

INFLUENCE OF WORKING PARAMETERS ON THE VISCOSITY OF THERMAL TREATED CORN STARCH SUSPENSIONS

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Abstract: The influence of three parameters (temperature, pre-treatment and shear rate) on the evolution of viscosity of medium concentrated starch suspensions (25% w/v) is investigated. The obtained viscosity curves allow the identification and analysis of the specific transformations of starch due to the thermal treatment (gelatinisation, pasting). Pregelatinisation has not a significant importance for the evolution of viscosity, whereas the increase of the shear rate shifts the viscosity.

INTRODUCTION

Starch is the cheapest and most abundant food biopolymer worldwide. Starch is often used as an inherent natural ingredient but it is also added for its functionality.

They are many challenges in the study of starch processing as result of the compositional, structural and rheological complexities of starch systems. The gelatinisation and pasting properties are of particular importance to starch science. The phenomena referred to as gelatinization are complex (Brouillet-Fourmann et al., 2003). Upon heating, the granules of starch with significant moisture contents swell and amylose and water start diffusing out of the granular entities especially when the granular structure is not totally perfect (Atkin et al., 1999). At higher temperatures, amylopectin melting begins and enables the release of the important amount of amylose that was trapped between amylopectin layers and of the small part that was confined within crystalline amylopectin (Atkin et al. 1999). Diluted starch suspensions are characterised by a temperature interval when the gelatinisation in the granular mass is produced (French, 1984).

When the starch content increases the pasting process is dominant. Pasting is defined as the point at which starch slurry begins to thicken and show an increase in viscosity when heated. The pasting temperature is normally several degrees higher than the endpoint of the gelatinisation range (Snyder, 1984).

For commercial reasons, control of gelatinization and pasting are important in food systems as they have a direct impact on final product quality (Alavi et al., 2002). The study of the gelatinization process is realized usually using DSC (Spigno et De Faveri, 2004) offering informations about state transformations, NMR techniques that allow the identification of intermediary compounds (Lewen et al., 2003), microscopically methods that indicates structural changes in products (Snyder, 1984).

Rheology is also a valuable tool in the analysis of starch, RVA (Rapid Visco Analyzer) or Brabender Viscograph being the most used instruments (Neiles et al., 2003). Rheology can help to optimise the process design (Thebaudin et al., 1998) (Drozdek and Faller, 2002) or to characterise starchy products (Hopkins and Gormley, 2000).

The goal of this research is to investigate the parameters influencing the gelatinisation of starch suspensions having a medium concentration (25%) by using rheometry. A special cylinder-flyer geometry adapted for suspensions easy to sediment is used and the influence of shear rate, temperature and thermal pre-treatment on the viscosity of starch suspensions is investigated.

Such a study is interesting for the food industry, especially for processes where thermal treatments combined with mixing are applied to starch-based systems (dough, sausages or starch-based soups preparation). The variation of the viscosity can then be correlated with structural changes in the product induced by gelatinisation and pasting processes (Whistler et al., 1984) (Carnali and Zhou, 1996) (Lewen et al., 2003).

MATERIALS AND METHODS

Corn starch C*Gel with 12% water content and having the ratio amylose/amylopectin 1/4 from Cerestar was used. Suspensions with 25% (w/v) starch were prepared, taking into account the water content of the initial starch samples (12%). All samples were maintained at 6-8°C (refrigerator) before analysis for 16 hours to equilibrate.

The measurements were performed using a rotational rheometer (Searle) MCR300 with temperature controlling system and cylinder-flyer geometry. This geometry was chosen because it has the advantage to limit the sedimentation of starch particles in suspension. The cylinder has a plastic cover that limited the water evaporation. The samples were submitted to constant shear rates and the evolution of viscosity (calculated as shear stress/shear rate) in time was measured. Such analysis can give valuable information about the gelatinization (Lagarrigue and Alvarez, 2001) or pasting (Varavinit et al., 2003) process.

For the analysis of the influence of cooking temperature on the viscosity of the medium concentrated corn starch suspensions three temperature profiles (0,12,°C/s, 0,2,°C/s and 0,32,°C/s) with linear ramp from 30° to 90°C and from 30° to 75°C were tested.

In order to study the influence of the preliminary thermal treatment on the gelatinization, two kinds of starch samples were used: non-pregelatinised and pregelatinised starch. The pregelatinised starch was obtained in two steps. In the first step the samples were maintained in the static cylinder at 50°C, indicated by the literature as pregelatinisation temperature (Neiles et al., 2003) (Varavinit et al., 2003); no mixing was performed but the flyer was maintained in the suspension during pregelatinisation to avoid mechanical disruptions of the pregel at the reuptake of mixing. In the second step the temperature was increased to 75°C in order to study the rheological behavior of starch in the gelatinization area.

In order to study the influence of the shear rate on the rheological properties of starch, analyses with 25% starch suspensions at variable shear rates (10s^{-1} , 20s^{-1} , 30s^{-1} and 50s^{-1}) were realised.

RESULTS AND DISCUSSIONS

Influence of cooking temperature

A typical viscosity curve at the thermal treatment of a corn starch sample with 25% (w/v) starch is presented in Figure 1. Nine behavioural types can be identified.

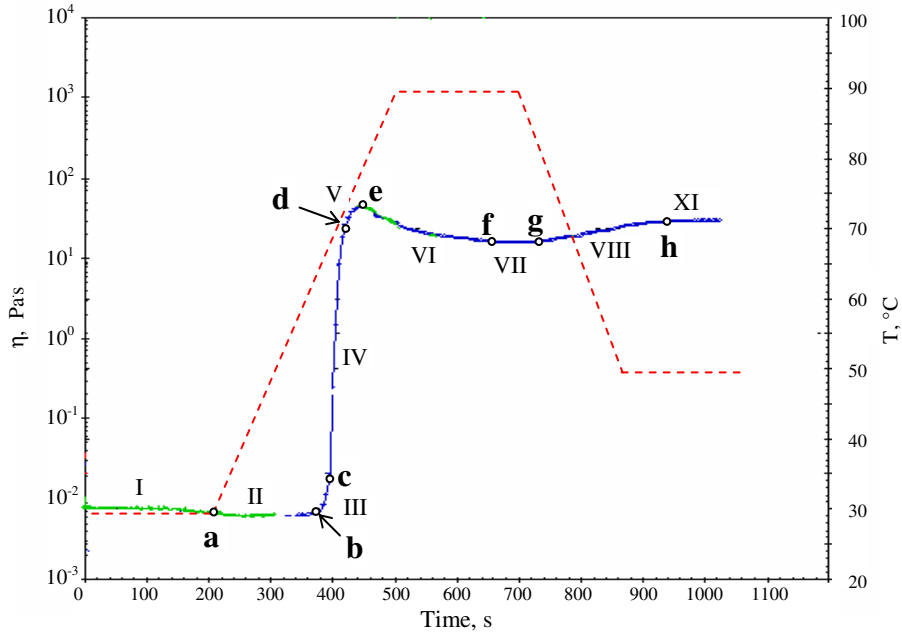


Figure 1: Evolution of viscosity of the C*Gel corn starch 25% (w/v) at mixing with continuous shear rate 50s^{-1} and heating from 30 to 90°C ($\sim 0.2^\circ\text{C/s}$)

During the initial step when no thermal treatment is applied and in the starch suspension no changes occurs viscosity remains constant at low values, near 10^{-2} Pa·s (phase I in Figure 1). A small decrease of viscosity is registered in the initial heating period at temperatures between 30° and 62°C , due to the influence of temperature on the water viscosity (phase II in Figure 1).

The behaviour of sample is very important in the interval 63° - 78°C , helping to identify the two main processes at the thermal treatment of starch suspensions having medium concentration. After a step characterised by a slow increase of viscosity when most probably swelling occur (phase III), in the temperature range between 66° and 72°C (temperature of gelatinisation T_{gel}) the process is characterised by a rapidly increase of viscosity with 1.5 Pa·s/s until approximately the maximal value (30 Pa·s) is attained (phase IV). This phase is identified as the gelatinisation phase, this temperature intervals corresponding with other literature data for the gelatinisation of corn starch. For example, (Snyder, 1984) identified the temperatures interval 62° - 73°C corresponding to the starch gelatinisation by using microscopically techniques.

Phase V is considered to correspond to the pasting interval (Snyder, 1984), the maximal viscosity (50 Pa's) being attained at the finish of the total pastification of corn starch, at the pasting temperature $T_{past}=78^{\circ}\text{C}$. Similar results are reported in the literature, (Neiles et al., 2003) and (Varavinit et al., 2003) obtaining a maximal viscosity peak around 80°C at the rheological analysis of corn starch (~15% w/w) by using RVA.

At temperatures higher as 80°C a decrease of viscosity (phase VI) due probably to the melting is observed. At 90°C a plateau in the evolution of viscosity is obtained (phase VII), indicating that the transformations in the product are finished.

The increase of viscosity in the phase VIII is due to the cooling.

When the same suspension is heated only to 75°C (Figure 2a), some differences are observed. The first four phases are similar with the phases identified at the treatment till 90°C . Because the temperature is smaller as T_{past} pasting is incomplete (phase V incomplete), the pasting peak being not obtained. The next phases, VI and VII are not clear separated because not all transformations in the product took place before.

Viscosity analyses of more concentrated starch suspensions (from 30% to 50% - data not shown) gave similar behaviours, a very small displacement of T_{gel} being registered ($T_{gel} = 73^{\circ}\text{C}$ for the 30% starch suspensions and 75°C for the 50% starch suspension), whereas T_{past} has the same value for all samples.

Influence of thermal pretreatment

In Figure 2 the results obtained at the analysis of corn starch 25% (w/v) without (2a) and with pregelatinisation at 50°C (2b) are presented. No significant differences between the samples are observed, the pregelatinisation step doesn't cause changes that could be detected with the geometry tested.

The gelatinisation time doesn't play an important role. Experiments realised with longer gelatinisation time didn't give significant variations of the viscosity curve.

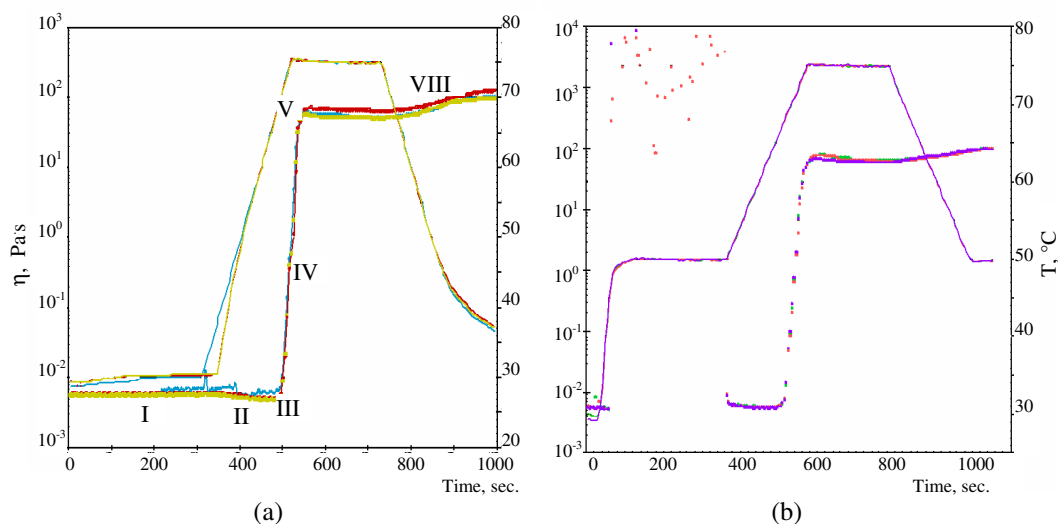


Figure 2: Evolution of viscosity of 25% corn starch suspensions heated to 75°C at constant shear rate of 30s^{-1} : (a) thermal treatment without pregelatinisation ($0,2^\circ\text{C}/\text{sec}$); (b) thermal treatment with pregelatinisation at 50°C (heating from $\sim 30^\circ\text{C}$ with $0,32^\circ\text{C}/\text{sec}$) for 3.5 min followed by heating to 75°C ($0,12^\circ\text{C}/\text{sec}$). Three parallel results from each analysis are presented.

Influence of shear rate

Analyses realised with 25% starch suspensions at different shear rates show a shift of viscosity, observed in all samples. The viscosity shift is displaced to higher temperatures with the increase of shear rate (Figure 3).

This displacement is significant (1°C for an increase of shear rate from 10s^{-1} to 30s^{-1}) and can be due to changes in the material properties induced by variable shear rates. Higher shear rates (50s^{-1}) give also a viscosity shift, in this case displaced to 73°C .

As observed in Figure 3, an increase of the shear rate causes a modification of the duration of gelatinisation, the time allowed to this process being shorter for higher shear rates.

Structural investigations (like microscopy or DSC) are necessary to verify and to elucidate this behaviour.

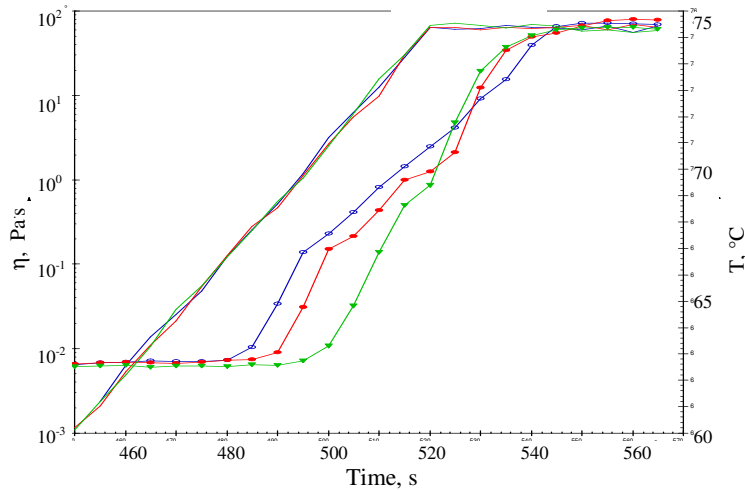


Figure 5: Viscosity shift at various constant shear rates during the treatment of C*Gel starch 25% in continuous shear mode with three different shear rates (10s^{-1} —○—, 20s^{-1} —■— and 30s^{-1} —▲—) and thermal ramp from 30 to 75°C (0.2°C/sec)

CONCLUSIONS

Viscosity curves offer valuable informations on the starch transformations during the thermal treatments (gelatinisation, pasting, melting) and could be used industrially to establish the optimal heating ratio and final temperature necessary in various processes in order to obtain products with certain characteristics (for example various gelatinisation or pasting degree).

In the tested conditions, pregelatinisation at 50°C don't modify the viscosity of starch samples. Shear rate seems to have a influence on the viscosity of starch suspensions, higher shear rates reducing the gelatinisation time.

More investigations using methods that allow the structural characterisation of starch (like DSC or SEC) are necessary in order to explain the viscosity shift observed around 65°C.

REFERENCES

1. Alavi, S., Chen, K-H., Rizvi, S.S.H., 2002, *Rheological characteristics of intermediate moisture blends of pregelatinized and raw wheat starch*, Journal of Agricultural and Food Chemistry, 50, p. 6740-6745
2. Atkin, N., Cheung, S., Abeysekera, R., Robards, A., 1999, *Localisation of amylose and amylopectin in starch granules using enzyme-gold labelling*, Starch/Stärke, 51, p. 163-172

3. Brouillet-Fourmann, S., Carrot, C., Mignard, N., 2003, *Gelatinization and gelation of corn starch followed by dynamic mechanical spectroscopy analysis*, *Rheologica Acta*, 42, p. 110–117
4. Carnali, J.O., Zhou, Y., 1996, *An examination of the composite model for starch gels*, *Journal of Rheology*, 40(2), p. 221-233
5. Drozdek, K., Faller, J., 2002, *Use of a dual orifice die for on-line extruder measurement of flow behaviour index in starchy foods*, *Journal of Food Engineering*, 55, p. 79-88
6. French, D., *Organisation of starch granules*, in “*Starch: Chemistry and Technology*” edited by Whistler R., Bemiller J and Paschall E., Academic Press, London, 1984
7. Hopkins, S., Gormley, R., 2000, *Rheological properties of pastes and gels made of starch from different potato cultivars*, *Lebensmittel Wissenschaft und Technologie*, 33, p. 388-396
8. Lagarrigue, S., Alvarez, G., 2001, *The rheology of starch dispersions at high temperatures and high shear rates: a review*, *Journal of Food Engineering*, 50, p.189-202
9. Lewen, K., Paeschke, T., Reid, J., Molitor, P., Schmidt, S., 2003, *Analysis of the retrogradation of low starch concentration gels using differential scanning calorimetry, rheology and nuclear magnetic resonance spectroscopy*, *Journal of Agricultural and Food Chemistry*, 51, p. 2348-2358
10. Neiles, E., Dewar, J., van der Merwe, C., Taylor, J., 2003, *Granule integrity and starch solubility during slow, extended pasting of maize starch- the second viscosity peak*, *Starch/Stärke*, 55, p. 72-79
11. Snyder, E.M., *Industrial microscopy of starches*, in “*Starch: Chemistry and Technology*” edited by Whistler R., Bemiller J and Paschall E., Academic Press, London, 1984
12. Spigno, G., De Faveri, D.M., 2004, *Gelatinization kinetics of rice starch studied by non-isothermal calorimetric technique: influence of extraction method, water concentration and heating rate*, *Journal of Food Engineering*, 62, p. 337-344
13. Thebaudin, J-Y., Lefebvre, A-C., Doublier, J-L., 1998, *Rheology of starch pastes from starches of different origins: applications to starch-based sauces*, *Lebensmittel Wissenschaft und Technologie*, 31, p. 354-360
14. Varavinit S., Shobsngob, S., Varayanond, W., Chinacoti, P., Naivikui, O., 2003, *Effect of amylase content on gelatinisation, retrogradation and pasting properties of flours from different cultivars of thai rice*, *Starch/Stärke*, 55, p. 410-415