Rheological Behavior of Native Sago Starch in Comparison with Other Native Starches

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ABSTRACT

A rheological model of native sago starch was developed by determining the shear stress at various temperatures, and at several shear rates, using an LVDVII+ Brookfield viscometer. The data were analyzed to obtain the consistency index (k) and the flow behaviour index (n) using an empirical power law model. Viscosity decreased with increasing temperature, and the activation energy (Eₐ) was estimated using the Arrhenius equation. For comparison, arenga sago, corn, and tapioca starches were also analyzed for measurement of pasting properties, was also used to obtain apparent viscosity a different rotational speed in rpm. An attempt was made to correlate the rheological behaviour data from these two viscometers. The result indicated that more fundamental rheological parameters usually measured with Brookfield viscometer could be estimated with high confidence by using the empirical RVA viscometer, within the conditions used in this study.

Keywords: food industries, sago, rheological, viscometer

1. INTRODUCTION

Rheological data of a food starch are essential, for predicting its behaviour of that food starch for further process engineering, formulation and intended use [1], [2]. A starch system possessing a high viscosity, would be required more force or power in its processing and would be more suitable for use as a thickener or bodying agent [3].

A review by Rao et al. has discussed the basic principles in measuring the rheological behavior of fluid foods [4]. The viscosity of a food starch is a measure of the internal friction within the starch liquid system. It is defined mathematically by the ration of shear stress and shear rate. The relationship between viscosity and shear rate has been used in classifying liquid systems into Newtonian, non-Newtonian, pseudoplastic, plastic, dilatant, thixotropic, and rheopectic. The viscosity of food is dependent upon temperature, time, shear rate, previous history, and composition of that food.

Rheological data of foods are mostly collected using well-established viscometers, such as Brookfield, Cannon Fenske, and other viscometers [4]–[8]. The Rapid Visco Analyser (RVA) which is usually used in assessing the pasting properties of food starch could be used to collect rheological behaviour data, in place of the previously mentioned viscometer [9]–[11]. The conditions during viscosity test such as rotational speed and temperature can be precisely controlled through the RVA software so that it is practically easier to run the analysis compared to the single temperature method using e.g. Brookfield viscometer. The objective of this study was to measure the rheological behaviour of native sago starch and other native starches like corn and tapioca, to measure their activation energy (Eₐ), and to correlate the rheological data obtained from Brookfield viscometer with those obtained from the RVA.

2. MATERIALS AND METHODS

Materials

Native sago starch (from Metroxylon sp.), designated as sago was obtained from Southeast Sulawesi, Indonesia. For comparison, other native starches were also analysed including sago arenga (from Arenga pinannata produced in Indonesia), corn (Hongkong produce), and tapioca (Thailand produce).

Viscosity Measurement with Brookfield LVDVII+

The concentrations of native sago starch in distilled water were 2, 3 and 4% (w/w), while those for sago arenga, corn and tapioca starches were 4% (w/w). The starch suspensions were gelatinized in a boiling water bath for 20 min with constant stirring. About 250 g of the paste was added to a 600 mL beaker to just cover the immersion groove. Viscosity was measured on triplicate samples at various temperatures using a Brookfield LVDVII+ Viscometer (Brookfield Engineering...
Laboratories Inc., Stoughton, Massachusetts) with five readings per samples at 3 min intervals. Cylindrical spindles No. #1, #4, and #UL-adapter were used, and measurements in centiPoise (cP) were taken at different rpm of the speed. Shear rates (1/sec) and shear stress (dyne/cm²) were calculated according to the manufacturer specification.

Viscosity Measurements with RVA

The gelatinized starch was prepared in the same way for the above Brookfield viscosity measurements. Then, 25.00 g of the gelatinized starch was placed in the RVA canister for viscosity measurements. A profile of the rheological test was developed at various temperatures. The shear-dependent rheological properties were measured using a shear hysteresis loop. With rotational speeds of 40, 80, 160, 320, 160, 80, and 40 rpm, each for 1 min. An example of the rheological profile is shown in Figure 1.

III. RESULTS AND DISCUSSION

A. Apparent Viscosity Measurements with Brookfield Viscometer

Apparent viscosities in cPoise were directly recorded from the Brookfield viscometer. It was shown in Figure 2 that apparent viscosity for all starch pastes decreased with increasing shear rates. Such a decrease indicated a non-Newtonian fluid with a pseudo-plastic behaviour [4]. Sim et al. observed a similar behaviour of sago starch pastes using a Brookfield cone and plate viscometer [7].

At similar concentrations, sago starch paste had the highest apparent viscosity; whilst decreasing the concentrations of sago starch resulted in a decrease in viscosity. Arenga starch, on the other hand, had the lowest apparent viscosity. Karim et al. and Nadiha et al. reported these observations could be attributed to the differences in their botanical factors, such as swelling capacity, granules sizes, and amylose/amylopectin contents [12], [13]. The higher viscosity of sago starch may be advantageous in some food applications, such as thickeners.

B. Consistency Coefficient Index (k) and Flow Behaviors Index (n)

The relationship between shear stress and shear rate can be constructed with the power law model. This model has been widely used to obtain the consistency coefficient index (k) and flow behaviour index (n) [14], [15]. The power law equation is described as follows:

$$\tau = k \gamma^n$$

Figure 2. The plot of apparent viscosity (µ) in cPoise at different shear rate of various starch pastes measured with Brookfield viscometer.

Figure 3. The plot of apparent viscosity (µ) in cPoise at different shear rate of 4% (w/w) sago starch paste and at various temperatures measured with Brookfield viscometer.
Where $\gamma$ is shear rate (1/sec),
$\tau$ is shear stress (dyne/cm$^2$),
k is consistency coefficient index (dimensionless),
n is flow behaviour index (dimensionless).

Data on the shear rate and shear stress were then converted to the log form, as given in Equation 2.
\[ \log \tau = \log k + n \log \gamma \] .......................... (2)

A linear regression method was employed to calculate the slope ($n$), and the intercept ($\log k$). This model appeared to be appropriate for all samples, which was indicated by the high value of correlation coefficient ($R^2$).

The temperature seemed to have a little influence on the $n$ values. This phenomenon has been also observed on other fluid food systems, such as Lepidium perfoliatum gum, tomato puree and soups [16], [17].

The flow behaviour of fluids is generally classified into Newtonian and non-Newtonian fluids [4]. Newtonian fluids would usually show a linear relationship between shear stress and shear rate, which has an $n$ value close to 1.0. On the other hand, a non-Newtonian fluid would have an un-proportional relationship between shear stress and shear rate to be further classified as pseudo-plastic, dilatant or plastic according to the viscosity changes in response to variation in shear rate. With an increasing shear rate, the pseudo-plastic type would display a decreasing viscosity, the dilatant type would show an increase in viscosity, and the plastic type would produce a ‘yield stress’, i.e. a force to be applied to induce a flow of the fluid. Results of this study indicated that all starch pastes exhibited a pseudo-plastic non Newtonian behaviour.

Among starch pastes analyzed, sago 4% (w/v) and tapioca 4% (w/v) had the highest $k$ values. Decreasing the concentration of sago starch resulted in a decrease of $k$ values. This seemed in line with their apparent viscosities. The $k$ values were increased with decreasing temperature, indicating that fragmented and soluble materials in the pastes tended to be re-associated at the lower temperature [7].

C. The Effect of Temperature on Viscosity

The apparent viscosity of all samples was decreased with increasing temperature. Figure 4 shows the apparent viscosity of sago starch at various temperatures, similar figures were obtained for other samples. The effect of temperature on viscosity was analysed using the Arrhenius equation [6], [17], as shown below in Equation 3.
\[ k = k_0 e^{(E_a/RT)} \] ..................................(3)

Where:
k is consistency coefficient index
$k_0$ is a constant
$E_a$ is activation energy of the flow in kcal/mol
$R$ is the universal gas constant (1.987 cal mol$^{-1}$oK$^{-1}$)
$T$ is temperature in oK

Values of $k$ at various temperatures obtained from the power model (Equation 1) were used to calculate the constant $k_0$, $E_a$ (activation energy).

The activation energy ($E_a$) is the sensitivity measurement of viscosity changes due to temperature changes. Three different concentration of sago pastes had different activation energies. Increasing concentration resulted in a lower $E_a$. This suggested that viscosity of a lower concentration solution would be more easily changed with the temperature change.

D. Correlation between Rheological Data from Brookfield LVDVII+ and RVA Viscometer.

The RVA is usually employed in measuring the pasting properties of a starch product. The variable shear and temperature facilities, which could be controlled from its software, enables a wider application, such as measuring the rheological behaviour of a starch paste. The clear advantage of this instrument was that a pasting test could be combined with a shear hysteresis loop test in one RVA test [18], as indicated in Figure 1. This obviously would provide much greater information on a sample.
A limitation of the instrument was that exact rates and shear stress could not be obtained. However, the apparent viscosity in cPoise obtained from the RVA can be assumed to be proportional to the changes of the rotational speed. The plots between apparent viscosity obtained from RVA and rotational speed in rpm of the sago starch paste at various temperatures, and in comparison with those of other starch pastes are shown in Figure 5 and 6 respectively.

Similar to the assumption described in Equation 1 and 2, an empirical mathematical relation between apparent viscosity and viscometer speed might also be constructed, as follows:

\[
\log b_R = \log b_R + a_R \log X_R
\] .............................. (4)

Where:
- \( b_R \) is the apparent viscosity at rotational speed of 1 rpm
- \( a_R \) is the slope between \( \log R \) dan \( \log X \)
- \( X_R \) is the rotational speed in rpm

Using a linear regression, the values of \( a_R \) and \( b_R \) parameters for all samples were estimated, along with their correlation coefficient (\( R^2 \)).

Values of \( b_R \) decreased with increasing temperature. These values were similar to the k values in Equation 1. The activation energy (\( E_a \)) and \( b_{Ro} \) for this experiment might also be determined using the Arrhenius equation, as in Equation 5 and the values shown in Table 5.

\[
b_R = b_{Ro} e^{(E_a/RT)}
\] .............................. (5)

where:
- \( b_R \) is the apparent viscosity at rotational speed of 1 rpm;
- \( b_{Ro} \) is a constant
- \( E_a \) is activation energy in kcal/mol
- \( R \) is the universal gas constant (1.987 cal mol\(^{-1}\) oK\(^{-1}\))
- \( T \) is temperature in °K.

Figure 5. The plot of apparent viscosity (\( \mu \)) in cPoise at different rotational speed in rpm of 4% (w/w) sago starch paste and at various temperatures measured with RVA.

The parameters of the relationship between apparent viscosity in cPoise and rotational speed in rpm, as shown in Equation 4, were estimated by using linear regression.

Apparent viscosities from these two viscometers were then estimated and correlated using a linear equation, as shown in Equation 6.

\[
\mu_B = p \mu_R + q
\] .............................. (6)

Where:
- \( \mu_B \) is the estimated apparent viscosity from Brookfield LVDVII+ viscometer;
- \( \mu_R \) is the estimated apparent viscosity from RVA viscometer;
- \( p \) is the slope of the correlation; and
- \( q \) is the intercept of the correlation.

Of all samples analyzed, the correlation coefficient (\( R^2 \)) of the relationship was more than 0.99. This suggested that a more fundamental apparent viscosity from Brookfield viscometer (\( \mu_B \)) might be estimated with high confidence from the RVA viscometer (\( \mu_R \)), within the condition ranges used in this study. Therefore, there were apparently some advantages of using the RVA over the Brookfield viscometer including the use of a relatively smaller amount of sample and the variations of shear and temperatures, which could be controlled accurately from the computer system. This would result in a relatively simple procedure in viscosity measurements.
IV. CONCLUSION

Rheological behaviour data obtained in this study would obviously be useful in utilizing sago starch in the food industries. The information of the flow behaviors obtained could be used in planning the suitability of the starch for food application, and in designing the process equipment to be used. In a case where a more fundamental viscometer would not be available, this study has indicated that proportional flow parameters could be predicted by the use of an empirical viscometer, such as the RVA. Therefore, the obvious advantage was that RVA could be employed to obtain the pasting properties and flow parameters on one sample at the same time.

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