

Flow and Thermal Behaviours of Pregelatinized Legume Starches

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Abstract

The native starches isolated from pigeon pea (*Cajanus cajan* L.), lima bean (*Phaseolus lunatus* L.) and jack bean (*Canavalia ensiformis*) were pregelatinized at 50 and 55 °C. The native starches and their derivatives were analysed for their flow and thermal behaviours. Both the native and pregelatinized starches possessed pseudoplastic flow behaviours ($n < 1$). Flow behaviour indices, n of the starch samples ranged from 0.62 to 0.86, consistency coefficient ($\text{Pa}\cdot\text{s}^n$), K , from 0.01 to 0.83, and yield stresses (Pa), σ_0 , from 0.18 to 2.86. The native starches possess higher shear viscosities than their pregelatinized derivatives, except for PPS. The values of the gelatinization temperatures were higher than the temperatures of pregelatinization of the native starches. After storage for 7 days at 4 °C, the values of transition temperatures of the starches were lowered, having undergone retrogradation. However, the native starch granules were more homogeneously distributed than their pregelatinized derivatives. These starches could be possible alternative sources of starch in meeting its ever-increasing demand in food and non-food industries.

Keywords: Starch, pregelatinization, flow behaviour, thermal properties

Introduction

Starch, versatile biopolymer, has found numerous applications in many industries, ranging from food to non-food industries. These include adhesives, agrochemicals, cosmetics and toiletries, detergents, paper making additives, pharmaceuticals, paints, textiles, water purification, biodegradable plastics, super – adsorbent materials, sugar market and so on. In its native form, starch suffers limitations under rigorous industrial processing, which can be eliminated or reduced significantly through modifications ^[1]. Hydroxypropylation has been earlier reported as a chemical modification process for legume starches ^[1]. Pregelatinization is one of the physical methods used to modify starch, resulting in alteration of physicochemical and functional properties of the starch significantly ^[2]. Due to starch granule disruption, pregelatinized starch can absorb water and increase viscosity immediately even with cold water ^[4, 5]. Adebayo and Itiola ^[4] have reported that swelling power of starch, among other functional properties, has been considered to be of great significance in tablet and capsule formulations, as it is believed that disintegrants work through a swelling and wicking action.

Depending on the application, specific starches are available for use as binders, diluents, and/or disintegrants in drugs, and as a thickening agent in pie fillings, puddings, sauces, and baby foods. Starches are being used as disintegrants because of the swelling properties of starch granules in water. Studies have shown that starches, in their various forms, have a variety of swelling abilities ^[6, 7].

The most commercially important sources of starch come from corn, wheat, rice, potatoes, tapioca and peas [8]. The high demand of starch necessitates the need to find alternative sources, hence, the importance of this present research.

Thermal properties of pregelatinized starches of jack fruit and glutinous rice have been studied and their temperatures relevant to gelatinization of were significantly higher than those of native starches, with a much lower enthalpy of gelatinization (ΔH_{gel}) [9, 10].

The present paper aims at: (a) sourcing starches from some selected legumes – pigeon pea (*Cajanus cajan* L.), lima bean (*Phaseolus lunatus* L.) and jack bean (*Canavalia ensiformis*), (b) modifying the starches via pregelatinisation process, and (c) examining the effects of pregelatinization on the flow behaviours and thermal properties of the starches. This is with the view to proposing possible applications of these starches.

Materials and Methods

Materials

Pigeon pea (*Cajanus cajan* L.) and lima beans (*Phaseolus lunatus*) were commercially purchased at Jattu Market, Etsako-West Local Government Area, Jattu, Edo State, Nigeria while jack beans (*Canavalia ensiformis*) were freshly from the orchard of the authors. All reagents were commercially purchased and were analar grade.

Isolation of Native Legume Starches

The native starches were isolated, using the method described by Oladebeye et al. [1], which is illustrated in Fig. 1.

Preparation of Pregelatinized Starches

The fully pregelatinized starches were prepared by adopting the method described by Herman et al. [6] with slight modifications. An aqueous slurry of each starch was made with 100 g of starch powder in 100 ml of deionised water and then heated at 50 °C with stirring for 10 min. The resulting paste was crisp-dried in a hot-air oven at 60 °C for 48 h, followed by grinding and sieving through a 250-mesh (250 μm) sieve before use. The same procedure was repeated for slurry of each starch at 55 °C to obtain two pregelatinized starch samples for each native starch type. The starch samples were labeled as PPS (native pigeon pea starch), PPS₅₀ (pregelatinized pigeon pea starch at 50 °C), PPS₅₅ (pregelatinized pigeon pea starch at 55 °C), LBS (native lima bean starch), LBS₅₀ (pregelatinized lima bean starch at 50 °C), LBS₅₅ (pregelatinized lima bean starch at 55 °C), JBS (native jack bean starch), JBS₅₀ (pregelatinized jack bean starch at 50 °C) and JBS₅₅ (pregelatinized jack bean starch at 55 °C),

Flow Behaviour Measurement

The flow behaviours of the starches were measured using CSL2100 Carri-Med Rheometer (AR 1000, TA Instruments Ltd) with cone and plate geometry (40 mm, 2° cone and 55 μm gap) by adopting the method of Lee et al. [11]. Starch sample (5%, w/w) was weighed into a 100 ml screw-cap conical flask and topped with deionized water to a total of 30 g. The mixture was heated on a hot plate while stirring with a magnetic bar at 160 rpm until the suspension turned from opaque to translucent solution. The flask was immediately transferred into a water-bath preset at 95 °C and held for 15 min. The flask was subsequently transferred to another water-bath preset at 80 °C for another 10 min for full viscosity development. The sample was held at 80 °C throughout the experiment to prevent gelatinization. Continuous flow test was carried out by monitoring the shear rate from 0 to 900 s^{-1} in 180 s and subsequently return to the initial rate. With this, a plot of shear stress (or viscosity) and shear rate was obtained. Torque was fixed at logarithmic ramp to minimize the inertia effect of the

rheometer. Herschel–Bulkley rheological model, $\sigma = \sigma_0 + K\dot{\gamma}^n$, was used to express the flow behaviour parameters. Each sample was freshly prepared and all measurements were carried out at 25 °C and in triplicates.

Thermal Properties

The thermal characteristics of starches were studied using a Differential Scanning Calorimeter (DSC-Q100, TA Instruments, New Castle, DE, USA). 3.00±0.01 mg of the starch sample was placed in a pre-weighed aluminium sample pan with the required amount of water to make slurry. A Starch slurry was prepared at 1:3 dry starch/water ratio and was immediately hermetically sealed using a DuPont encapsulation press (DuPont Co., Delaware, USA), and reweighed. The samples were allowed to stand at room temperature for minimum of 1 hour to equilibrate. The instrument was conditioned at 75 °C for 120 min, followed by indium check, using a standard reference pan (empty pan) and indium pan (16.6 mg) at the rate of 10 °C/min between 30–180 °C for 20 min. The samples were run for thermal properties by replacing the indium pan with the sample pans at heating rate of 5 °C/min from 20–100 °C, using the standard reference pan (empty pan) as reference. The DSC cell was purged with nitrogen gas at a flow rate of 100 ml/min. Onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and enthalpy of gelatinization (ΔH_{gel}) were computed from the thermograms, using TA Instruments Universal Analysis software. The gelatinization temperature range (R) and peak height index (PHI) were calculated as ($T_c - T_o$) and $\frac{\Delta H}{(T_p - T_o)}$ respectively. After the DSC run, gelatinized starch samples (in the original sealed pan) were stored at 4 °C for 7 days for retrogradation studies. After 7 days, samples were removed and allowed to equilibrate at room temperature for 1 h before being rescanned using the DSC with the same heating programme. Likewise, Onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and enthalpy of retrogradation (ΔH_{ret}) were evaluated automatically and percentage of retrogradation (%R) was calculated as:

$$\%R = \frac{\text{Enthalpy of Retrogradation}}{\text{Enthalpy of Gelatinization}} \times 100$$

Statistical Analysis

Means were compared using Duncan's least significant test at the 5% significance level. SPSS 17.0 software (SPSS Inc., Chicago, IL) was used to analysis the data for Pearson Correlation coefficients.

Results and Discussion

Flow Behaviours

The flow parameters, the yield stresses (σ_0), consistency coefficient (K) and flow behaviour index (n) deduced from the flow curves by Herschel-Bulkley model for the native and pregelatinized starches are depicted in Table 1. All the starches, native and pregelatinized, exhibit non-newtonian behaviour, evidenced by $n < 1$. This implies that the starches are pseudoplastic, resulting from decrease in their viscosity values with corresponding increase in shear rate (Fig. 2). The flow behaviour indices (n) of the native starches increase upon pregelatinization, except in JBS ($p < 0.05$). High values of flow behaviour indices of the pregelatinized starches indicate less pronounced shear-thinning behaviours than their native starches. The values of consistency coefficient (K) and yield stresses (σ_0) are significantly higher ($p < 0.05$) in native starches than the pregelatinized derivatives, except in PPS with slight deviation. High K and σ_0 values are mainly due to the existence of interactions between swollen granules and/or between swollen granules and an extra granular network of exudates [12]. This in turn means that the structural elements formed by molecular interactions that resist the flow are more when the viscosity of one starch pastes is high [13]. A study of the

rheological properties of the starch pastes also enables the engineering scale up in production, quality control as well as improvement of final products ^[14, 15]. Figure 2 shows the shear viscosities (0–900 s⁻¹) of both native and their pregelatinized derivatives. The native starches possess higher shear viscosities than their pregelatinized derivatives, except for PPS.

Thermal Properties

Table 2 shows the gelatinization profile of the native starches and their pregelatinized derivatives. The gelatinization temperatures, that is, onset (T_o), conclusion (T_c) and peak (T_p) are significantly different ($p < 0.05$). The values of the gelatinization temperatures are higher than the temperatures of pregelatinization of the native starches. Significant increase in all the gelatinization temperatures is observed for PPS₅₀ and JBS₅₀ whereas LBS₅₀ and LBS₅₅, interchangeably, possess increase in the gelatinization temperatures. The onset temperature is influenced by short amylopectin branch-chains and low gelatinization temperatures are characteristic of starches with larger proportions of short amylopectin branch chains ^[16]. Peak temperature is an indication of granular architecture (crystalline quality) and a high peak temperature might be due to a higher proportion of longer chains in the amylopectin as these require higher temperatures to dissociate completely than required for shorter double helices ^[17]. Increase in the enthalpies of gelatinization, ΔH_{gel} after pregelatinization is significant at 55 °C with slight deviation observed for PPS. Gelatinization temperature is considered to be a reflection of the degree of orderly arrangement of molecules in the starch granule while gelatinization enthalpy reflects the loss of molecular order. Higher gelatinization temperatures and enthalpy indicate the presence of strong bonding forces within the granule interior, that is, more orderly arrangement of molecules and thus higher degree of crystallinity ^[18]. The temperature range and PHI are an indication of the distribution of starch granules. Sasaki ^[19] has reported that the more heterogeneous the granules, the broader the temperature range and the lower the PHI. The data obtained in this present work reveal that at 55 °C, the granules of pregelatinized derivatives of PPS and LBS are less homogeneous than their native forms whereas an opposite trend is observed for JBS. Invariably, the values of PHI of the native starches are significantly higher than their derivatives.

The retrogradation profiles of the native and their pregelatinized derivatives were studied after 7 days of storage at 4 °C are presented in Table 3. The retrogradation temperatures, that is, onset (T_o), conclusion (T_c) and peak (T_p) of the pregelatinized starches are significantly higher than their native form ($p < 0.05$) with slight deviation observed for PPS in terms of their peak temperature. The peak enthalpy of retrogradation, ΔH_{ret} (8.21 J/g), is obtained in LBS₅₀ while the least (2.79 J/g) in PPS₅₀. Upon pregelatinization, there is noticeable increase in the value of ΔH_{ret} . After storage for 7 days at 4 °C, the granules of the pregelatinized starches are more heterogeneous than the native starches. In other words, the granules of the native starches are more homogeneously distributed and arranged than their derivatives. This may suggest the possible rearrangement of the granular network during retrogradation. Among the pigeon pea starch type, the peak value of %R, 118.8% is obtained in native starch while the least, 45.70% in pregelatinized starch at 55 °C (PPS₅₅); lima bean starch type, the peak value of %R, 67.33% is obtained in LBS₅₀ while the least, 39.11% in LBS₅₅ and jack bean starch type, the peak %R, 87.63% is obtained in JBS₅₅ while the least, 44.99% in the native starch.

However, the transition temperatures, temperature ranges and enthalpies of transition of the retrograded starch gels after 7 days of storage at 4 °C were lower in values than the gelatinized starch gels. This is in agreement with the previous report by Oladebeye et. al ^[1]. This might be due to the fact that recrystallization of amylopectin branched chains occurred in a less ordered manner in stored gels, as it is present in native form ^[20].

Conclusion

Pregelatinization of starches extracted from pigeon pea, lima bean and jack bean was successfully carried out. All the gels of the native starches and their derivatives exhibited pseudoplastic flow behaviour. Pregelatinization affected the orderliness of the starch granules. The native starch granules were more homogeneous than their derivatives. Retrogradation of the starches lowered their transition temperatures and enthalpies of transition after storage for 7 days at 4 °C. These starches could serve as alternative sources of starch to meet the ever-increasing demand of starch in both food and non-food industries.

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Table 1: Herschel-Bulkley parameters for native and pregelatinized starches

Starch	σ_0 (Pa)	K (Pa.s ⁿ)	n
PPS	0.18±0.05 ^a	0.02±0.01 ^a	0.86±0.02 ^b
PPS ₅₀	0.26±0.07 ^{ab}	0.25±0.07 ^b	0.66±0.04 ^a
PPS ₅₅	0.15±0.07 ^a	0.01±0.00 ^a	0.86±0.03 ^b
LSB	2.86±0.08 ^c	0.83±0.03 ^c	0.62±0.00 ^a
LBS ₅₀	0.57±0.17 ^{ab}	0.05±0.01 ^a	0.75±0.07 ^b
LBS ₅₅	0.45±0.13 ^a	0.10±0.03 ^b	0.71±0.04 ^b
JBS	0.65±0.13 ^c	0.08±0.02 ^b	0.76±0.02 ^a
JBS ₅₀	0.36±0.05 ^b	0.04±0.01 ^a	0.77±0.05 ^a
JBS ₅₅	0.32±0.02 ^a	0.05±0.01 ^a	0.75±0.04 ^a

Results are expressed as means±standard deviations ($n = 3$). Values in the same column with the same superscript letters are not significantly different ($p < 0.05$)

Table 2: Gelatinization profile of native and pregelatinised starches

Starch	T_0 (°C)	T_c (°C)	T_p (°C)	ΔH_{gel} (J/g)	^a R (°C)	PHI (J/g.°C)
PPS	76.82±0.32 ^b	89.39±0.06 ^b	81.22±0.12 ^b	6.29±1.02 ^a	12.57±0.38 ^b	1.43±0.16 ^c
PPS ₅₀	82.75±0.83 ^c	92.12±2.70 ^c	87.37±1.77 ^c	6.10±0.01 ^a	9.40±1.87 ^a	0.67±0.02 ^b
PPS ₅₅	53.09±8.18 ^a	74.93±2.66 ^a	67.48±2.16 ^a	8.99±1.12 ^b	21.84±1.84 ^c	0.41±0.06 ^a
LSB	75.45±0.77 ^{bc}	86.41±0.68 ^a	79.89±0.11 ^a	8.34±0.41 ^a	10.97±0.45 ^a	1.89±0.17 ^c
LBS ₅₀	72.88±1.07 ^a	91.40±1.77 ^b	94.48±0.66 ^c	12.25±0.37 ^c	18.52±0.69 ^b	0.67±0.01 ^b
LBS ₅₅	75.08±1.26 ^b	99.00±1.13 ^c	81.00±1.06 ^b	9.52±0.56 ^b	23.92±2.39 ^c	0.41±0.06 ^a
JBS	77.54±0.01 ^a	88.99±0.39 ^{ab}	80.93±0.15 ^a	10.51±0.71 ^b	11.45±0.38 ^b	3.10±0.07 ^c
JBS ₅₀	80.42±1.42 ^b	91.92±0.70 ^c	83.90±0.35 ^b	13.45±0.48 ^c	11.50±0.28 ^b	1.17±0.07 ^b
JBS ₅₅	80.72±0.66 ^b	88.32±0.43 ^a	83.21±1.07 ^b	7.24±0.36 ^a	7.60±0.23 ^a	1.40±0.06 ^a

^aR = range of temperature ($T_c - T_0$); PHI – peak height index ($\frac{\Delta H}{(T_p - T_0)}$); Results are expressed as means±standard deviations ($n = 3$). Values in the same column with the same superscript lowercase letters are not significantly different ($p < 0.05$)

Table 3: Retrogradation profile of native and pregelatinized starches

Starch	T _o (°C)	T _c (°C)	T _p (°C)	ΔH _{ret} (J/g)	^a R (°C)	%R
PPS	43.21±0.57 ^a	74.83±5.48 ^b	56.05±1.69 ^a	7.54±2.02 ^b	31.62±6.05 ^{bc}	118.83±12.92 ^c
PPS ₅₀	50.87±0.35 ^c	72.61±0.66 ^a	56.62±1.47 ^a	2.79±0.08 ^a	21.74±1.01 ^a	45.70±0.70 ^a
PPS ₅₅	45.05±1.17 ^b	75.68±2.89 ^b	56.91±0.37 ^a	7.91±2.18 ^c	30.64±4.05 ^b	91.86±4.16 ^b
LSB	43.01±0.64 ^a	71.67±0.47 ^a	56.55±0.00 ^a	5.45±0.13 ^b	28.66±1.10 ^b	65.35±2.04 ^b
LBS ₅₀	44.58±0.62 ^b	76.30±4.96 ^{ab}	57.26±0.40 ^b	8.21±2.25 ^c	31.72±5.57 ^c	67.33±2.04 ^c
LBS ₅₅	51.41±1.01 ^c	76.67±0.78 ^b	60.89±0.52 ^c	3.71±0.14 ^a	25.27±1.79 ^a	39.11±3.78 ^a
JBS	44.62±0.54 ^a	71.53±0.37 ^a	59.28±0.13 ^a	4.73±0.37 ^a	26.91±0.92 ^a	44.99±0.47 ^a
JBS ₅₀	46.80±0.30 ^b	75.47±0.64 ^b	60.52±0.57 ^b	7.10±0.16 ^c	28.67±0.34 ^{bc}	52.85±3.05 ^b
JBS ₅₅	47.30±0.68 ^b	75.92±0.41 ^b	62.61±0.40 ^c	6.33±0.29 ^b	28.55±1.09 ^b	87.63±8.37 ^c

^aR = range of temperature; %R – percentage retrogradation; Results are expressed as means±standard deviations (n = 3). Values in the same column with the same superscript lowercase letters are not significantly different (p < 0.05)

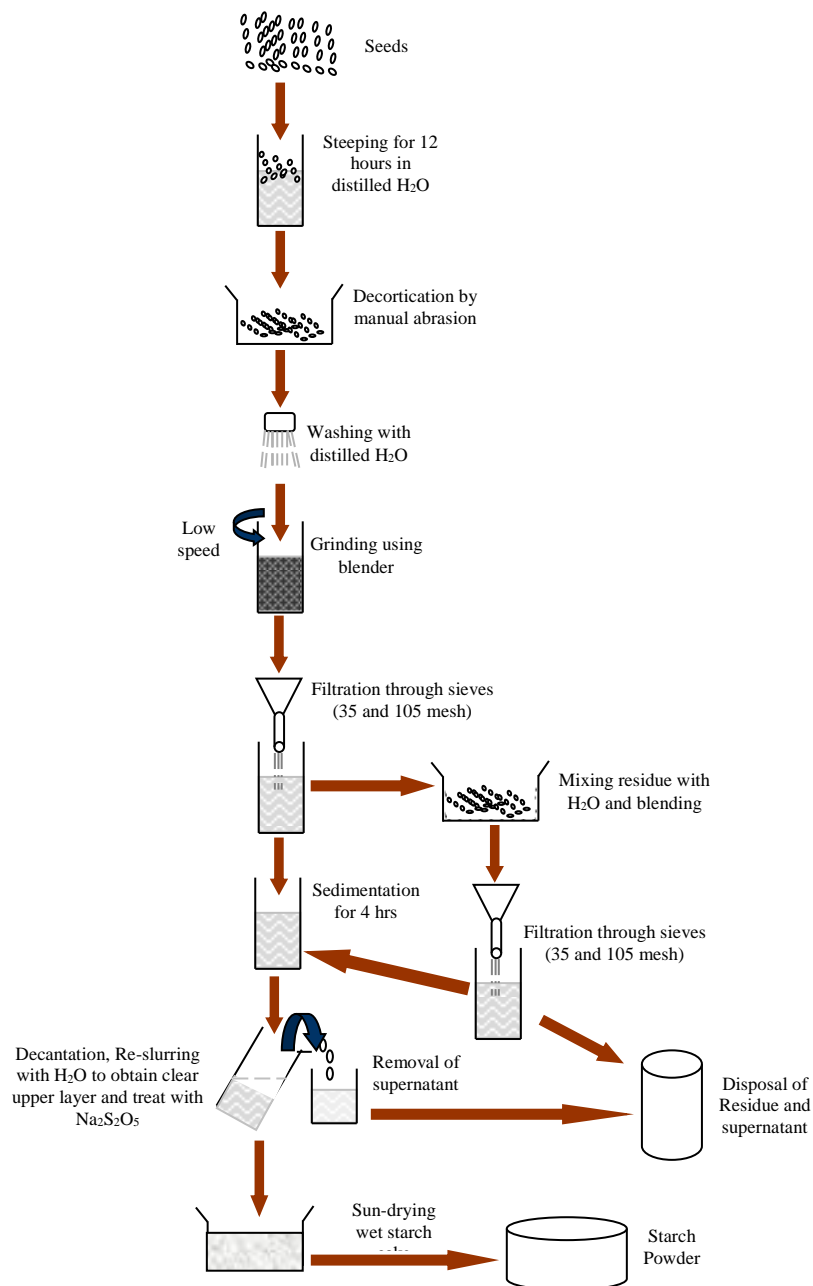


Figure 1: Isolation of Legume Starches

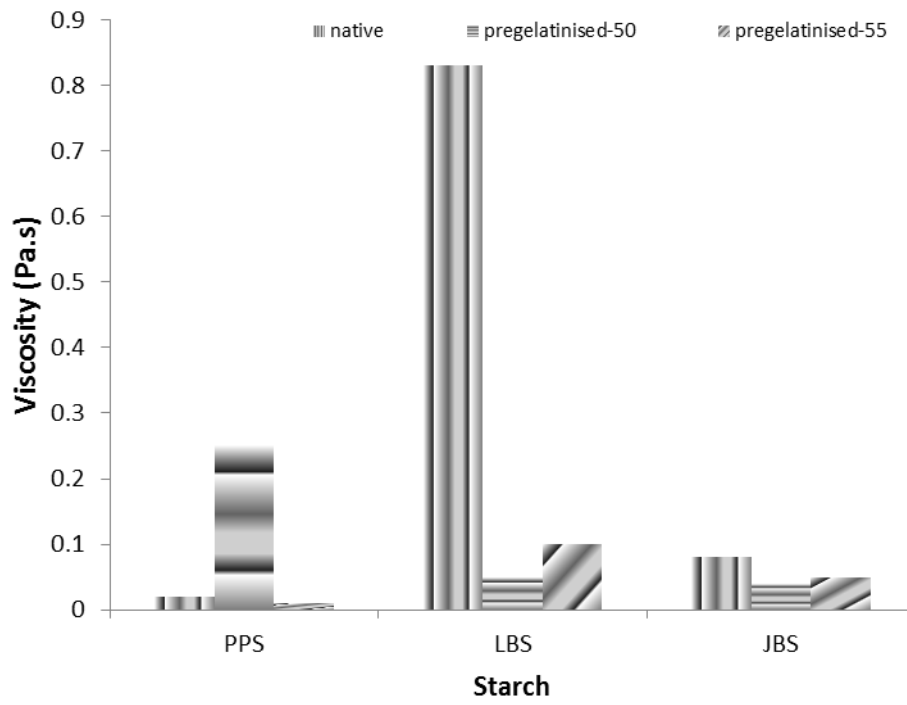


Figure 2: Viscosity of native and pregelatinised (50°C, 55°C) starch samples. Measurements were made at 25°C.