COMPARATIVE STUDY OF THE PHYSICOCHEMICAL PROPERTIES OF STARCH BLENDS-PIGEON PEA AND RICE STARCHES VERSUS BAMBARRA GROUNDNUT AND CASSAVA STARCHES

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ABSTRACT

Pigeon pea starch (100PPS), rice starch (100RS), bambarra groundnut starch (100BBS) and cassava starch (100CS) were blended in different ratios: (70PPS/30RS; 50PPS/50RS; 30PPS/70RS) (PPS/RS) and (70BBS/30CS; 50BBS/50CS; 30BBS/ 70CS) (BBS/CS) and their physicochemical properties were compared. The apparent amylose contents of the PPS/RS blends ranged from 33.14% (30PPS/70RS) to 42.63% (50PPS/50RS) compared with 33.23 (30BBS/70CS) to 41.53% (70BBS/30CS) of the BBS/CS blends. Significant differences were observed in the bulk density, dispersibility and pH of both blends (PPS/RS and BBS/CS). In the PPS/RS blends, the swelling power and the water solubility index were lower than that of the control starches while these parameters fluctuates as the temperature increased in the BBS/CS blends. While the pasting parameters (with the exception of pasting time and pasting temperature) of the PPS/RS blends were non-additive compared to the BBS/CS blends that were additive (with the exception of peak and breakdown viscosities) of their individual components. The under-utilized 100PPS could be more important industrially by substituting part of it into the more expensive 100RS. Overall results indicate that blending of native starches from different botanical sources improves their properties.

Key words: Physicochemical, Pasting, Dispersibility, Blending, Viscosity.

INTRODUCTION

The importance of starches lies in their abundant availability, cheapness, renewability, biodegradability, non-toxic nature and possession of ubiquitous hydroxyl groups. The uniqueness and individuality of starches from different botanical origin had been widely attributed to differences in morphology, amylose/amylopectin ratio and soil type during growth. It is these differences in its entirety that accounted for the different applications of these starches in the food and non-food industries.

The industrial utilization of native starches is limited due to inherent high rate of retrogradation, insolubility in water and fluctuation in viscosity during thermal processing[1]. Furthermore, instability of pastes and gels under various temperatures, shears and pH conditions also restricted the commercial applications of native starches. This deficiency of native starches is mitigated by physical and chemical modification, enzymatic and biotechnological modification, or their combinations. The introduction of chemicals (e.g. epichlorohydrin) in starchy food that tend out latter to be carcinogenic and banned is part of the problem associated with chemical modification[1]. Nowadays, market trends are towards natural food components, avoiding as much as possible any chemical treatments[2].

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Blending of starches from different botanical origin has come as a good alternative. It is cheap and does not involve the addition of chemicals or biological agents into the starches. Blending of starches is not an entirely new process. Cocoyam starch had been previously blended with wheat starch[3]; pigeon pea starch (100PPS) blended with rice starch (100RS)[4], bambarra starch (100BBS) blended with cassava starch (100CS)[5] and Irish potato starch blended with 100PPS[6]. Blended starches have been reported to exhibit either additive or non-additive properties depending on the combination of starch counterparts, mixing ratio and concentration of the starch mixture[2]. According to Waterschoot et al.[7], tremendous disparity in granule size and swelling power (SP) between blended starches lend to uneven moisture distribution during heating of starch suspension. The consequence is that the behavior of the blend differ from what would be expected based on the behavior of the individual starches.

Amylose (AM) and amylopectin (AP), the major components of starch granules plays an important role in the determination of SP, solubility, pasting and gelatinization of the starches. The role of the anti-swelling and anti-solubility minor components (mainly lipids and proteins) has been widely reported in the literature[8]. The functionality of the two main components of starch differs significantly. AM has a high tendency to retrograde and produce tough gels and strong films[1]. In contrast, AP, when dispersed in water, is more stable and produces soft gels and weak films[9].

There are plenty of works on pigeon pea (*Cajanus cajan*) starch[10], rice (*Oryza glaberrima*) starch[11], bambarra groundnut (*Voandzeia substerranean*) starch[12] and cassava (*manihot esculenta*) starch[13]. It was observed from literature review that there are limited works on blending of native starches from different botanical sources in the areas of bulk density, dispersibility, pH and potential industrial applications of these blended starches. It is a rarity to see the comparative study of physicochemical properties of blended starches in different proportions; (70PPS/30RS, 50PPS/50RS and 30PPS/70RS) versus (70BBS/30CS, 50BBS/50CS and 30BBS/70CS) from different botanical origin in the literature. Therefore, the aim of this work is to study the physicochemical properties of these blended starches. Furthermore, their physicochemical properties will be compared and the likely potential industrial applications stated depending solely on their physicochemical properties.

EXPERIMENTAL

Materials

Pigeon pea seeds were purchased from a local market at Igbokoda, Ondo State, Nigeria. Rough hulled rice grains called Nerica 11 rice were generously donated by International Institute of Tropical Agriculture (IITA), Ibadan, Oyo State, Nigeria. Bambarra groundnut seed (BGS) and cassava roots (CR) were purchased from a local market at Ikare, Ondo State, Nigeria. The Nerica 11 rice is the product of a cross between *Oryza sativa* and *Oryza glaberrima*. The BGS were screened to remove the defective ones. The CR was peeled and those with dark spots were eliminated. All other chemicals were of analytical reagent grade.

Starch isolation

Pigeon pea starch (100PPS) was isolated from pigeon pea seeds by the method reported by Singh et al.[14] Rice starch (100RS) was isolated from rice flour using the alkaline deproteinization method of Lim et al.[15] as modified by Ashogbon and Akintayo[11]. Manually dehusked and dried bambarra groundnut was ground to a powdery form in a laboratory grinder. Starch was isolated from the powdery form by a procedure of Adebowale and Lawal[16] as modified by Sirivongpaisal[12]. Isolation of native cassava starch was carried out by a method described by Benesi[17].

Preparation of starch blends

Starch blends were prepared from the isolated control starches (100PPS, 100RS, 100BBS and 100CS) in six proportions (70PPS/30RS, 50PPS/50RS, 30PPS/70RS) and (70BBS/30CS, 50BBS/50CS, 30BBS/70CS) (%, w/w). The starches were sieved and mixed in a laboratory blender.

Gross chemical compositions of isolated starches

Apparent amylose (AAM) content (%) was determined by a colorimetric iodine assay index method[18]. The moisture, protein, lipid, and ash content in the starch samples were determined using procedure of AACC method[19].

Bulk density

This was determined by the method of Wang and Kinsella[20] as modified by Ashogbon and Akintayo[21].

Dispersibility

This was determined by the method described by Kulkarni et al.[22] as modified by Akanbi et al.[23]

pH

Starch samples (5 g) were weighed in triplicate into a beaker and mixed with 20 mL of distilled water. The resulting suspension was stirred for 5 min and left to settle for 10 min. The pH of the supernatant was measured using a calibrated pH meter[17].

Swelling power and solubility

Swelling power (SP) and water solubility index (WSI) determinations were carried out in the temperature range 55-95°C at 10°C intervals using the method of Leach et al.[24]

Pasting properties

The pasting properties of the starches were evaluated using a Rapid Visco Analyzer (Newport Scientific, RVA Super 3, Switzerland). Starch suspensions (9%, w/w, dry starch basis; 28 g total weight) were equilibrated at 30°C for 1 min, heated at 95°C for 5.5 min, at a rate of 6°C/min, held at 95°C for 5.5 min, cooled to 50°C at a rate of 6°C/min and finally held at 50°C for 2 min. Parameters recorded were pasting temperature (PT), peak viscosity (PV), trough viscosity (TV), final viscosity (FV), and peak time (Pt). Breakdown viscosity (BV) was calculated as the difference between PV minus TV, while total setback viscosity (SV) was determined as the FV minus TV. All determinations were performed in triplicate and expressed in rapid viscosity unit (RVU).

Statistical analysis

Experimental data were analyzed statistically using Microsoft Excel and SPSS V. 12 .0. The least significant difference at the 5% probability level (P < 0.05) was calculated for each parameter.

RESULTS AND DISCUSSION

Gross chemical composition of control starches and their blends

For the purpose of this discussion, the blends (70PPS/30RS, 50PPS/50RS and 30PPS/70RS) will be represented with PPS/RS and the blends (70BBS/30CS, 50BBS/50CS and 30BBS/70RS) with BBS/CS. The

gross chemical composition of the control starches and their blends are summarized in Table 1. All other things been equal, the higher is the moisture content of starch samples, the more vulnerable they are to spoilage. The moisture content of all the starch samples falls within the commercially accepted range (less than 14.00% moisture content[25]). For the blends (PPS/RS), the moisture content of the blended starches was higher than that of the control starches. This seems to indicate that blending of starches in different proportions increases their moisture content. In the blends (BBS/CS), the moisture content was additive of their individual components.

The ash content of the blended starches was non-additive of their individual components. Generally, the ash contents of most of the blended starches were higher than their control starches. For the control starches that constitute the PPS/RS blends, 100RS had the higher values for lipid and protein. Furthermore, the lipid content was additive of their individual components. In contrast, for the blends (BBS/CS), the lipid content was higher than in the control starches and the protein content was additive.

Apparent amylose (AAM) of the control starches and their blends differed significantly ($P < 0.05$). With the exception of the characteristic high AAM content of the legume starch (100BBS), the AAM contents of the blended starches were higher than the control starches. This shows that blending of starches from different plant origin increases the AAM content of the blended starches. The AAM contents of the blended starches (PPS/RS and BBS/CS) were non-additive of their individual components. The blends (50PPS/RS and 70BBS/CS) with higher AAM could be desired in the manufacture of noodles. High AM starches could be very useful film-forming material due to their strong gelation properties and helical linear polymer structure[18]. Furthermore, these high AM blended starches have been associated with the formation of resistant starches[26].

The manifestation of higher AAM depends on the proportion of 100BBS in the blends (BBS/CS), since the blends with the highest AAM had the ratio (70BBS/30CS) (Table 1). In the other blends (PPS/RS), the proportion of 100PPS and 100RS were equal in the blend with highest AAM content. But the next higher AAM was observed in the blend (70PPS/30RS) with higher proportion of 100PPS. In a nutshell, the display of higher AAM content in the blended starches depends on the proportion of the legume starches (100BBS or 100PPS) in it.

Table 1: Gross chemical composition of control starches and their blends

Sample	Moisture	Ash	Lipid	Protein	AM
100 PPS	8.72 ± 0.30	0.10 ± 0.00	0.15 ± 0.03	0.20 ± 0.10	28.40 ± 0.00
70PPS/30RS	13.00 ± 0.01	0.40 ± 0.10	0.33 ± 0.00	0.18 ± 0.01	37.85 ± 0.10
50PPS/50RS	13.50 ± 0.20	0.20 ± 0.01	0.49 ± 0.05	0.26 ± 0.02	42.63 ± 0.01
30PPS/70RS	12.00 ± 0.10	0.40 ± 0.01	0.56 ± 0.10	0.18 ± 0.02	33.14 ± 0.02
100RS	11.74 ± 0.02	0.24 ± 0.02	0.40 ± 0.20	0.40 ± 0.01	26.04 ± 0.10
100BBS	11.00 ± 0.02	0.05 ± 0.01	0.31 ± 0.02	0.18 ± 0.01	37.30 ± 0.10
70BBS/30CS	11.52 ± 0.10	0.30 ± 0.01	0.38 ± 0.10	1.80 ± 0.10	41.53 ± 0.02
50BBS/50CS	11.95 ± 0.20	0.21 ± 0.10	0.49 ± 0.05	0.80 ± 0.02	36.26 ± 0.01
30BBS/70CS	12.36 ± 0.01	0.12 ± 0.02	0.33 ± 0.00	0.18 ± 0.02	33.23 ± 0.10
100CS	12.65 ± 0.30	0.20 ± 0.01	0.10 ± 0.03	0.10 ± 0.01	20.20 ± 0.01

Functional properties of the control starches and their blends

The values of bulk density (BD), dispersibility and pH of the control starches and their blends are presented in Table 2. The bulk densities of the starch samples ranged from 0.62 to 0.88 g/mL. The highest bulk density was observed for 70BBS/30CS and the lowest for 100RS. BD is a measure of the degree of coarseness of the starch particles. This means that the 70BBS/30CS blend had the coarsest particles. It also implies that 100RS particles are very smooth and could be useful for making expicient for pharmaceutical tablet, paper and photographic paper powder, cosmetic dusting powder and laundry stiffening agent[27,28]. Furthermore, the small BD of 100RS could provide smooth texture that exhibits fat mimetic properties[29]. The bulk densities of the blends (PPS/RS) were additive of their individual components. In contrast, the BD of the blends (BBS/CS) was non-additive.

Table 2: Bulk density, dispersibility and pH of the control starches and their blends

Sample	Bulk density (g/mL)	Dispersibility (%)	pH
100PPS	0.82 ± 0.04	82.00 ± 0.07	7.60 ± 0.02
70PPS/30RS	0.76 ± 0.01	83.00 ± 0.06	7.17 ± 0.05
50PPS/50RS	0.73 ± 0.02	81.00 ± 0.03	7.39 ± 0.03
30PPS/70RS	0.64 ± 0.01	80.00 ± 0.05	7.39 ± 0.01
100RS	0.62 ± 0.03	89.00 ± 0.04	7.24 ± 0.04
100BBS	0.86 ± 0.03	86.00 ± 0.04	7.38 ± 0.04
70BBS/30CS	0.88 ± 0.01	86.02 ± 0.05	7.32 ± 0.01
50BBS/50CS	0.83 ± 0.02	83.00 ± 0.03	7.29 ± 0.03
30BBS/70CS	0.87 ± 0.01	87.00 ± 0.06	7.21 ± 0.05
100CS	0.72 ± 0.01	85.00 ± 0.07	7.03 ± 0.02

Dispersibility is a measure of reconstitution of starch in water. The higher is the dispersibility, the better the flour reconstitutes in water[22]. The non-additive tendency of the blends (PPS/RS and BBS/CS) in respect to dispersibility was obvious as seen in Table 2. The dispersibility of the blended starches ranged from 80.00 to 87.00%. Since the higher is the dispersibility, the better the starch flour reconstitutes, the values obtained for 100RS and the 30BBS/70CS blend were better than that of other investigated starches. Furthermore, these values are better than 40.67% obtained by Akanbi et al.[23] for breadfruit starch. The implications are that high dispersibility starches (100RS, 30BBS/70CS and 70BBS/30CS) will probably be suitable for applications where large quantity of starches occupy small surface area. The high dispersibility starches could be useful for adsorptive removal of ions from contaminated water system. The percentage dispersibility of the BBS/CS blends was higher and better than that of the PPS/RS blends.

pH is a property in starch industrial applications, being generally used to detect the acidic or alkaline properties of liquid media. Blending of starches from different plant sources do not significantly impacted on the pH of the blended starches. All the control starches and their blends are slightly alkaline. Lower pH values had been previously reported for some legumes (6.20-6.88), rice starch (4.30) and cassava starch (5.56)[30]. Furthermore, higher acidic values (3.71-3.99) had been reported by Ahmed et al.[31] for some cultivar of rice starches.

AP had being widely reported to be responsible for SP and AM for WSI. The importance and influences of residual proteins, lipids, native and temperature-induced amylose-lipid complexes on these two

parameters were also emphasized[5]. The SP and WSI of the control starches and their blends, heated from 55 to 95°C at 10°C interval were summarized in Figures 1 and 2, respectively. Generally, the SP and WSI of the PPS/RS blends increased with temperature compared to the BBS/CS blends where these parameters fluctuate.
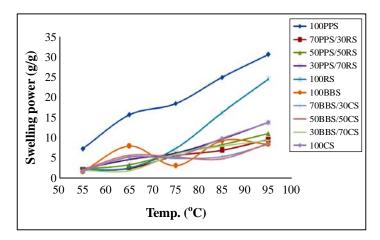

Fig. 1: Effects of temperature on swelling power

Unexpectedly, in these PPS/RS blends, as the proportion of 100PPS was decreased, the SP and WSI increased for all temperatures investigated and vice versa in the case of RS and the blends. The SP and WSI of the starch blends (PPS/RS) were lower than that of the individual starches. Blending inhibited the SP and WSI of the blended starches (PPS/RS) because the starches share the available solvent[32]. This decreased swelling as a result of blending might result in increased rigidity of swollen starch granules[32] and an increase in AAM content of the blends[4]. The low SP of the blends (PPS/RS) was attributed to their low AP content. In contrast, SP and WSI of the blends (BBS/CS) increased as the temperature was raised up to 65°C and subsequently decreased to 75°C (except for the 30BBS/70CS blend) before astronomically increasing as the temperature was further raised to 90°C. This decreased in SP and WSI at 75°C were probably due to the effects of residual proteins, lipids, native and temperature-induces complexes[33]. More amylose-lipid complexes might have been formed at 75°C; therefore, swelling was inhibited and exudation of AM from starch granules that enhance solubility was also limited. Furthermore, denatured residual protein could have been deposited on the granules and further inhibited swelling and solubility[34].
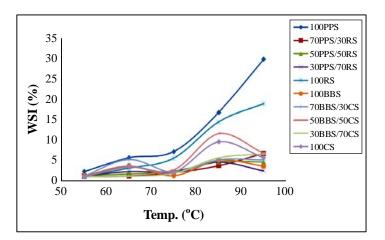

Fig. 2: Effects of temperature on WSI

Pasting properties of control starches and their blends

The pasting properties of the control starches and their blends are summarized in Table 3. Generally, blending of various starches tend to reduce their PV values. The peak viscosities of the blended starches (PPS/RS and BBS/CS) were non-additive of their individual components. As seen in Table 3, the legume starches (100PPS and 100BBS) were observed to be responsible for the manifestation of higher PV. This is expected because of the high PV value of the individual legume starch. The contribution of the high PV value of 100CS to the blends seems to have been inhibited by factors inherent in the mixing ratios. The higher is the proportion of legume starches in the blends, the greater the ability of the starch blends to swell. The PV of the control starches and their blends ranged from 171.08 to 558.00 RVU. Higher PV values were observed in 100CS, 100PPS and the blends (50PPS/50RS and 70BBS/30CS). These high PV starches and blends could be used in products where high SP is required, e.g., in tablet and capsule formulations[35]. Furthermore, these viscous starches and blends may also be utilized as thickeners, binders, fillers and disintegrants for fast release of drugs[29]. High paste viscosity suggests suitability as a finishing agent in the textile and paper industries[36].

Breakdown viscosity (BV) is a measure of the ease of disrupting swollen starch granules and suggests the degree of stability during cooking[37]. The BV values ranged from 40.92 to 392.17 RVU. It was highest for 100CS and lowest for 100RS. The lower BV values of 100RS and the 30PPS/70RS blend could be the most thermally stable and highly resistant to mechanical fragmentation of their granules during agitation. Furthermore, the high BV values in 100CS and the 50PPS/50RS blend indicated the weak internal structures of their granules. The high thermal stability of 100RS and the 30PPS/70RS blend could be useful in canned foods and those products that require sterilization[38]. The BV of the starch blends (PPS/RS and BBS/CS) was non-additive of their individual components.

Table 3: Pasting properties of control starches and their blends

Sample	PV(RVU)	TV(RVU)	BV(RVU)	FV(RVU)	SV(RVU)	Pt(min)	PT(^{0}C)
100PPS	558.00 ± 0.20	333.40 ± 0.10	224.60 ± 0.10	510.00 ± 0.20	176.60 ± 0.30	4.37 ± 0.20	74.00 ± 0.20
70PPS/30RS	320.33 ± 0.10	149.75 ± 0.10	170.58 ± 0.30	332.25 ± 0.20	182.50 ± 0.20	4.40.40 ± 0.10	81.65 ± 0.30
50PPS/50RS	429.42 ± 0.20	163.92 ± 0.20	265.50 ± 0.20	347.25 ± 0.10	183.33 ± 0.10	4.53 ± 0.10	83.25 ± 0.20
30PPS/70RS	171.08 ± 0.30	78.75 ± 0.10	92.33 ± 0.20	196.83 ± 0.30	118.08 ± 0.10	4.93 ± 0.10	87.30 ± 0.10
100RS	268.25 ± 0.10	227.33 ± 0.20	40.92 ± 0.30	329.92 ± 0.10	102.50 ± 0.20	6.36 ± 0.20	83.02 ± 0.10
100BBS	432.38 ± 0.20	247.04 ± 0.20	185.34 ± 0.30	401.34 ± 0.10	154.29 ± 0.20	4.73 ± 0.20	84.13 ± 0.20
70BBS/30CS	416.21 ± 0.30	246.67 ± 0.10	169.54 ± 0.30	395.05 ± 0.30	148.38 ± 0.10	5.24 ± 0.10	95.25 ± 0.10
50BBS/50CS	362.34 ± 0.20	212.75 ± 0.20	149.59 ± 0.20	345.13 ± 0.10	132.38 ± 0.10	5.33 ± 0.10	94.95 ± 0.10
30BBS/70CS	360.38 ± 0.20	186.30 ± 0.10	174.08 ± 0.30	299.21 ± 0.20	112.92 ± 0.20	4.10 ± 0.10	70.28 ± 0.20
100CS	553.75 ± 0.10	162.58 ± 0.10	391.17 ± 0.10	274.63 ± 0.20	112.05 ± 0.30	3.34 ± 0.20	69.98 ± 0.30

The TV or holding strength of the starch samples ranged between 78.75 and 333.40 RVU with the 100PPS having the highest value and the 30PPS/70RS blend the least. The BV and the SV values were computed using the TV values.

Setback viscosity (SV) involves the reordering of starch molecules and shows the tendency of the starch to associate and retrograde[37]. The high retrogradation values of some of the starch blends (70PPS/30RS and 50PPS/50RS) were expected due to their high AAM content. This implies that they could be used in gluten-free paste and noodles[39] where high retrogration is desired. In contrast, lower SV values of some blended starches (30BBS/70CS and 30PPS/70RS) could be utilized in refrigerated foods, desserts and cake filling[38].

The higher retrograded blended starches were due to the high proportions of the legume starches in the blends. The legume starches (100BBS and 100PPS) were responsible for the manifestation of higher SV values. This was expected because the legume starches are known for their characteristic high AM and retrogradation, when compared to the cereal starch (100RS) and root starch (100CS). In relation to SV, the blended starches were additive for the blends (BBS/CS) and non-additive for the blends (PPS/RS) of their individual components.

A high final viscosity indicates that the paste is more resistant to mechanical shear and may form a more rigid gel. FV values of the control starches and their blends ranged from 196.83 to 510.00 RVU and they vary significantly ($P < 0.05$). The characteristic high PV values of the legume starches (100PPS and 100BBS) and some blends (70BBS/30CS and 50PPS/50RS) could be desired in many food products (soups and sauces); they can also be used in the textile industry and wet stage paper production where high viscosity is required[40]. The lower FV starch blend (30PPS/70RS) could be significant in the dry stage paper-making[40].

It was observed just as in SV, that the manifestation of high FV values depended on high proportions of legume starches in the blends. In relation to FV, the blended starches were additive (BBS/CS) and non-additive (PPS/RS) of their individual components (Table 3). The same reason (high AM content) is responsible for high SV and FV values. This is not ignoring the contribution of non-random highly branched AP molecules[41]. The impacts of the anti-swelling and anti-solubility minor components (lipid and protein) were not negligible.

Generally, the PT values of the blended starches were higher than that of the control starches. The 70BBS/30CS blend showed the highest PT value and 100CS the least. The pasting temperature is the minimum temperature needed to cook starch. High PT value (long cooking time) of starch blends (70BBS/30CS and 50BBS/50CS) could be utilized in retort (canned foods) and sterilized foods processed at high temperatures[29]. The lower PT value starch (100CS) and blend (30BBS/70CS) could be preferred in food industries because of their reduced energy cost and time during production.

In the blends (PPS/RS) the manifestation of high PT values was due to high proportion of 100RS in the blends. In contrast, in the blends (BBS/CS), this same tendency was due to the presence of high proportion of BBS in the starch blends. The PT values of the blends were additive of their individual components.

CONCLUSIONS

The physicochemical properties of the blended starches (70PPS/30RS, 50PPS/50RS and 30PPS/70RS) (PPS/RS) and (70BBS/30CS, 50BBS/50CS and 70BBS/30CS) (BBS/CS) were significantly different. This study displayed that blended starches show large dissimilarity in their physicochemical properties hence can have different applications in both food and non-food industries. In the PPS/RS blends,

the swelling power (SP) and the water solubility index (WSI) were lower than that of their control starches while these parameters fluctuates as the temperature was increased in the BBS/CS blends. The pasting parameters also differ significantly; some were additive and others non-additive of their individual components.

The high apparent amylose content of these blends (50PPS/50RS and 70BBS/30CS) could be desired in the manufacture of noodles. The high percentage dispersibility blended starches could be required for the adsorptive removal of ions from contaminated water system. Furthermore, SP and pasting properties of blended starches have useful industrial applications, especially in the pharmaceutical, paper and textile industries. Blended starches can produce meritorious characteristics without the need for costly starch modification.. In a nutshell, blending of native starches from different botanical sources improve their industrial applicable properties.

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