate degree of gelatinisation above ninety percent, even at the beginning of the experiment, for all sodium hydroxide concentrations.

Sample calculations of degree of gelatinisation based on viscosity (Eq. 2) and based on fluidity (Eq. 3) are shown in Table 2 for 22g/dm³ NaOH concentration.

5 CONCLUSION

Starch gelatinisation under strong alkali conditions can be studied rheologically by using the coaxial cylinder viscometer to study the change in sample viscosity and fluidity with time. Fitting the fluidity-time curve to a model of the form, $F = F_e \exp(Kt^n)$, where $n < 0$ and F_e is the equilibrium fluidity, will give the equilibrium fluidity, which on inversion gives the equilibrium viscosity.

The degree of gelatinisation can be defined in terms of

$$\text{viscosity as } x = \frac{\mu - \mu_o}{\mu_e - \mu_o}$$

6 REFERENCES

- Austin, G. T. 1985. *Shreve's Chemical Process Industries*, 5th ed., McGraw-Hill Book Company, 456 – 458.
- Chandler Engineering, 2004. *3506 Six Speeds Direct Reading Viscometer*, (Available at: www.chandlereng.com).
- Freitas, R. A., Paula, R. C., Feitosa, J. P. A., Rochas, S. and Sierakowski, N. 2002. Structure, Rheological Properties and Gelatinisation Kinetics of Yam (*Discorea alata*) and Cassava (*Manihot utilisima*) Starches (Available at: www.rheofuture.De/papers/2002/).
- Halley, P. and Sopade, P. 2004. Starch Gelatinisation, *CHEE 4007 Individual Inquiry B*, (Department of Chemical Engineering, The University of Queensland).
- Kubota, K., Hosokawa, Y., Suzuki, K. and Hosaka, H. 1979. Studies on the Gelatinisation Rate of Rice and Potato Starches, *J. Food Sc.*, 44:1394 – 1397
- Leach, H. W. 1965. Gelatinisation of Starch in *Starch: Chemistry and Technology*, Vol. 1, 2nd ed., edited by Whistler, R. W., Paschall, E. F. and Bemiller, J. M., Academic Press, New York, 289 – 307.
- Nelson, E. B. et al, 1990, *Well Cementing*, Schlumberger Dowell, Sugar Land, Texas, 4-6 – 4-13
- Stickle, D. F., Mathews, K. R. and Landmark, J. D. 2004. Quantitative Assay for Starch by Colorimetry using a desktop Scanner, *J Chemical Education*, 8(5): 702 – 704.
- Www.cerestar.com, 2004. *A Glossary of Terms and Products for the Starch Industry*, Cargill Cerestar, 2004.
- Yamamoto, H., Makita, E., Oki, Y. and Otani, M. Flow Characteristics and Gelatinisation Kinetics of Rice Starch Under Strong alkali Conditions, *J Food Eng* (in press). (Available at: www.arxiv.org.ftp/physics/papers).

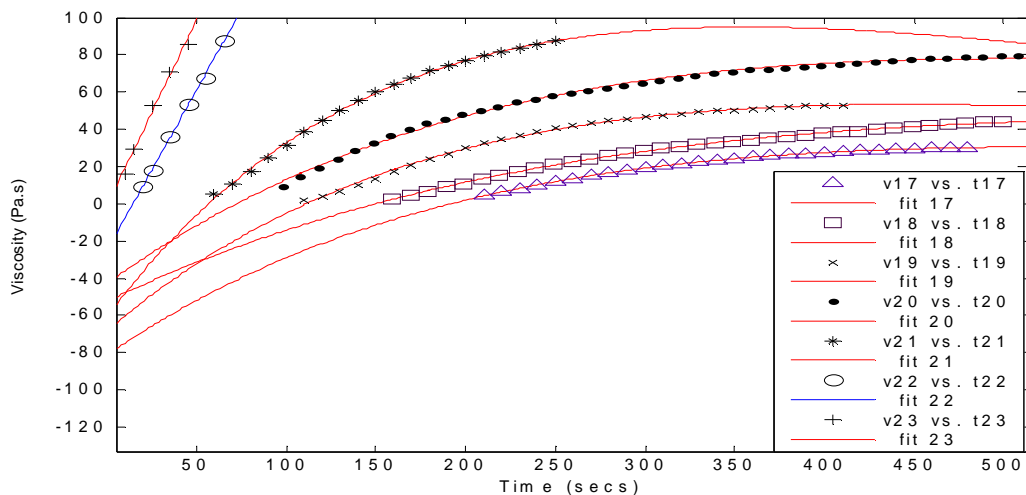


Figure 1: Viscosity vs. Time for 17g/dm³ – 23g/dm³ NaOH concentration

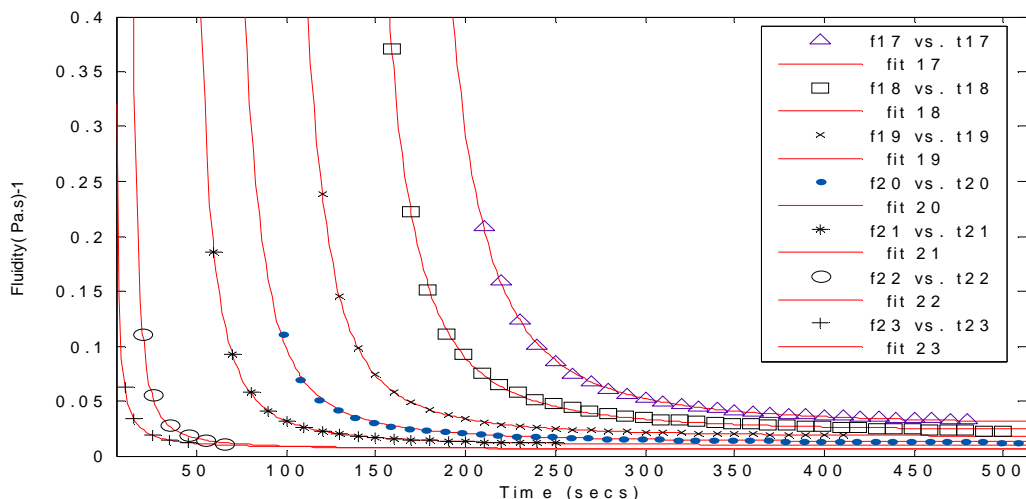


Figure 2: Fluidity vs. Time for 17g/dm³ – 23g/dm³ NaOH concentration

Table 1: Numerical fit results for Fluidity-time curve and equilibrium viscosity for 17g/dm³ – 23g/dm³ NaOH concentration

NaOH Conc.(g/dm ³)	F _e (Pa.s) ⁻¹	K	n	R ²	RMSE	SSE	μ _e (Pa.s)
17	0.02799	7.584e+7	-3.263	0.9995	9.33e-4	2.176e-5	35.7270
18	0.02240	1.595e+7	-3.069	0.9991	2.141e-3	1.467e-4	44.6429
19	0.01708	9.2e+5	-2.666	0.9999	3.227e-4	2.915e-6	58.5480
20	0.01196	1.7721e+4	-1.970	0.9992	5.199e-4	1.054e-5	83.6120
21	0.008742	3088	-1.690	0.9999	1.921e-4	6.271e-7	114.3963
22	0.005515	90.75	-1.138	0.9996	9.528e-4	2.724e-6	181.3237
23	0.004965	12.95	-0.7073	0.9997	5.141e-4	5.285e-7	201.4099

Table 2: Sample Computation of Degree of Gelatinisation for 22g/dm³ NaOH concentration

Time (secs)	20	25	35	45	55	65
x _v (Based on viscosity (Eq. 2))	0.0488	0.0985	0.1979	0.2939	0.3717	0.4813
x _f (Based on fluidity (Eq. 3))	0.9841	0.9925	0.9967	0.9980	0.9986	0.9991



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