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Full Length Research Paper

Contribution to light transmittance modelling in starch media

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Light transmittance (%T) studies were carried out at 650 nm in several types of starch-based media such as natural tropical and non tropical starch pastes and simplified model media. With natural starch pastes (1% db), the clarity ranged from 8%T (ginger starch) to 79%T (potato starch), with intermediate values for cassava starch (47%T) and waxy maize (35%T). These values depended mainly on the spectrophotometer type, starch concentration, treatment temperature and storage time. In simplified media (treatment at 150°C, acid hydrolysis and DMSO solubilization), all paste (1% db) transmittances were improved and the maximum dispersion (using DMSO) was the main factor influencing the transmittance. In effect, the average values were classified as following: 79.5%T (DMSO) > 64.7%T (HCl 2.2 N hydrolysis) ≈ 54.7%T (heating at 150°C) > 22.8%T (control). Thus, a model was proposed to explain that in a dilute and purified starch paste, the quasi totality of incident light passing through the media was transmitted, which made the medium clear.

Key words: Paste clarity, light transmittance, model, solute, tropical starch.

INTRODUCTION

Starch is the most important source of carbohydrates in human diet. It is a mixture of essentially linear α-glucans (amylose) and branched α-glucans (amylopectin). Starch is found in the roots, tubers or fruits (Buléon et al., 1990). Functional properties of starches are the major assets to make starch marketing. They depend much on the amylose/amylopectin ratios that even depend on the botanical origin (Swinkels, 1985). In the food field, starch is used as ingredient and provides a texture of several food. Thus, it can be used as thickeners, stabilizers, binders, adhesives, tonics, coagulants, gelling and forming agents, emulsions and foams stabilizers and water retention agents (Luallen, 1985; Friedman, 1995).

Among these properties, starch pastes clarity is one of the important attributes: starch used to thicken fruit pies is preferably transparent, but that used in the spoonable salad dressing should be opaque (Craig et al., 1989).

Pastes clarity varies considerably with the starch source, the amylose/amylopectin ratio, chemical or enzymatic modifications and addition of solutes. The starch granules swelling and the brittleness would affect the paste clarity (Craig et al., 1989). These authors classified the starches according to their paste (1% db) clarity as following: potato ≥ Maize > waxy maize > amylomaize.

The multiplicity in the methods of clarity determination led some confusion, hence reversing the classification order of some starch pastes clarity compared to others. Indeed, Schoch (1942a) used percentage of reflectance and obtained with starch paste (3.5% db), the following order: waxy maize > cross-linked waxy maize > potato ≥ maize and these observations could vary with the paste concentrations. These results differed from those of Marrs et al. (1977) who obtained with gel (9%), the following order using the degree of "whiteness": potato > corn ≥ waxy corn ≥ tapioca.

Works undertaken on the influence of solutes on starch paste clarity indicated variations of clarity according to solutes content and nature. Thus, sucrose and glucose increased considerably starch pastes clarity (Osman, 1984; Craig et al., 1989; Bello-Perez and Paredes-Lopez, 1996). As for lipids, they contributed to starch pastes opacity (Craig et al., 1989) contrary to the observations made previously (Bello-Perez et al., 1998) with stearic acid, palmitic acid. Addition of NaCl to starch paste did

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Table 1. Origin of starches samples.

Origin	Variety	Species	Histological nature
Yam	Florido	*Dioscorea alata*	Tuber
Yam	Kponan	*Dioscorea cayenensis-rotundata*	Tuber
Yam	Esculenta	*Dioscorea esculenta*	Tuber
Cassava	Bitter cassava	*Manihot esculenta*	Tuber
Cocoyam	Macabo	*Xanthosoma sagittifolium*	Tuber
Ginger	Ginger	*Zingiber offinale*	Root
Sweet potato	White variety	*Ipomea batatas*	Root
Potato	Potato	*Solanum tuberosum*	Tuber
Maize	Normal maize	*Zea maïs*	Cereal
Maize	Waxy maize	*Zea maïs*	Cereal
Rice	Normal rice	*Oryza sativa*	Cereal
Wheat	wheat	*Tricicum aestivum*	Cereal

not present a well defined effect on clarity (Bello-Perez et al., 1996), whereas it reduced considerably transmittance and visual clarity but increased whiteness on potato starch paste (Craig et al., 1989). Moreover, phosphorylation generally increases starch paste transmittance at low degree of substitution but clarity decrease with the increase in the degree of substitution (Mahmoud et al., 2000).

Starch media clarity would also be influenced by the macromolecular characteristics of amylose and amylopectin. Thus, clarity of reconstituted starch pastes (1% db) with amylopectin (80%) and amylose (20%) from various origins decreased with the molar mass of amylose and the degree of polymerization of amylopectin (Jane and Chen, 1992). Moreover, it revealed a good correlation between the hydrodynamic coefficients (ν_G) and pastes clarity (1% db) of yam starches from Côte d'Ivoire (Amani, 2002).

Taking into consideration this diversity of results, the aim of this work is to harmonize and explain the factors which influence the starch pastes clarity by studying the light transmittance in starch pastes obtained with starches from different botanic origin.

MATERIALS AND METHODS

Raw materials

Twelve starches from different origin were used in that study (Table 1). Yam tubers were obtained from the experimental farm of the Genetics Department (FAST) of the University of Abidjan (in the forest zone). Starches from potato, cocoyam, cassava, sweet potato and ginger were extracted from tubers and roots identified and bought on the greatest market in Abidjan. Commercial starches were obtained from several origins: waxy maize, normal maize and wheat starch (Roquette Frères, Lestrem, France), rice starch (Remy Industries, Leuven-Wijgnaal, Belgium).

Starch isolation

The starches were purified according to the previously described procedure (Amani, 1993). Tubers and roots were peeled and immediately cut into small pieces. The freshly cut pieces were suspended in distilled water containing 0.1% (w/v) sodium metabisulphite. The material was crushed in a Warring blender (Moulinex, Lyon, France) and suspended in a large excess of distilled water containing 4% NaCl. The slurry was filtered through a 100 µm sieve. The starch was allowed to settle and the supernatant decanted off. This process was repeated four times and the recovered white prime starch was then oven-dried at 45°C for two days. The moisture content was determined by oven-drying for 2 h at 130°C.

Clarity measurement (%T) on starch paste

Clarity was determined by reading the light transmittance (%T) as described previously (Craig et al., 1989). A 1% db aqueous suspension (100 mg in 10 mL) was heated in boiling water bath for 30 min with constant stirring. The solution was cooled and held for 1 h at 25 ± 1°C. The sample was then stored for 28 days at 4°C, during which time, light transmittance (%T) was determined every 24 h at 650 nm against a water blank with both Genesys.5 (Thermo Electron Corporation, MA, USA) and Jasco V-530 spectrophotometer (Jasco Corporation, Tokyo, Japan). As for concentration influence study, 1, 2, 3 and 4% db aqueous suspensions were treated in the same conditions above. Moreover, in order to study the cooking level influence on light transmittance in starch paste, sample were heated at different temperatures (55, 65, 75, 85 95 and 150°C).

Effect of NaCl and sucrose on %T of starch paste

Samples (1% db) were prepared as above but after cooling, 1.0, 2.0 and 3.0 g sucrose were added to different sets of tubes (corresponding to 10, 20 and 30%) and thoroughly shaken until the solute was dissolved. The same procedure was followed for NaCl, with the amounts of 0.5, 1.0 and 2 g NaCl corresponding to 5, 10 and 20%. The light transmittance (%T) was determined as above.

Effect of acid hydrolysis on %T of starch paste

Native starches were suspended (5%db) in 2.2 N HCl. The containers were placed at 37°C for 1 h and the suspension was shaken every 20 min to resuspend the sedimented granules (Robin et al., 1974). The suspension was withdrawn and centrifuged (10 min, 10000g, 15 - 20°C) (YOUAN SA, Saint Herblain, France). Total

Table 2. Light transmittance at 650 nm of starch pastes (1% db) determined after 1 h of storage at temperature of laboratory (25 ± 1°C).

Starch	A	B
Florida	10.1±0.3	19.3±0.9
Kponan*	20.4±1.7	33.1±4.4
Esculenta*	9.4±0.2	17.2±2.1
Potato	79.1±0.6	94.2±1.4
Cocoyam*	15.8±0.8	24.9±1.3
Ginger*	8.6±1.1	12.1±2.4
Cassava*	47.1±2.5	50.3±1.4
Sweat potato*	16.7±0.5	14.5±1.9
Wheat	12.2±1.4	14.2±2.1
Normal maize	11.2±0.7	14.2±1.2
Waxy maize	35.4±0.7	ND

A and B representing respectively Jasco V530 and Genesys. 5 Spectrophotometers. *Starch from the same batch which were used for ANOVA analysis in order to compare the spectrophotometers results.

solubilized sugars were measured in the supernatant by the sulphuric acid-orcinol colorimetric method (Planchot et al., 1997) and the extent of degradation was expressed as the percentage of dry substrate solubilized. The base was withdrawn and dried by exchange of water using acetone and diethylether. Dry hydrolyzed starch was suspended in water (1% db) and was prepared as above. Thus the light transmittance (%T) was also determined as above.

Effect of DMSO dispersion on %T of starch paste

Sample (0.5 g) was first dissolved in 95% di-methylsulphoxide (DMSO) (20 mL) with a moderate magnetic stirring for 3 days at room temperature. The sample was then precipitated with ethanol (200 mL), stored overnight at 4°C and then centrifuged (28000 g, 15 - 20°C and 10 min) (YOUAN SA, Saint Herblain, France). The precipitate was filtered over a glass filter (G 4) and dried by exchange of water using successively acetone (10 mL) and diethylether (10 mL). The glass filter was then stored overnight in dessicator. The purified starch was suspended in water (1% db) and was prepared as above. Thus the light transmittance (%T) was also determined as above.

Statistical analysis

All the experiences were made in triplicate and Analyses of variances (ANOVA) were performed using NCSS6.0 statistical software (NCSS, Kaysville, USA).

RESULT

Influence of apparatus on the transmittance of natural starches paste (1% db) With Jasco spectrophotometer, the light transmittance (%T) values ranged between 8%T

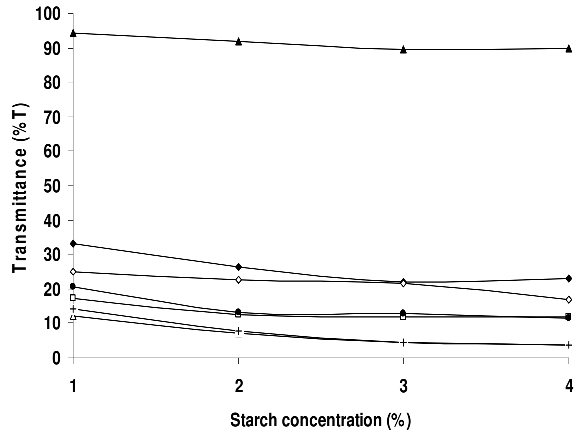


Figure 1. Influence of starch concentration on light transmittance of starch pastes. ♦, Kponan; □, Esculenta; ▲, Potato, ◊, Cocoyam; Δ, Ginger; ●, Sweet potato; +, Normal maize.

(ginger starch) and 79%T (potato starch) (Table 2). Relatively high intermediate values were obtained with cassava starches (47%T) and waxy maize (35%T). The major part of the samples had clarity ranging between 10 and 20%T. With regard to Genesys spectrophotometer, the %T values were slightly higher than those obtained on Jasco spectrophotometer. A variance analysis was carried out on the results obtained with samples resulting from the same batch (starches from Kponan, Esculenta, cocoyam, ginger, cassava and sweet potato). Thus, the results obtained with Genesys spectrophotometer were higher than those of Jasco spectrophotometer (Table 2).

Influence starch concentration on clarity

The light transmittance decreased with a weak slope when the starch concentration increased from 1 to 4% db (Figure 1). Ginger starch and of normal maize starch formed opaque and white paste starting from 2% db (clarity < 10%T), whereas, potato starch paste remained clear (clarity>90%T).

Influence of treatment temperature on paste (1% db) clarity

The light transmittance increased with the increase in the temperature of treatment (Figure 2). However, the clarity evolution for each starch presented two zones of increase: a zone of progressive and little increase ranging between 55 and 75°C and the zone of significant increase starting from 75°C.

Influence of storage at cold temperature (4°C) on pastes (1% db) clarity

Starch pastes light transmittance decreased during storage (Figure 3). Pastes from Florido, Esculenta, ginger

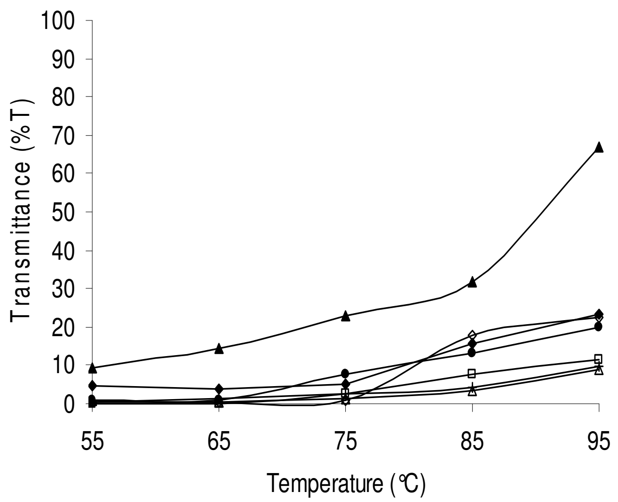


Figure 2. Influence of treatment temperature on light transmittance of starch pastes (1% db):♦, Kponan; □, Esculenta; ▲, Potato, ◊, Cocoyam; Δ, Ginger; ●, Sweet potato; +, Normal maize.

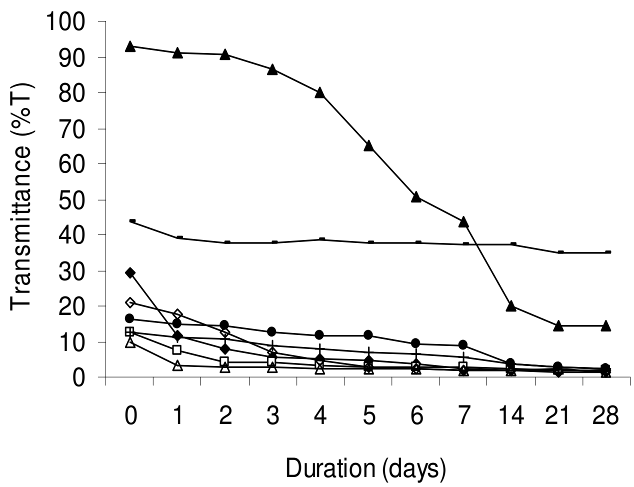


Figure 3. Influence of storage time at 4°C on light transmittance of starch pastes (1% db): ♦, Kponan; □, Esculenta; ▲, Potato, ◊, Cocoyam; Δ, Ginger; ●, Sweet potato; +, Normal maize; ⁻, Cassava.

and normal maize starch were initially turbid and their turbidity increased more and more starting from the third day (%T lower than 10%T). A macroscopic phase separation was observed. These starch pastes became completely opaque after 5 days in these storage conditions. Thus, they were the least stable at cold.

Cocoyam and sweet potato starch pastes became turbid after 3 and 7 days respectively but any macroscopic phase separation was not observed into them. At the end of the 7th day, the %T of potato starch paste was being reduced by half (45%T). From the 14th day, potato starch pastes were less clear than cassava starch pastes (Figure 3). Cassava starch pastes were most stable at cold temperature. No macroscopic phase separation was observed into them and they presented a transparent aspect for the storage period (28 days).

Table 3. Light transmittance of starch paste in the presence of NaCl.

Samples	Control	5%	10%	20%
kponan	33.1±4.4	29.1±2.3	32.5±1.2	37.9±1.3
Esculenta	17.2±2.1	12.1±1.8	14.5±1.9	16.8±1.5
Potato	94.2±1.4	64.2±0.7	69.1±2.5	70.3±1.3
Cocoyam	24.9±1.3	20.2±1.6	25.2±1.5	30.1±1.8
Ginger	12.1±2.4	16.2±1.6	20.5±1.4	22.3±2.1
Cassava	50.3±1.4	55.3±2.1	55.7±2.1	65.8±2.2
Sweat potato	20.7±1.9	20.3±0.7	22.3±0.5	27.3±1.6
Normal maize	14.5±2.1	11.7±1.8	14.1±1.6	17.1±0.7

Table 4. Light transmittance of starch paste in the presence of sucrose.

Sample	Control	10%	20%	30%
Kponan	33.1±	38.1±1.5	42.1±2.2	42.9±1.6
Esculenta	17.2±2.1	17.7±1.7	23.1±1.3	26.9±1.4
Potato	94.2±1.4	93.1±2.5	93.1±2.1	93.3±2.7
Cocoyam	24.9±1.3	29.2±1.3	33.7±1.7	38.2±1.8
Ginger	12.1±2.4	15.1±2.2	19.5±1.5	25.2±1.8
Cassava	50.3±1.4	60.9±1.8	68.8±1.6	72.2±2.3
Sweat potato	20.7±1.9	26.4±2.1	34.7±2.6	40.5±1.4
Normal maize	14.5±2.1	16.8±2.1	23.4±1.8	27.3±1.6

Influence of NaCl on the starch pastes (1%db) clarity

Two phases of variation of clarity were observed when NaCl was added to the starch pastes (Table 3): a phase of slight decrease with addition of 5% NaCl, but an important decrease was observed with potato starch (from 94 to 64%T) and an increase phase when the NaCl content increased. This increase was observed on an interval of 4 - 10%T compared to the pastes containing 5% NaCl. On the other hand, in the case of potato starch, transmittance remained very low compared to the control (23%T of fall). That was not the case for the other starches whose %T increased compared to their respective control, except the starch of Esculenta for which clarity returned to the initial values.

Influence of sucrose on starch pastes (1% db) clarity

Light transmittance increased with the sucrose concentration; except the potato starch whose clarity remained unchanged (Table 4). Pastes transmittance containing 30% sucrose was raised by 10%T (yam starch) and 22%T (cassava starch).

Table 5. Light transmittance of starch paste (1% db) after treatment of starch in different conditions: 150°C, heating at 150°C; HCl, treatment of starch in HCl for 1 h before determination of %T; and DMSO, dispersion in DMSO before determination of %T.

Sample	Control	150^{oc}	HCl	DMSO
Florida	10.1±0.3	61.4±0.1	25.2±0.3	74.5±0.4
Kponan	20.4±1.7	69.9±0.4	65.3±0.1	83.6±0.3
Esculenta	9.4±0.2	19.4±0.2	78.7±0.3	85.9±0.6
Potato	79.1±0.6	95.2±0.2	98.7±0.1	91.4±0.6
Cocoyam	15.8±0.8	45.4±0.3	87.7±0.8	80.2±0.9
Ginger	8.6±1.1	35.3±0.2	23.5±0.5	82.5±0.3
Cassava	47.1±2.5	79.1±0.3	90.1±0.6	87.1±0.5
Sweat potato	16.7±0.5	61.2±0.1	75.6±0.3	70.4±0.2
Wheat	12.2±1.4	41.9±0.4	55.3±0.4	69.8±0.3
Normal maize	11.2±0.7	41.4±0.3	35.2±0.4	82.5±0.5
Rice	19.8±	50.7±0.2	76.3±0.2	66.7±0.4
Average values of each treatment	22.8a	54.7b	64.7b	79.5c

Values followed by the same letter within a line do not differ significantly (p<0.05).

Influence of dispersion by heating at 150°C on starch pastes (1% db) clarity

Light transmittance ranged between 19%T (Esculenta starch) and 95%T (potato starch) after heating at 150°C (Table 5). Higher values (%T>60) were obtained with starch pastes from Kponan, sweet potato and manioc, potato. Values of the other starches pastes were lower than 45%T. The average values of treated starches pastes clarity was 54.7%T.

Influence of molecular weight reduction on starch pastes (1% db) clarity

Light transmittance of the hydrolyzed starch pastes ranged between 23%T and 98%T (Table 5). Lowest values were obtained with starch pastes from ginger (23%T), Florido (25%T) and normal maize (35%T). The transmittance of the remainder starches was higher than 55%T. The average values of hydrolyzed starches pastes clarity was 64.7%T.

Influence of total dispersion on starch paste (1% db) clarity

Light transmittance of treated starch (in DMSO) pastes were higher and varied between 67%T and 91%T (Table 5). The average values of hydrolyzed starches pastes clarity was 79.5%T.

DISCUSSION

This difference relative to apparatus would be due to detector's acceptance angles. Thus, for the samples scattering and or refracting most of light, the light was spread out over various angles and the resulting quantity which arrived at the detector varied according to the internal layout of each spectrophotometer. These differences were also found previously (Craig et al., 1989). For the continuation, starch pastes transmittances could be compared only if they were obtained with the same apparatus. Moreover, the most significant fact was the order of classification of the starches in terms of their paste %T. Thus, natural starch paste could be classified as following: Potato >Cassava > Waxy maize > other cereal. These observations are in agreement with those of several authors (Craig et al., 1989; Wang et al., 1993, Bello-Pérez and Paredes, 1996; Jacobson et al., 1997; Amani et al., 2005). However, these results were definitely higher than those obtained by Singh et al. (2004) on potato; difference probably due to the samples or the treatment temperature which was 90°C.

The reduction in transmittance with the increase in the concentration would be due on the one hand to the cumulative effect of the amylose concentration in the medium that would induce opaque and white gel formation; and on the other hand to the fact that the beam of light met more structures (swollen granules) in the medium, thus, it was more and more reflected or refracted.

The first zone observed when heating starch suspendsion at low different temperature corresponded to a beginning or an absence of starch gelatinization. Thus, starch pastes were opaque and the light transmittance (%T) values were lower than 5%T for the majority of them except potato starch whose clarity was about 22%T. This low clarity would be explained by the fact why the not swollen starch granules remained dense, thus, they reflected the maximum of light entering the medium. Consequently, pastes appeared turbid or opaque, in agreement with literature (Craig et al., 1989).

The zone of increase in transmittance showed that it evolved with the gelatinization phenomenon. Pastes obtained after gelatinizations were more transparent than native starch suspension (Lizuka and Aishima, 1999; Nuessli et al., 2000). The increasing in starch paste clarity could be due to reduction in light refraction by the granules remnants.

The rapid opacification of the starch pastes of Esculenta, Florido and ginger would be due to the phenomenon of retrogradation. Amylose reorganized by forming amylose aggregates on the one hand and on the other hand binds to the granules remnants to form amylose aggregates and granules remnants (Whistler, 1954). Thus, they sedimented and generated the phase separation. The plate of transmittance values could represent a stabilization of the mediums by amylose aggregates associated with the granules remnants.

Addition of NaCl in starch pastes involved an association between starch chains that led to collapsed structure which would reflect light in a significant way and consequently, it would induce a reduction in the transmitted light. In the same way, the covalent bound phosphates groups of potato amylopectin which would generate high clarity by electronegative repulsions were neutralized by sodium ions, explaining the high fall of clarity (of 23%T) observed into potato paste. This behavior was also reported previously (Craig et al., 1989; Bello-Pérez and Paredes-Lopez, 1996).

The phase of rise in clarity would be due to the increase in the medium refractive index which involved a reduction in the relative refractive index. Consequently, it led to both a reduction in medium refraction and an increase in transmittance as described (Bello-Pérez and Paredes-Lopez, 1996).

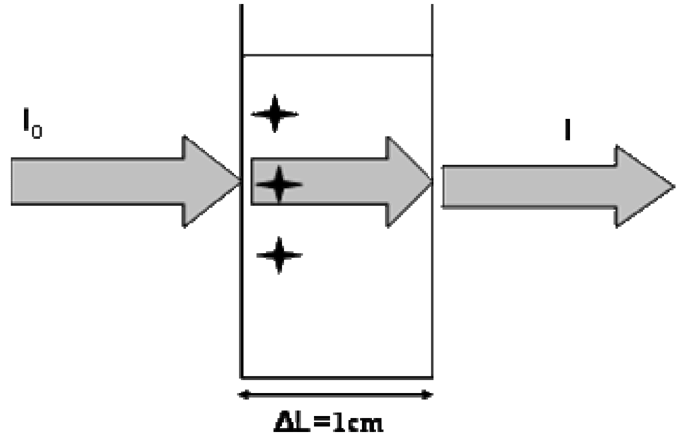
The absence of transmittance variation observed with potato starch pastes could be due to a probable saturation of the apparatus. The increase in pastes clarity after addition of sucrose was in agreement with literature (Bello-Pérez and Paredes-Lopez, 1996). As announced above, the increase in %T after addition of sucrose would be related to the medium refractive index.

Comparison of treated (at 150°C) starch paste transmittance with the control revealed that values were increased between 1.2 times (potato starch) and 6 (Florido starch). The lowest ratio of transmittance values obtained for potato starch could be due to its higher initial value (79%T). These results reveal that clarity would be influenced by the residues dissolved granules remnants.

As for hydrolyzed starch paste, the comparison of light transmittance with the control revealed an increase ranging between 1.2 times (potato starch) and 8.3 (Esculenta starch). Clarity could be influenced by the residues dissolved granules remnants. Acid hydrolysis did not only reduce starch molar mass (Erkki et al., 1992) but also the starch granules density. It allowed an increase in both swelling capacity and solubility at low temperature (Leach et al., 1959). Moreover, amorphous zones of starch granules were preferentially hydrolyzed and that had an important influence on starch pasting behavior by lowering its temperature of gelatinization (Jenkins and Donald, 1997). Thus, the increase in clarity after acid hydrolysis would be not only ascribable with a molecular weight reduction but also with the reduction in density of starch granules inducing a lowering of refractive index.

Comparison of purified starch paste transmittance with the control revealed an increase of 1.2 (potato starch) and 9.6 times (ginger starch). Purification with DMSO consisted of starch granules destruction, rupture of the crystalline zones and dispersion of the macromolecules in solvent without any structural degradation (Everett and Foster, 1959). It also consisted of lipids removal (Lansky et al., 1949). The highest transmittance observed with purified starch pastes revealed that, a better dispersion would be one of the main factors influencing starch paste clarity.

Thus, a synthesis consisting of the comparison of each treatment effects on pastes clarity was made in order to classify them. For the whole of the samples, the averages calculated with various treatments were 22.8%T (control), 54.7%T (heating at 150°C), 64.7%T (HCl 2.2 N hydrolysis) and 79.5%T (DMSO) (Table 5). The comparison of these average showed that when starch was purified and dispersed well, it formed at low concentrations (≈1% db) clearer pastes (light transmittance ≥70%T) than when it was not. Thus, this model (Figure 4) is proposed to show and explain that, in these conditions (dilute media), quasi totality of incident light passed though a starch medium that appeared clear.



✦ : Raleigh scatterer.

Figure 4. Schematic representation of light transmission through a dilute purified starch paste (1% db): I_0 and I representing incident and transmitted light respectively.

Conclusion

The results above make it possible to conclude that light transmittance in starch pastes could depend on: starches botanical origin, starches granules degree of dispersion, medium concentration, medium refractive index and the starch molecules aggregation or association capacities according to both temperature and time conditions. Moreover, starches from potato and cassava generated the clearest pastes.

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