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Pasting, Thermal and Gel Texture Properties of Three Varieties of Nigeria Rice Flours and Starches

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Authors' contributions

This work was carried out in collaboration between all authors. Author OJO initiated the idea and designed the work. Author MMI supervised the work. Author KAA is the student that carried out the experimental work at a research institute in Nigeria. All authors read and approved the final manuscript.

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ABSTRACT

Flours and starches from three Nigeria rice varieties CISADANE (Faro51), OS_6 (Faro11) and NERICA 19 were evaluated for their pasting, thermal and gel texture properties. Their thermal properties were evaluated with Differential Scanning Calorimeter (DSC) and pasting properties were obtained using a Rapid Viscography Analyser (RVA). Light transmittance of their gel textural properties was determined using UV-vis spectrophotometer. The results showed that Glass transition temperature (Tg) was highest in CISADANE (Faro51) (222ºC) and almost the same in OS_6 (Faro11). Melting point (MP) temperature was highest for OS_6 (Faro11)(264ºC) and almost the same for

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NERICA 19 and CISADANE (Faro51) flour. Tg values of starches were almost the same in CISADANE (Faro51) and NERICA 19 (264ºC). CISADANE (Faro51) starch showed highest melting point (237ºC), almost the same for the other two starches. It was observed that defatting caused degradation in the physical properties of flours and starches of all the three rice varieties investigated. It was concluded that proteins and fats could influence the glass transition and other physical properties of rice flours and their respective starches.

Keywords: Flours; starches; pasting characteristic; thermal properties; gel texture properties.

1. INTRODUCTION

Quite often in recent years food processing industry has been employing starches or flours derived from roots, tuber and cereals as ingredients to impart specific functional properties in a wide range of formulated foods. The ultimate success of utilizing any starch or flour source as food ingredients or some other industrial applications depends largely on their physical properties [1-3].

Raw or native starches are often modified in order to obtain combinations of properties suitable for specific industrial applications and also to make them more versatile in their applications by introducing new properties. The most commonly used physical method for modification of starch is through its hydrothermal treatment [4]. This involves heating the starch slurry coupled with stirring. Heating alters the structure of starch granules irreversibly during gelatinization. The granular structure is destroyed, the system of hydrogen bonds is broken and the state of free hydroxyl group is fixed in the starch paste.

In Nigeria, rice is grown in all ecological and dietary zones, with different varieties possessing adaptation traits for each ecology [5-6]. Though, there are ample information on the physicochemical and cooking characteristics of rice varieties grown in U.S.A. and Asia, there are less information on same properties in Nigeria rice varieties. Rather, breeding, agronomy and crop production have received considerable attention.

For example, the National Cereals Research Institute (NCRI) at Badeggi Bida Nigeria has continued to introduce farmers to improved rice varieties for different ecologies. In recent years breeding has become a veritable means of obtaining new varieties of rice with specific or new properties incorporated.

Although rice is usually processed and consumed in whole kernel form, its conversion to flour and starch would provide a more stable form of the product as well as increase its versatility and broaden its industrial application. Native starch in many starch-based products is subjected to some thermal treatments during its processing or manufacturing. Hence thermal analysis will be particularly valuable in evaluating effects of hydrothermal treatment on starch-based products.

In addition, evaluation of other functional properties of the starch pastes or gels will further help in understanding of the nature of these starches and thus their suitability for various functional purposes. Hence, the objectives of the current research were to determine the effects of changes in temperature and starch concentration on the pasting, thermal, gel texture, clarity and other physicochemical properties of rice flours and starches. The results of this study are expected to improve the understanding of how temperature and starch concentration affects various properties of rice flours and starches for further application in product development.

2. MATERIALS AND METHODS

2.1 Materials

Rough rice samples of the three varieties of Nigeria rice, CISADANE (Faro51), OS_6 (Faro11) and NERICA 19 were collected from the International Institute of Tropical Agriculture (IITA), Ibadan, Oyo State, Nigeria.

2.2 Preparation of Full-Fat Flour Samples

A dehusker (THU-35, Satake, Hiroshima, Japan) was used to dehusk 150g rough rice samples. The brown rice recovered was weighed and then milled for 30 sec in a McGill NO.2 mill. Head rice was separated from the broken kernels through a double tray sizing device. Flour samples were obtained by grinding the sample with a cyclone mill fitted with a 100 mesh sieve.

2.3 Preparation of Defatted Flours

The defatting of the full-fat flours was carried out with 85% methanol for 18-24 hours. The defatted samples were exposed to room temperature for 48 hours.

2.4 Preparation of Starch Samples

Starch samples were prepared based on the alkaline-steeping method of Yang et al. [7] with slight modification. Head rice sample (10g db) was soaked in 40ml of 0.1% Sodium hydroxide (NaOH) for 24 hour, washed once with tap water, wet-milled in a osterizer blender for 4 min at speed 6, filtered and then centrifuged for 15minutes at 1,500 rpm. The supernatant was transferred into a 250-ml volumetric flask while the top yellow curd-like layer of the residue was discarded by carefully scraping it off with spatula. The remaining residue was again extracted with 0.1% NaOH, centrifuged using the same speed, and the supernatant collected into the same 250ml volumetric flask. The residue was then adjusted to pH 6.5 with 0.2 M HCL and washed with 40ml of deionized water three times. For each washing, the supernatant was also transferred into the same 250 ml volumetric flask. The starch residue was then dried at 40°C for 24hr. The dried residue so obtained was ground using a Retsch ultra centrifugal mill.

2.5 Methods

2.5.1 Pasting characteristics of rice flours and starches

A Rapid Viscography Analyser Model 3D (RVA) (Newport Ply Ltd, Warriewood NSW 2102, Australia) was employed to determine the pasting properties of the rice flour and rice starch samples. The sample (3.5g) was made equivalent to 14% moisture and mixed with water in an RVA aluminum canister to make the total weight of the slurry to 28g. A programmed heating and cooling cycle was followed. As the sample was installed on the rotor of the RVA and heated from 50 to 93ºC (at 50ºC for 1 min and 4 min to reach 93ºC). It was held at 93ºC for 7 minutes cooled from 93ºC to 50ºC in 4 minute, and allowed to stand at 50ºC for 3 minutes. Readings were displayed on the monitor in a numerical and graphical form. At fixed peak viscosity value, various ratios of breakdown (H/P), setback (C/P), and total setback (C/H), and relative breakdown (BDr) were calculated by taking the ratio of P-H to C-H.

Where: P is peak viscosity; H is hot paste Viscosity and C is cold paste viscosity.

2.5.2 RVA Gel textural properties of rice flours and starches

The gel so obtained after the viscography analysis in RVA was immediately removed, mixed with a spatula, transferred into an aluminum cup of 40mm diameter and 10mm depth, covered with aluminum foil, and kept for 4hr at room temperature. Its texture was measured by a Tensipresser. The gel was compressed to 9.8mm or 0.2 mm clearance by means of a plunger of 10mm diameter in the cup of dimensions mentioned above, and measurements were based on the texture profile method of Bourne [8]. The textural parameters of hardness, stickiness, adhesiveness, and cohesiveness were determined. In the calculation of these parameters, some of the values were divided by the area of the plunger in order to express the values as dynes per square centimeter.

2.5.3 Thermal analysis by differential scanning calorimeter

The thermal properties of each rice flour and starch sample were determined with a DSC 22ºC instrument. Silver crucible of P/N 560-004 AG 15 capsule was used for the experiments. About 5mg of the sample was used in each experiment. Heating was carried out from 30 to 350ºC at the rate of 10ºC/min. The sample was placed in the silver cup, covered with the silver lid, and sealed very carefully with the sealer supplied by the manufacturer. Another empty cup was used after sealing as before, making this the reference (air). The instrument was calibrated using melting temperature and enthalpy of indium. Mainly glass transition, melting point, and dextrinization or degradation or decomposition point were measured.All experiments were carried out in replication except DSC, where the melting point and decomposition point were reproducible even by carrying out experiments two or three times. Hence, only one experiment was carried out in this instrument.

2.5.4 Amylose content determination

The sample (100mg) was treated with 1ml of ethyl alcohol in a 50ml conical flask, slowly stirred treated with 9ml of 1N Sodium hydroxide, and heated in boiling water for 10 minutes with occasional stirring. The sample was cooled to room temperature, transferred and finally made up to volume with water. Five milliliters of the dispersion was taken, 50ml of water was added. 1N Acetic acid was added and whole contents were shaken and 2ml of 0.2% Potassium iodide solution was added to make up to volume with water and kept at 27ºC for 20 minutes. Colour was read at 620 nm in a UV-2010 spectrophotometer with a blank (without sample). A standard graph was prepared by using different proportions of amylose and waxy rice starch (0% amylose and 100% waxy starch amylopectin) similarly different proportions and finally 100% amylose and 0% waxy starch amylopectin) wetted with 1ml of alcohol followed by 9ml of alkali and following the same procedure as above for developing the colour. A standard graph was drawn with absorbance on y-axis and amylose content on x-axis. A regression equation was prepared for estimating amylose content in the unknown sample.

2.5.5 Light transmittance and amylose content absorbance of soluble rice flour and starches

Light transmittance was measured according to the method of Singh et al. [9]. In the experiments (0.1%) aqueous suspension of sample was heated in water bath at different temperatures ranging from 50 to 90ºC for 30 minutes at each temperature. The suspension was cooled to room temperature and transferred to a 50ml volumetric flask after being made up to volume with water. After this, the remaining dispersion was centrifuged at 3,000 rpm for 15min, and the supernatant was carefully transferred to a beaker. Five milliliters of this was taken for the measurement of the soluble amylose content at an absorbance of 620nm after the colour had been developed as described above.

3. RESULTS AND DISCUSSION

3.1 Pasting Properties

The transition from a suspension of starch granules to a paste, when heat is applied, is accompanied by a large increase in viscosity [10]. The pasting properties of samples of rice flours and their respective starches are presented in Table 1. In this table P is the peak viscosity observed when the slurry is heated and the granules swell, highest was recorded as peak. It is the hot paste viscosity, which is an indication of disintegration of granules after reaching maximum viscosity (generally at higher concentrations of slurry the value of P will be greater than H), and C is the cold paste viscosity, which is obtained while the hot paste slurry is cooled from H onwards. P-H is the breakdown; instead of this, the ratio has been expressed. Breakdown is a measure of the ease of disrupting swollen starch granules and indicates the degree of stability during cooking [11]. The breakdown ratio of H/P was high in the case of CISADANE (Faro51) rice flour, taking into consideration the H/P values, CISADANE (Faro 51) rice comes under group III rice quality as enumerated by Bhattacharya et al. [12], OS_6 (Faro11) rice comes under group VI and NERICA 19 rice comes under group VI and NERICA 19 rice flour fits authentically very well in group VIII. Depending on the total, soluble and insoluble amylose contents, equilibrium moisture content on soaking in water at room temperature, alkali score, stickiness, consistency, and relative breakdown. Existing rice varieties in the world have tentatively been classified into eight quality groups; group I cooks flaky and hard whereas group VIII cooks extremely sticky and soft and group IV is scented rice varieties [12]. Other values do not shed much light except relative breakdown for NERICA 19 rice flour, which very well fits into the quality profile of rice varieties. Probably, conditions with RVA and Brabender amylograph need to be standardized in a separate study. Among corresponding starches, there was a remarkable difference in the case of OS_6 (Faro11), for which the H/P value was high compared to its flour and the value for NERICA 19 rice starch for C/H (total setback ratio) was almost the same as that of its flour. In fact, the comparison has been made by equalizing the concentration of starch in the flour along with the pure isolated starch, still some differences have been shown, which may be due to the presence of fat and a negligible quantity of protein. This pasting behavior illuminates peculiar properties of OS_6 (Faro11) and NERICA 19 rice starch, which demands further testing by other experimental data.

Table 1. Pasting characteristics and viscography indices of rice flour and respective rice starches at a peak viscosity of 200 RVA units

Rice/Form	H/P	C/P	C/H	BDr
Flour				
CISADANE (Faro51)	0.61	1.00	1.63	1.00
OS_6 (Faro11)	0.48	1.00	2.10	1.00
NERICA 19	0.49	0.68	1.57	2.78
Starches				
CISADANE (Faro51)	0.54	1.00	1.85	1.00
OS_6 (Faro11)	0.60	1.00	1.60	1.00
NERICA 19	0.60	0.63	1.60	2.66

3.2 RVA Gel Texture Properties of Rice Flours and Starches

At the end of the RVA run, the texture of the gel was measured using the Tensipresser and some of the parameters are shown in Table 2. Among the three types of rice flours and starches, at lower concentrations, the gel texture could be measured only in CISADANE (Faro 51) and OS_6 (Faro11). However, in NERICA 19 rice flour, it was not possible to measure even at higher concentrations up to 10.6% except its flour at 12.5% concentration, which is 3.5g in the present experiment. In the case of CISADANE (Faro51) flour and starch, starch shows a higher hardness, lesser stickiness, higher adhesiveness, lower cohesiveness and lower balance degree (balance degree is the ratio of hardness to stickiness) compared to its rice flour. OS_6 (Faro11) starch showed higher hardness, lesser stickiness, higher adhesiveness, lesser cohesiveness, and lesser balance degree compared to its rice flour. NERICA 19 rice starch could not register any measurement under the conditions employed here. However NERICA 19 rice flour showed lower hardness, higher stickiness, almost the same adhesiveness, higher balance degree, and higher cohesiveness compared to other rice flours. Further work is needed to reach generalized conclusions in the case of OS_6 (Faro11) and NERICA 19 varieties of rice.

During storage, the gel system starts to retrograde and gel firmness increase. This is mainly due to the rearrangement of amylose and recrystallization of side chains of amylopectin to form a three-dimensional network [13-14]. The changes in textural properties during storage is an indication of retrogradation tendency of starch gels; the greater the textural changes during storage, the greater is the tendency of starch to retrograde [13]. Parameters of textural properties of starch gel are influenced by various factors, including the rheological characteristics of the amylose matrix, the volume fraction, the rigidity of the gelatinized starch granules as well as the interactions between dispersed and continuous phase of the gel [15]. Other components naturally present in the starchy material or additives interact with starch and influence pasting behaviors. The presence of proteins with disulfide linkages has been reported to confer shear strength and gelatinized paste rigidity to starch [16-17].

3.3 Thermal Properties of the Rice Flours and Starches

Some of the thermal analysis properties of the three types of rice flours and their starches before and after defatting are presented in Table 3. Special care was taken to measure glass transition (T_g) points. The glass transition is ill-defined below 13% moisture. In this work, there were sharp peaks before melting, but in some cases very weak peaks were observed. Therefore, the scales were enlarged, and the peaks before melting points were taken into consideration for comparison purposes. Also, there is no perfect method; there are several literature reports of different methods of addition of moisture and measurement of glass transition. Hence, in this method, samples per sec were taken for experiment and the observations were made. Moisture content varied from 9 to 11% in the isolated starches and from 13 to 14.5% in their respective rice flours.

Early stage of the experiments revealed that great variations in the results were not seen in these moisture ranges. Melting point (M_p) and degradation peaks (D_p) were very clear and sharp. The very first melting point of rice flour in all the three types remained almost the same; the highest (264.1ºC) was shown by OS_6 (Faro11) rice flour followed by NERICA19 rice flour (261.4ºC) and CISADANE (Faro51) rice flour (259.8ºC), indicating that the presence of protein and fat does not have significant effect on this property. After defatting, the melting points increased marginally in each flour. Thus, the highest increase (12.2ºC) was observed in CISADANE (Faro51) followed by OS_6 (Faro11) (6.6ºC) and the least (1.0ºC) in the case of NERICA 19 rice flour, indicating that the presence of the lipids may interfere with the starch and protein matrix of each type of flour. The degradation or dextrinization point of flour after melting occurs generally at 18^{o}C higher than the melting point in the case of CISADANE (Faro 51) rice flour, around 10^{o}C higher in OS_6 (Faro 11) and around 8ºC higher in NERICA 19 rice flour. Hence, both protein and fat have a tremendous effect on degradation point of these types of rice flours.

Table 2. Some textual parameters of the gels of different rice flours and their corresponding starches

Name	H1	-H1	Adh	Balance	Coh
CISADANE (FARO51)					
Flour	1.51×10^5	7.07×10^4	1.29×10^6	0.47	0.52
Starch	2.89×10^5	6.27×10^4	2.87×10^6	0.22	0.46
OS6 (FARO 11)					
Flour	1.63×10^5	7.21×10^4	1.21×10^6	0.40	0.54
Starch	2.08×10^5	7.09×10^4	1.41×10^6	0.31	0.46
NERICA 19					
Flour	9.98×10^5	7.18×10^5	1.23×10^5	0.72	0.74

Surface hardness (H1); Surface stickiness (-H1); Adhesiveness in dyn/cm2 (Adh); Cohesiveness (Coh); Balance degree (Balance)

After defatting an 8-9.5ºC rise in temperature was observed in CISADANE (Faro51) and OS_6 (Faro 11) but there was less of an increase in NERICA 19 rice flour indicating the least effect of fat in the case of NERICA 19 rice flour and substantial effect on OS_6 (Faro 11) and CISADANE (faro 51) rice flours. Glass transition (T_g) (221.8ºC) was highest in CISADANE (Faro 51) rice flour and almost the same in OS_6 (Faro11) (210.7ºC) and NERICA 19 rice flours (209.3ºC). After defatting, the T_g value decreased for OS_6 (Faro11) but increased in CISADANE (Faro 51) by 5.9ºC, and that for NERICA 19 rice flour by 17.2ºC although the peak was not sharp in the case of this NERICA 19 rice flour indicating the presence of amylopectin and protein; that is, defatted NERICA 19 rice flour behaves differently. The change in T_g can be taken as a type of cross-linking between starch and protein or fat or both, although they exist as globules or protein matrix along with starch granule in the cell compartments of the endosperm of rice grain, and it is well reported that cross-linking increases T_g.

Starches have higher melting points compared to their respective flours, probably because they are free from protein to a greater extent, although not completely. The highest melting point (276.2ºC) was shown by CISADANE (Faro 51) starch followed by OS_6 (Faro11) (268.5ºC) and NERICA 19 starch (267.0ºC). Degradation or dextrinization takes place at the temperature of 2-5ºC above their respective points. After defatting, in starch, the melting point of CISADANE (Faro51) and OS_6 (Faro11) increased to the same extent (8ºC), but the increase in NERICA 19 was only 6.5ºC indicating that the absence of protein and fat enhances the melting point of starches (defatted) to a greater extent, whereas the presence of these did not have much effect, as seen by the melting point of respective flours. However after defatting, degradation occurs at a higher temperature compared to the non-defatted ones. The degradation point increased from 1.4 to 5ºC after defatting in all three types of starches compared to the melting points of defatted ones. These interesting observations indicate the influence of protein and fat (or Lipids) on the physical properties of these rice flours and their starches. The T_g values among the starches were almost the same in CISADANE (Faro51) (235.8ºC) and NERICA 19 (237.6ºC) but were lower in OS_6 (Faro11) starch (215.5ºC). These values decreased after defatting; the extent of decrease varied by 23.5ºC in CISADANE (Faro51) by 6^{o}C in OS_6 (Faro11) and by 23.4ºC in NERICA 19 starch. These observations led to some speculations. If these fat or lipid globules are attached to the starch granules or encapsulated to granules, in flexible types of side groups, their T_g could decrease after defatting.

Table 3. Some of the parameters derived from the thermograms of the DSC instrument for various rice flours and their starches before and after defatting

Type of rice	M_p (^{o}C)	D_p (^{o}C)	T_g (^{o}C)	ΔH Top peak (mJ/mg)	ΔH Bottom peak (mJ/mg)
CISADANE (FARO 51)					
Flour	259.8	278.6	221.8	-318.0	320.8
Defatted flour	262.0	269.9	227.7	-232.2	263.3
Starch	276.2	278.0	235.8	-059.3	119.4
Defatted starch	284.4	212.3	212.3	099.3	055.0
OS6 (FARO 11)					
Flour	264.1	273.6	210.7	-210.9	276.2
Defatted flour	265.1	274.6	204.6	-206.5	193.8
Starch	268.5	272.8	215.5	-202.8	125.9
Defatted starch	276.4	281.4	209.8	-213.3	132.7
NERICA 19					
Flour	261.4	269.3	209.3	-335.1	178.1
Defatted flour	261.3	226.5	226.5	-041.7	266.3
Starch	267.0	237.6	237.6	-034.1	109.4
Defatted starch	273.5	214.2	214.2	-017.7	190.9

Moreover, starch consists of two major chemically distinguishable polysaccharides, amylose and amylopectin. Amylopectin is a highly branched molecule. The crystalline nature of starch seems to be associated with the amylopectin molecule. If this is the case, the melting point of NERICA 19 starch which is fully amylopectin is supposed to be correct, because crystalline molecules will have sharp melting point. A similar explanation can be given for the amorphous nature of linear polymer present in CISADANE (Faro51) and OS_6 (Faro11) starches. The glass transition is mainly due to the amorphous polymer (linear i.e amylose) where the molecules slide over each other.

3.4 Light Transmittance and Amylose Content Absorbance

The light transmittance of the flours and starches of the three rice varieties are shown in Fig. 1. In the case of the respective rice flours there were difficulties in the measurements of the transmittance, as irrespective of the temperature of cooking, the values were abnormal; hence, values are not presented. It is seen from Fig. 1 that respective starches showed a particular pattern. Up to 70ºC the capacity was higher, as light transmittance was lower and dramatic changes took place after 70ºC, which was in and around the gelatinization temperature of all three types of starches, indicating the cooking of the starch granules, loss of crystallinity and reaching the Birefringence End Point Temperature (BEPT). NERICA 19 rice starch recorded the highest light transmittance, indicating the peculiar nature of the amylopectin molecules and clear clarity of this starch. At 50ºC the light transmittance was high in OS_6 (Faro11) starch, then decreased at 60ºC, and further increase was observed beyond this temperature. This is a peculiar observation. In other words, percent transmittance was inversely related to the amylose content of these starches, as is clearly seen from Fig. 1. NERICA 19 starch had the highest value and CISADANE (Faro51) the lowest. Light transmittance provides information on the behaviour of starch paste when the light passes through it and it depends on granule size, swelling capabilities, amylose content, amylose/amylopectin ratio, the level of swollen and insoluble granule remnants [18-20].

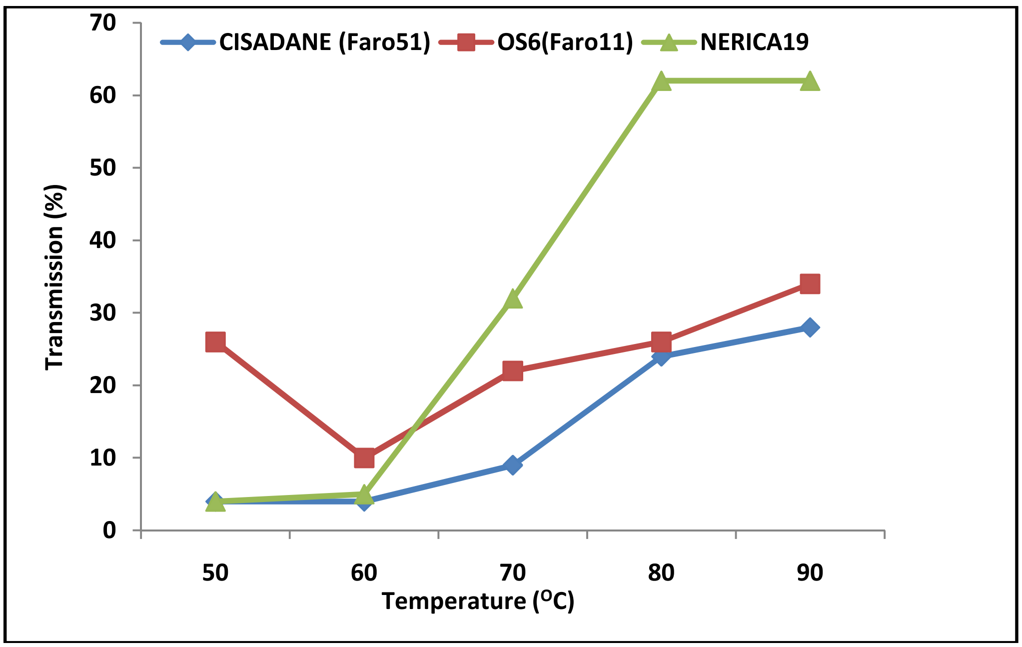

Fig. 1. Percent transmission of various rice starches (0.1% Conc.)

It is also clear from Fig. 2 that the amylose content absorbance of solubles was highest in CISADANE (Faro 51) starch followed by OS_6 (Faro11) and then NERICA 19 rice starch. These observation suggest that the higher the amylose content, the higher will be leaching of the linear polymer from each type of starch while cooking. Thus 50% less leaching occurred in the case of rice flours especially at 90°C, when compared to their respective starches. Leaching of linear polymer was very high in starches compared to that in their respective flours as it is seen from Fig. 3 that absorbance was high in starches.

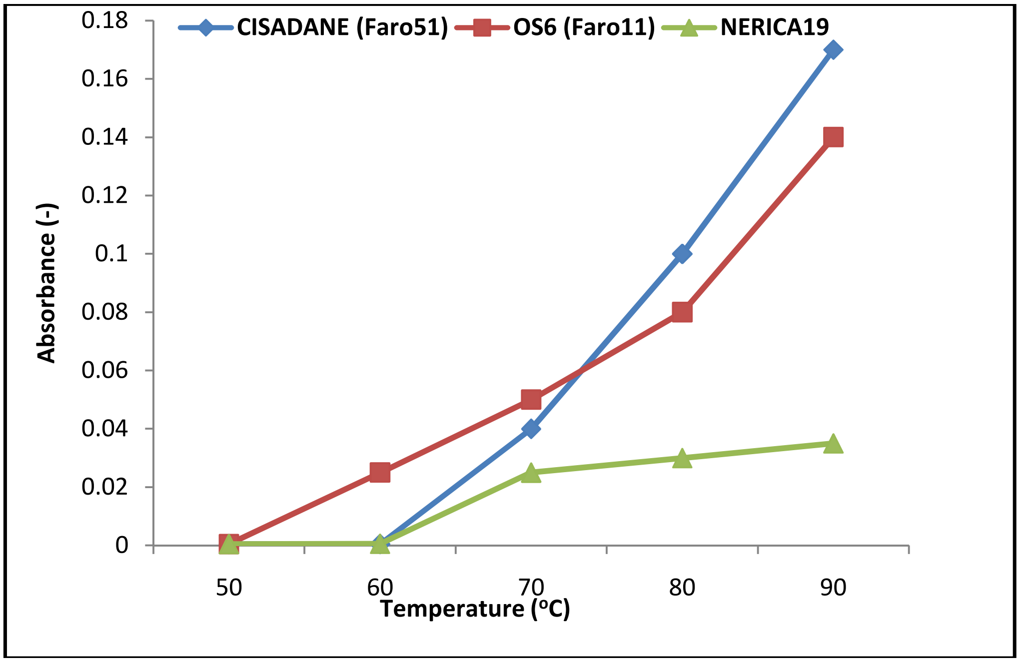

Fig. 2. Amylose content absorbance of solubles of various rice starches

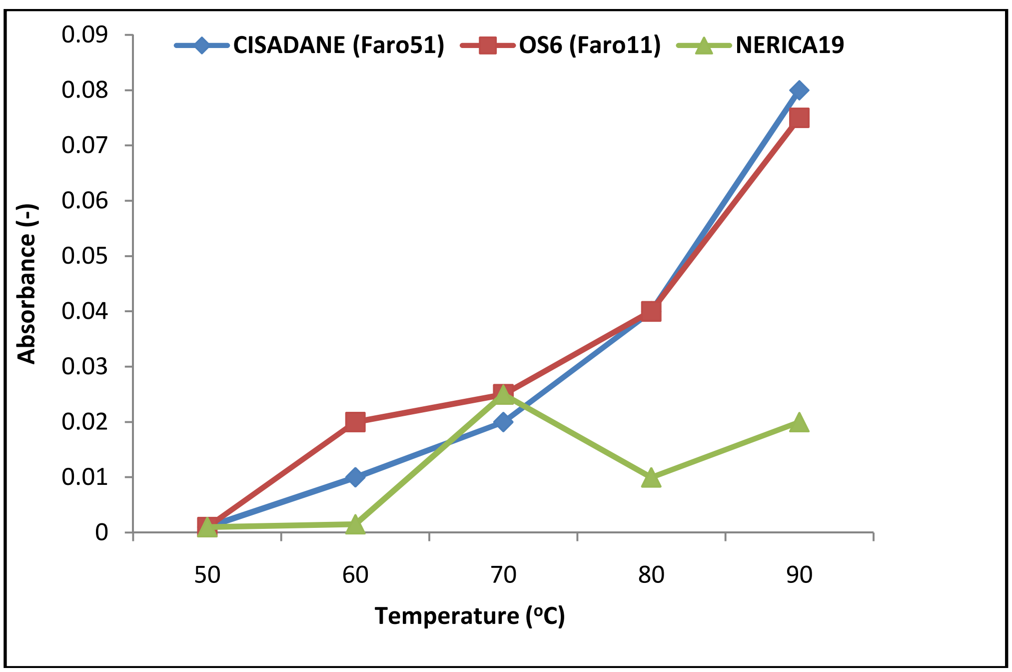

Fig. 3. Amylose content absorbance of solubles of various rice flours

Again, contents of amylose, though negligible in NERICA 19 flour and its starch there is a change at a particular temperature (70ºC), which was the same in the swelling and solubility experiments of this rice. It appears that proteins and lipids hinder the leaching of linear polymers, as it is observed in their respective rice flours that amylose content absorbance was less in these flours compared to their respective starches (Figs. 2 and 3), where fat is present to a greater extent but proteins to a negligible extent, may be one of the reasons for the easy leaching of linear polymers; hence, there is higher amylose content absorbance in starches and in a rice of higher amylose content. It has been reported that amylose standards obtained from various sources may vary widely in terms of quality, the presence of lipids that could interfere with the assay, and the pH of the final solution are other possible sources that contribute to the wide variation [15].

4. CONCLUSION

It was concluded from the present study that the presence of protein and fat does not have significant effect on the melting point of the flour of three varieties of rice investigated. However, after defatting, the melting points increased marginally in the flour of each variety. It was further concluded that both the protein and fat have a tremendous effect on degradation point of rice flours, and that the cross-linking increases the glass transition temperature T_g. Starches have higher melting points compared to their respective flours, however, it was inferred from the study that after defatting, degradation of flours and starches for the three varieties of rice occurs at a higher temperature compared to the non-defatted ones. It was finally deduced that the percent transmittance was inversely related to the amylose content of the starches of the examined rice varieties and that the leaching of linear polymer was also very high in their starches compared to their respective flours.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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