CHAPTER ONE

INTRODUCTION

1.1 Background to the study

Root and tuber are a group of industrially underutilised and underexploited crops which are also the basic local staples for millions of people in the developing countries of the world. They are the main source of food, nutrition and income generation for the developing world's rural poor and smallholder farmers (Scott *et al.,* 2000), and are important for poverty alleviation and reduction efforts in sub-Saharan Africa (Hartmann, 2007). Tropical root crops provide unique opportunities for the sustainable development and sustenance of around 600 million rural poor people in the tropical and subtropical regions of Africa, Asia, South Central America, and Oceania (Chandra, 2007). The global diversity of tropical root and tuber crops is very wide. It includes cassava, sweet potatoes, potatoes, yam, cocoyam and many minor tuber crops. Root and tuber crops are similar in that they are usually bulky, perishable and propagated by vegetative means but they are highly differentiated in terms of origin, production, nutritional traits and use (Scott *et al.*, 2000).

Cocoyam, a generic term for both *Colocasia esculenta* and *Xanthosoma sagittifolium* is an important stem tuber crop that is widely cultivated throughout the tropical and sub-tropical regions of the world (Onyeka, 2014). Cocoyam is used mainly as subsistence staple and source of dietary energy in many parts of sub-Saharan Africa and provide about a third of the food intake of more than 400 million people in the tropics (Onyeka, 2014). Cocoyam is the third most important root and tuber crop (after cassava and yam) in Nigeria (NRCRI, 2008). Nigeria is the largest producer of cocoyam in the world with a production of 3.3 million metric tonnes in 2014, a 32.3% share of the world production (FAOSTAT, 2015) and accounts for 57.7% production in Africa and 72.2 % production in West Africa (Chukwu *et al*., 2008). The corms of cocoyam are known to have a high content of tiny, easily digestible starch grains ranging in content between 22 and 40%, making it a good source of starch (Adane *et al*., 2006; Moorthy *et al*., 1993). Cocoyam leaves are consumed as vegetables and used in soup making. It may also be used as an ornamental plant. Its edible corms are consumed mainly after roasting, pounding or frying. Its dried slices may also be milled and used in the production of composite flour for baking purposes similar to potato flour (CABI, 2008).

Yam tubers of genus *Dioscorea* have more than 600 species cultivated mainly in the tropical and subtropical regions especially of West Africa but only a few of these are cultivated as major staple food crops or medicine in these areas (Zhu, 2015). The predominant edible species of African origin are the white Guinea yam (*D. rotundata* Poir.), yellow Guinea yam (*D. cayenensis* Lam.), and trifoliate or bitter (*D. dumetorum* Kunth) (Diop, 2008). Edible species from Asia include water or greater yam (D. *alata* L.), and lesser yam (*D. esculenta* [Lour.] Burkill). Cush-cush yam (*D. trifida* L.) originates from the Americas. White Guinea yam and water yam are the most important food yams in terms of cultivation and utilization. These global distributions of *Dioscorea*'s different species vary widely across continents in genotype, and whether they grow wild or are cultivated (Bhandari and Kawabata, 2004). These crops are consumed by a third of the world's population, usually comprising the lower socio-economic urban groups (Chandra, 2007) and the rural poor. Annual average of about 68 million metric tonnes of yams was produced worldwide from 2010 to 2014 (FAOSTAT, 2015). Of this figure, over 96.1% was produced from Africa with Nigeria alone accounting for about 36.68 million metric tonnes, a figure translating to 56.88% of world production with average of 258 kCal yam consumption per capita per day (IITA, 2009).

Trifoliate yam, also known as bitter yam (*Dioscorea dumetorum* (Kunth) pax), is indigenous to tropical Africa. It is mainly found wild or cultivated in West Africa, primarily eastern and western Nigeria and Cameroon and can be grown from sea level up to 1500 m of elevation in the tropics in both dry and humid areas (Medoua *et al.*, 2005a). It has been described as the most important yam in Cameroon (Agbor-Egbe and Treche, 1995) and as one of the eight most important yam species in West Africa (Medoua *et al*., 2007). Trifoliate yam is rich in protein (9.6%), with fairly balanced essential amino acids (having a chemical score of 0.94), and easily digestible starch (Medoua *et al.*, 2007). This yam specie has been found to be high-yielding (40 tonne/hectare) and may not require staking, thus saving on labour (Lyonga and Ayuk-Takem, 1982). The oval-shape and shallow growing tubers could also permit mechanized harvesting. Bitter yams are locally consumed by eating with sauce directly after boiling, roasting, or frying in oil. The tubers may also be mashed or pounded into dough after boiling, processed into flour, or cooked into pottage with added protein sauce and oils. A means of adding value to *Dioscorea* *dumetorum* could be processing its tubers into starch. Though it has a comparative higher nutritional potential than other yam species (Medoua *et al*., 2007), however the post-harvest hardening phenomenon which reduces its use as food and decreases its produce life makes its cultivation and production discouraging to farmers. In a bid to produce value added product from it and to find alternative use for this underutilised crop, instant flour has been produced from *D. dumetorum,* and the sensory properties were evaluated (Mbome and Treche, 1994). The physical and functional properties of *D. dumetorum* flours and starches have also been studied to evaluate their potential for use industrially (Sahoré *et al.*, 2007; Abiodun and Akinoso, 2014). Flour from *Dioscorea dumetorum* has been used to produce acceptable stiff dough ‘amala’ (Abiodun and Akinoso, 2015) that is comparable to the stiff dough from white yam.

Starch, the main constituent of root and tuber crops, is an important raw material for a wide range of food and non-food industries. Processing of root and tuber crops into starch will contribute to minimizing post-harvest losses, reduce wastages, increase the crops’ storability and shelf life and reduce cost of transportation. This will help to explore diversification of uses through value addition, thereby increasing income for smallholder resource-poor farmers who are the major producers of these crops. Starch provides over 70% of the calorific intake of man and has extensive applications as raw materials locally and industrially (Kavlani *et al.,* 2012). The uses of starch in the food industry includes canning, frozen foods, bakery, dairy, flavors and beverages, microwavable products, confectionery and cereals/snack industries as thickeners, stabilizers, binders, gelling and dusting agent etc. the non-food industries that utilize starch include adhesives, textile, metal, paper, cosmetics, pharmaceuticals, mining/explosives, construction and other miscellaneous uses (Satin, 2000). The specialized uses of starch in these systems are determined by their unique physicochemical, functional and structural properties (Singh *et al.,* 2010) which vary by botanical origin, environmental condition, season of planting, varietal differences, age of tubers and time from harvesting to processing (Sahore *et al.*, 2007, Farhat *et al.,* 1999; Afoakwa and Sefa-Dedeh, 2001; Abiodun and Akinoso, 2014). Each of the applications requires particular characteristics that make the starch competitive.

1.2 Justification of study

In Nigeria, corn and potato starches are currently the major sources of starch imported for industrial food and non-food use with some contribution from cassava as the only indigenous starch source. This results in significant losses in foreign exchange, discourages local production of starch and reduced patronage and utilisation of local crops with huge potentials. In the recent past, cassava was a cheap staple (processed to garri, fufu and lafun), affordable and consumed daily by even the poorest households. The recent attention on cassava as industrial raw material for starch, fuel and feed has resulted in increased value and prices for its local consumption and thereby contributing to food insecurity. Focus may be shifted to less important and underexploited staples like the cocoyam and bitter yam as starch source. These crops have the potential to alleviate poverty, create wealth for the farming community through enterprise development and generate employment while assuring food security of the nation. Farmers often record significant losses on the harvests of cocoyam and bitter yam due to the fact that they are not required in appreciable quantity for any industrial large scale applications and the production of value added products. Harvests that the farmers are unable to sell as fresh tubers therefore go to waste resulting in reduced income. Extracting starch from the freshly harvested tubers is a feasible way to prevent such losses.

Furthermore, starches from various botanical sources such as rice, wheat, cassava, maize and potato have received greater attention in terms of study of functional and physicochemical properties (Eke *et al*., 2009; Mweta *et al*., 2008; Mishra and Rai, 2006; Amenorpe, 2010). Although, some properties of native starches of few cultivars of the commodities have been studied (Falade and Okafor, 2013), however, comprehensive study of native and modified starches from the many cultivars of cocoyam and bitter yam grown in Nigeria have not been carried out so as to identify intrinsic properties that show their suitability for various end use purposes. This had so far considerably hindered the development of these crops as sustainable crops. In addition, significant quantities of tubers are lost due to poor post-harvest handling and storage practices. There is therefore a need to harness the potentials of these underutilised root and tuber crops as cheap and available sources of starch so as to reduce the burden of increasing demand on the well-known sources like potato, maize and recently, cassava (Mweta *et al*., 2008).

1.3 Research Objectives

This research was carried out to evaluate the physical, chemical, physicochemical and thermal properties of native and modified starches from nine cultivars of cocoyam and two cultivars of bitter yam. Specifically, this study intended to:

1. extract and study the physical, chemical, physicochemical and thermal properties of native starches from nine cultivars of cocoyam and two cultivars of bitter yam,
2. determine the effect of heat-moisture treatments (at 18, 24 and 27% moisture levels and 110°C), annealing and acid thinning modifications on physical, chemical, physicochemical and thermal properties of starches from nine cultivars of cocoyam and two cultivars of bitter yam,
3. propose food applications where the properties of the native and modified starches could be useful.

CHAPTER TWO

LITERATURE REVIEW

2.1 Root and Tuber crops

Tropical regions of the world (Africa, the Caribbean and Pacific) span across continents and many countries and cover about 31% of total land area of the earth with a land mass of about 1700 million hectares (FAO, 2015). Root and tuber crops produced in these areas are important foods that serve as subsistence staples for majority of the populace. They are the main source of inexpensive carbohydrates in the diet of millions of the people and are composed primarily of starch within their parenchyma cells. Principal tropical root and tuber crops belonging to a number of different plant families are derived from about nine species which include cassava (*Manihot esculenta* Crantz), yams (*Dioscorea spp*.), sweet potato (*Ipomoea batatas* L. (Lam), cocoyam (*Colocasia esculenta* and *Xanthosama sagittifolium* and other minor crops like arrowroot, African yam beans, winged beans, water chestnut etc. These crops play a significant role in the global food system by enhancing food security, providing cash income and serving as source of revenue generating activities for most rural dwellers. They are referred to as ‘insurance’ crops and safety shields in time of drought and other disturbances (Hartmann, 2007). In recent years, they have also become important economic drivers, yet their potentials for use have to a large extent, not been fully explored. They have underexploited potentials for contributing to food security, nutrition and industrialisation. They have traditional use as food, animal feed (Agwunobi *et al.,* 2002) in addition to their medicinal use (Eleazu *et al.,* 2013). Total average production share of major root and tuber crops by region between 2000 and 2013 showed Africa as the second largest producer with over 30% production after Asia (41.8%), Americas (10.6%), (Europe 16.1%) and Oceania (0.5%) (FAOSTAT, 2014).

In Nigeria, production of root and tuber crops spiked to an all-time high of over 100million tonnes in 2013 with progressive increase from 2010 (FAOSTAT, 2014). This showed a targeted interest in the cultivation of these crops as a result of greater attention been focused on industrial utilization. Cassava and yams were the most produced crops in Nigeria in 2013 at over 53 and 40.5 million tonnes, followed by maize, oil palm and sorghum at 10.4, 8 and 6.7 million tonnes (FAOSTAT, 2014). Table 2.1 shows Nigeria as the second top average producer of root and tuber crops between 1990 and 2010. Average annual production for Nigeria thereafter increased steadily to over 86.7, 91.0, 90.6 and 107.8 million metric tonnes in 2011, 2012, 2013 and 2014 respectively with a yield of 73,507 thousand Hg/Ha in 2014 (FAOSTAT, 2015). These crops may be transformed to value-added and durable products due to their perishable nature through drying, fermentation, detoxification etc. to ensure long-term maintenance of supply. Further value addition to these crops will help to reduce imports while enhancing self-reliance in production and utilisation.

2.2 Yams (*Dioscorea spp.*)

Yam is a generic name for the plants of twining climbers that form tubers in the genus *Dioscorea* of the monocot family *Dioscoreaceae*. *Dioscorea* is a large genus with over 600 species of which about 10 are staple yams, while many wild forms become famine food in times of food scarcity (Salda, 1999; Lebot, 2009). Yams are produced on 5 million hectares in about 47 countries in tropical and subtropical regions of the world (FAOSTAT, 2015). Tropical areas of the developing world alone, in particular, the ‘yam zone’ (Cote d’Ivoire, Sierra Leone, Ghana, Nigeria, Cameroun and Ethiopia) produces more than half of the world supply of yam (Farhat *et al.*, 1999) while Africa as a whole accounts for 96% of world production (FAOSTAT, 2014). Nigeria is the largest producer of yam in the world, accounting for about two-thirds of global production each year (FAOSTAT, 2015) with 36 million tonnes average annual production from 2010 to 2013 (Fig 2.1). The most commonly cultivated species include *D. alata* (water yam), *D. cayenensis* (yellow yam), *D. esculenta* (lesser yam), *D. opposita* (Chinese yam), *D. rotundata* (white yam), and *D. trifida* (cush-cush yam), while there are the less cultivated species but still with traditional relevance and limited utilization such as *D. abyssinica*, *D. bulbifera, D. dumetorum*, *D. persimilis,* and *D. septemloba* (Zhu, 2015). Some species of African origin are the *D. cayenensis, D. rotundata* and *D. dumetorum* while those from Asia include *D. alata, D. esculenta. D. trifida* originate from the Americas. Of all these, the white guinea yam and water yam are the most important in terms of cultivation and utilisation. Yam which is the major staples of people in most developing countries is also an income crop with high value cultural significance in festivals, marriages ceremonies and fertility. The starch yield from these various species vary considerably with *D. rotundata* tubers having the highest starch content (Moorthy, 2002).

Table 2.1. Top Producers of Roots and Tuber crops by countries

	Total		Per annum growth	
	(Million tonnes)	(Million tonnes)	(%)	(%)
	2009	2010	1990-1999	2000-2010
China	156.27	162.46	2.9	-1.5
Nigeria	72.61	83.26	8.9	2.5
India	45.13	45.73	3.5	3.6
Brazil	28.56	28.77	-0.8	0.8
Indonesia	25.75	27.51	-0.4	3.6
Thailand	30.54	22.46	-3.7	1.5
Ghana	19.64	20.94	8.4	4.7
USA	20.51	19.42	2.5	-2.1
Germany	11.62	10.20	-3.5	-2.9
Uganda	8.63	8.82	3.4	1.2

Source: FAOSTAT (2014).

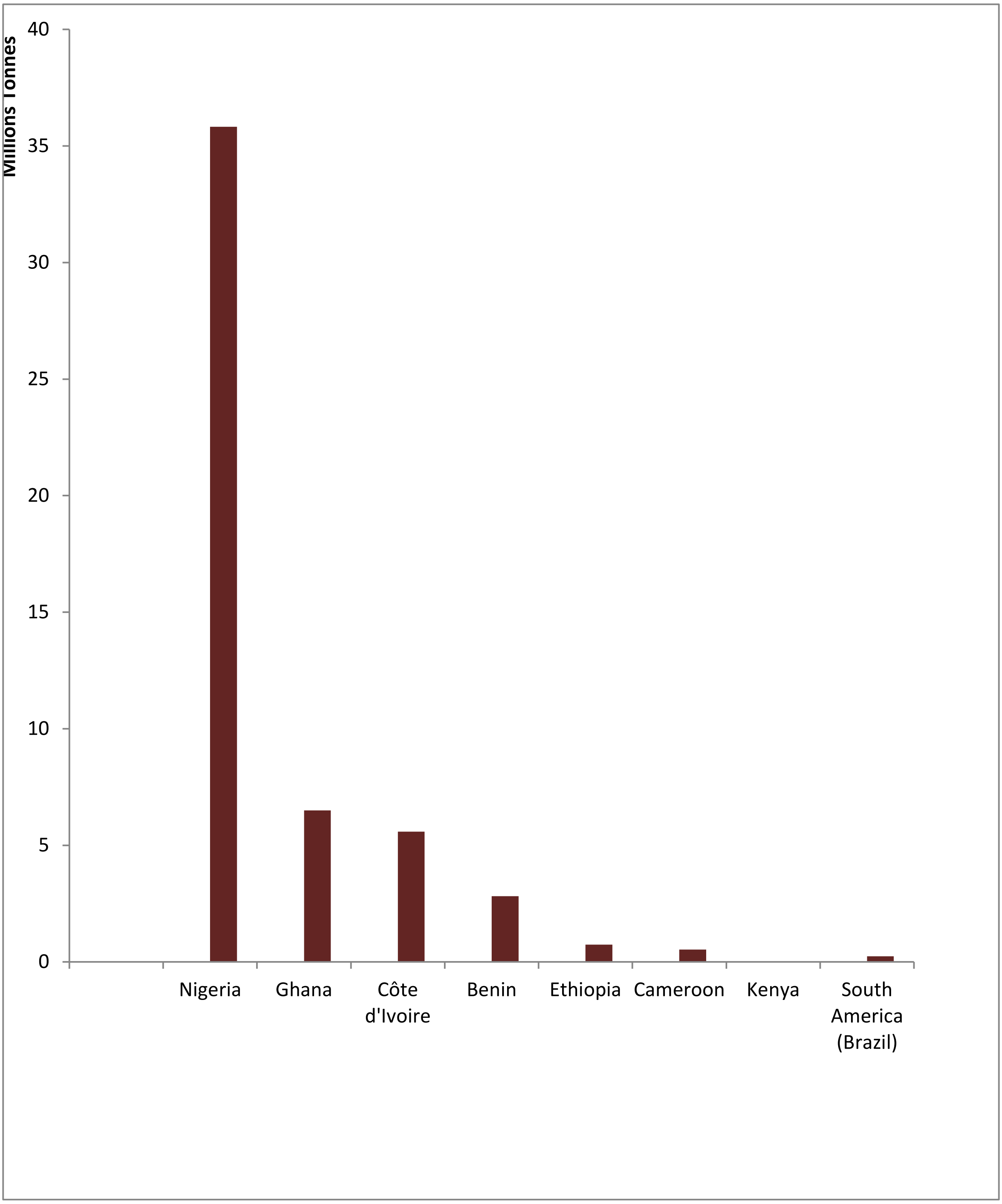


Figure 2.1. World highest producers of yams by country (Average 2010-2013) (FAOSTAT, 2014)

Yams are one of the most expensive crops to produce; the planting and harvesting processes require significant labor input, expensive yam seed, increasing pest issues, declining soil fertility and limited supply of seed. Despite these constraints, cultivation of yam is considered profitable (Maikasuwa and Ala, 2013). Yam consumption per capita per day is highest in Bénin (364 kCal) followed by Côte d'Ivoire (342 kCal), Ghana (296 kCal), and Nigeria (258 kCal) (IITA, 2015).

2.2.1 Bitter yam

Dioscorea dumetorum (Kunth) Pax. (Lasiophyton), of the family *Dioscoreaceae* (Bai and Ekanayake, 1998) commonly called African bitter yam, Quinim, cluster yam, trifoliate or three-leaved yam is also locally called Esuru (South West Nigeria), Ikamba (Gabon), Amargo (South Americas), Ono (West Africa). The species is found cultivated and wild throughout tropical Africa between 15°N and 15°S, and is cultivated in West Africa, especially in Nigeria and Cameroun (Medoua *et al*, 2005a). *D. dumetorum* is an important food crop in Nigeria and several central and western African nations. It has been shown to be less demanding of manpower in its cultivation than *D. alata* and *D. cayenensis* (Fasidi and Bakare, 1995). It grows as a spiny, climbing vine with robust stems that may reach up to 6-8 m in length. The leaves are trifoliate with ovate leaflets, 12-15 cm long and 6-9 cm wide. The underground tubers may be single or in a cluster weighing several kilograms with white, pale or dark yellowish flesh (FAO, 2007). *D. dumetorum* tubers are larger than those of *D. esculenta*, and a single plant could produce a cluster of tubers, which often contain a bitter alkaloid, dioscorine especially in the uncultivated wild variety (Degras, 1993; Palaniswami and Peter, 2008; Bhattacharjee *et al.*, 2011). Bitter yam is also used as food vegetable. Unlike other yam species like *D. rotundata*, it is not pounded into dough because of its soft texture when pounded while the aged populations with poor teeth prefer it (Kay, 1987). The wild forms are regarded as famine food, and the tubers may be detoxified by slicing, soaking, boiling usually with addition of salt; and the slices may then be subsequently dried (Mbome and Treche, 1994). The dried tubers can be used to prepare flour. In the Sudan, wild detoxified tubers have been ground into flour and used as a base for the preparation of beer (Kay, 1987). Wild varieties of bitter yam which are usually poisonous have been mixed with bait and used for killing animals in some localities in Africa while reports of their use for criminal purposes have also been recorded (Kay, 1987). This specie may be deliberately cultivated together with other edible yam species to discourage thieves in the field. Its use in traditional medical therapy as anti-diabetics, antiarthritis, anti-rheumatism and in the control of hyperlipidaemia, hypercholesterolaemia and hyperketonaemiamia has been reported. Evidences of some of these claims have been scientifically substantiated (Undie and Akubue, 1986; Nimenibo-Uadia, 2003).

Among pests affecting stored yams, the insects *Araecerus fasciculatus* and *Lepidobregma minuscula* have been identified as the major pests of tubers of *D. dumetorum* (NRI, 1987). *D. dumetorum* is the most nutritious of the six yam species consumed in Ghana (Afoakwa and Sefa-Dedeh, 2001). A typical analysis of the edible portion of the tubers was given by Degras (1993) as: water 79%; protein 2.78%; fat 0.28%; carbohydrate 17%; fibre 0.3%; ash 0.72%; calcium 92 mg/100 g and ascorbic acid 6.6 mg/100 g with a mean protein content of 9.6% (dry matter basis) compared to 8.2% for water yam (*D. alata*) and 7.0% for white yam (*D. rotundata*). Its protein is balanced in the essential amino acids (with a slight deficiency of lysine) and has an average chemical score of 93 against 86 for *D. rotundata*, when compared with the FAO/WHO (1973) reference protein (Mbome-Lape and Treche, 1994). The carbohydrate consists mainly of starch, with relatively small granules sizes which are small, rounded or polyhedral in shape. Average size of granule was reported as 1-4 microns (Farhat *et al*., 1999). Fasidi and Bakare (1995) reported higher sugar contents in the yellow variety than the white variety during sprouting. The physicochemical properties of fresh tubers have been elucidated (Farhat *et al.,* 1999; Sahore *et al.,* 2007; Otegbayo *et al.,* 2014) while the amino acids of the varieties of *D. dumetorum* were reported by Alozie *et al.* (2009).

Despite the impressive nutritional data reported for *D. dumetorum,* its production as a food resource in Nigeria has been found to be declining. This may be due to local importance of other food yams as storable food processing raw materials and materials of inter-state trade (Scott *et al.,* 2000; Ukpabi and Oti, 2010). This is more so as the plant is now considered as an endangered species in Nigeria (Ukpabi, 2015). *D. dumetorum* also presents a post-harvest hardening phenomenon that has been widely reported (Afoakwa and Sefa-Dedeh, 2001; Farhat *et al*, 1999; Siadeju *et al*, 2016; Medoua *et al*., 2005a). The storage of harvested tubers under warm, humid conditions (the typical condition of the tropical regions) render them susceptible to hardening that is characterised by an inability to soften even when cooked. In a bid to find utilisation for hardened tubers of bitter yam, several researchers have studied some changes accompanying this phenomenon in its flours and starches. Anti-nutritional changes during storage (Medoua *et al*, 2007), physicochemical changes after harvest (Sefa-Dedeh and Afoakwa, 2002; Medoua *et al.*, 2005a), soaking and salt treatment effects on pasting, textural and functional properties of starch (Abiodun *et* *al*., 2010; Medoua *et al*., 2005b) are some of the reported works. The hardened tubers have also been used in flour production for instant meals (Agbo-Egbe and Treche, 1995).

2.3 Cocoyam

Cocoyam (*Colocasia esculenta* L. Schott and *Xanthosoma sagittifolium*) is a member of the Araceae family made up of about 100 genera and more than 1500 species that are mostly epiphytes. It is one of the oldest crops known to man and grown for its edible corms, cormels, leaves and as a traditional ornamental plant (Onwueme, 1994). *Colocasia* (cocoyam) and *Xanthosoma* (new cocoyam) are the most important of the edible genera. Cocoyam is an important stem tuber crop that is widely cultivated throughout the tropical and sub-tropical regions of the world. The aroids, as they are often called, grow in humid or shady habitats. Some are terrestrial while others are vines, creepers or climbers (Ekanem and Osuji, 2006). It is used mainly as subsistence staple and source of dietary energy in many parts of sub-Saharan Africa and provide about a third of the food intake of more than 400 million people in the tropics (FAO, 1990). Cocoyam is believed to have originated from Asia and the Pacific region (where it is commonly known as taro or tannia), before it spread to the Mediterranean region, West Indies and West Africa. It is an important staple crop throughout these regions where the corms may be pounded into dough and eaten with soup, roasted, baked, boiled or fried. Cocoyam was first recognized as a major staple crop in Nigeria in 1969, cultivated by resource-poor smallholder farmers but is now the third most important root and tuber crop (after cassava and yam) (NRCRI, 2011). Nigeria is presently the largest producer of cocoyam in the world with an average annual production of 3.27 million metric tonnes in 2014 (FAOSTAT, 2015) and accounts for over 45% of global production, 57.7% production in Africa and 72.2 % production in West Africa (Chukwu *et al*., 2008). Production of cocoyam in Nigeria has suffered from challenges like apathy, low genetic base, high post-harvest losses, poor value addition and pests and diseases (NRCRI, 2011). A cocoyam rebirth initiative of the National Root Crops Research Institute, Umudike, Nigeria launched in 2011 has contributed to addressing the challenges of apathy and storage problems through the 'gocing' storage method. Through recent advances in cocoyam breeding and genetic improvement research, 14 accessions of edible cocoyam are currently available in Nigeria. *Colocasia species* have 10 landraces (NCe 001, 002, 003, 004, 005, 006, 007, 008, 009 and 010) while *Xanthosoma specie* has 3 landraces (NXs 001, 002, and 003) and a hybrid from Cameroun (NXS 004) (NRCRI, 2011). Yields from cocoyam cultivation in Nigeria has been recorded to be about 30-60 tonnes/ha which is poor compared to results obtained elsewhere (Okoye *et al*., 2008). Post-harvest loss of cocoyam has been reported be as high as 50-95% (Nwufo and Atu, 1987) which may be attributed to high deterioration in storage caused by lack of effective storage methods, low value addition, pests and diseases problems. The pests of cocoyam include the white ants which cause damage on the tubers at any stage of development or even in storage. Fungal attack on field may cause the plants to wilt and the seedlings damp off while rodents may also eat the corms and cormels on field (IITA, 1996). Diversifying the utilisation of cocoyam through the production of value added products like starch will contribute to reduction of post-harvest losses, increased consumption, enterprise development, improved market access and increased income for farmers.

2.4 Root and tuber starches

Starch, a renewable complex biopolymer, is a versatile agricultural raw material for local and industrial applications (Koh and Long, 2012). It is an inexpensive resource, relatively easy to handle, completely biodegradable and widely available in nature from sources such as cereals (maize, millet, sorghum, rice, and wheat), roots and tubers (cassava, yam, cocoyam and potato), fruits (banana, plantain and breadfruit), palms and seeds **(**Santana and Meireles, 2014). Starch has great potentials for economic and technological development in the developing countries of the world if properly harnessed. It is the third most abundantly produced commodity (after wood and vegetable oil) according to Daramola and Falade (2006) and is widely used in variety of food and non-food products with its quality determining the quality of products obtained from it. Starch is the major carbohydrate in root and tubers and can amount up to 80% of the dry matter (Zhu, 2015). It is a carbon reserve that occurs in two main forms: amylose, a linear chain of glucose monomer and amylopectin, a highly branched chain which may comprise up to a million glucose units. Starch is formed and stored as a product of the photosynthesis reaction in roots and tubers, with little content of proteins, vitamins, fibre and minerals. On fresh weight basis, starch component of cassava, sweet potato, yams and the aroids have been reported to be in the range 27-37, 18-28, 20-25 and 15-25% repectively (Lebot, 2009). Properties of starches from the roots and tubers vary widely by geographical location, botanical origin, cultivars, season of planting and a number of other factors which predispose them to a wide range of local and industrial food and non-food applications.

2.5 World sources of starch

Currently, the world starch market is dominated by starches from corn, potato, wheat (Mweta, 2009) and to a lower extent, cassava. World starch production and utilisation was estimated as 68 million metric tonnes in 2009 with projections of 72 million metric tonnes in 2015 (Xiaohui, 2007). Out of this quantity, corn starch and other cereals alone accounted for about 90% (Patil, 2012) while major root and tuber crops like cassava (where Nigeria has a competitive production advantage) accounted for only 7.5%. About 54% of this total starch production was utilized in local and industrial food applications and 46% was put to non-food uses (Omojola, 2013) while the paper industry is the largest non-food end-user of starch (de Bragança and Fowler, 2004). Although cassava production is reported to be growing with starch from cassava competing favourably with that of corn (Patil, 2012), corn still remains the main starch source in the world, together with starch from potato, wheat and cassava. Demand for cassava starch has recently grown considerably and it is actually the most widely traded form of native starch in the world, mainly in Thailand and East Asia (Bertolini, 2010). Asia however account for about 90% of industrial cassava starch with the main producing countries being Thailand, China and Indonesia (LMC, 2008). World's highest cereals producers in 2010 were China with 497, 943 and the USA with 401, 670 thousand metric tonnes. Africa as a whole produced 164, 536 out of which Nigeria accounted for only 24, 590 thousand metric tonnes (FAOSTAT, 2015). Progressive increase in import of cereal crops by Nigeria was reported by FAOSTAT (2015) (Figure 2.2). Although, because of their lower moisture contents, cereals have been reported to have longer storage times and their starch extraction easier and faster than in roots and tubers (Bertolini, 2010), to adopt a starch source for industrial utilization requires that it be cheaply available, have high calorific value, possess excellent physicochemical and functional properties with ease and versatility of modification. Research focus shift to other sources of starch to explore their industrial potentials would enhance Nigeria's advantage, being the world highest producer of underutilized and cheaply available root and tuber crops like cocoyam and bitter yam. Though compared to starches from other tuber and root crops, such as potato, cassava, and sweet potato, there is much less information on yam and cocoyam starches (Zhu, 2015). The shift will also serve to promote these crops' utilisation, break their subsistence mode, promote enterprise development, enhance economic growth and development (Otegbayo *et al.*, 2014) while increasing their competitiveness in the global starch market.

Table 2.2. Volume of total cereal trade by Nigeria (in thousand metric tonnes)

Year	Imports	Exports
2000	3051	29
2008	4066	5
2009	4981	0
2010	5872	0.23
2011	6245	1.97
2012	6555	1.5
2013	6556	14.3

(Adapted from FAOSTAT, 2015)

2.6 Starch synthesis in plants

Leaves and stems of green plants through photosynthesis produce sugar during the day time which is then stored as small compact starch granules in their chloroplasts (transitory starch) (Martin and Smith, 1995). These are hydrolyzed and translocated to the amyloplasts (leucoplasts) which are the major storage organs of the plant cell (Martin and Smith, 1995). For long term storage, starch may be synthesized in the amyloplast of the heterotrophic and non-photosynthestic plant tissues like seeds, rhizomes, roots, underground stems and tubers. The major storage form in most plants is starch but in some plants such as sugar beet and sugarcane, sucrose is the primary storage form (Turesson *et al.,* 2014). Synthesis of starch occurs in their plastic cellular compartment while that of sugar occur in the cytosol (Streb and Zeeman, 2012). Starch as a complex polysaccharide has properties which vary depending on the relative amount of its primary components: amylose and amylopectin. Starch is synthesized by the reaction of hexose phosphates (glucose-1-phosphate) and sugar nucleoside ATP in the presence of ADP-glucose pyrophosphorylase (AGPase) enzyme as catalyst. Three important classes of enzymes that regulate starch synthesis and production of the final structure of amylose and amylopectin chains are the starch synthases (which are involved in the production of new α-1, 4 glucosidic bonds between glucose molecules), the branching enzymes (which introduce branching points) and the debranching enzymes (which remove some of the branched points) (Streb and Zeeman, 2012). The ADP glucose, a highly reactive compound is formed with the liberation of pyrophosphate. More glucose unit residues are then transfered from the ADP glucose in linear chains by starch synthase enzymes to the pre-existing starch molecules to add to the non-reducing end of the starch thereby liberating ADP. Branching is introduced into the chain helices by starch branching enzymes through the hydrolysis of 1, 4 glycosidic bonds to create 1, 6 glycosidic bonds (Figure 2.2).

2.7 Isolation of Starch

Separation of starch granules from tubers for commercial industrial utilisation must yield as pure a form as possible of the granules The process of starch isolation involves the preparation and extraction of starch by washing and peeling of the roots, cutting into smaller sizes, then crushing of the cells and separation of the granules from other insoluble matter, dirt and contaminants with addition of water. The mixture is allowed to sediment and filtered by sieving of the homogenized slurry, then allowing the mixture to sediment again. The supernatant is discarded and sediments re-suspended in water.

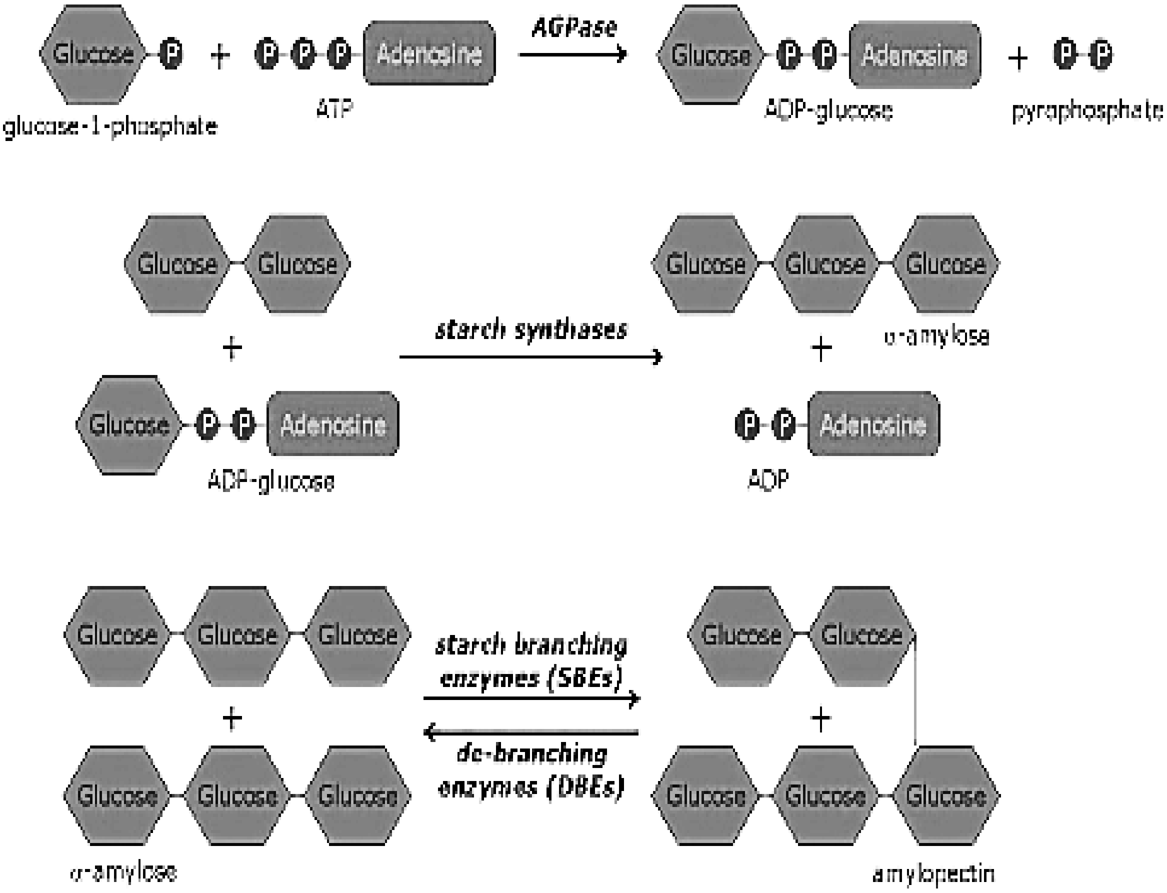


Figure 2.2. Representation of pathway of starch synthesis in plants

(Source: andrewgray.com/essays/starch)

This sedimentation, decanting and washing process is repeated severally to purify the starch granules before finally being centrifuged and dried. There are many variations to this general procedure of starch extraction due to differences in crop types and species, composition and structure. As the granules are locked together with other secondary constituent of the tuber like proteins, fats, and fibre in the protoplasm, they present difficulty in obtaining the pure form of the starch and so, purification may be done by the use of chemicals. The use of different solutions other than water for homogenizing cut tubers have been reported, sodium bisulfite solution (0.075%), or alkaline solution in a blender (Alves *et al.*, 1999; Riley *et al.,* 2004; Otegbayo *et al.*, 2014). Starch has also been extracted from tubers without peeling (Woodward, 1982). Whole roots were milled and pressed to separate the solids and to obtain the starch with the juice. The starch is then separated from the juice which is returned to the initial mixture for recycling. The process does not involve addition of any liquid other than the natural juice (Woodward, 1982). This starch extraction process seems feasible for industrial processing, though the purity of the resulting starch has not yet been ascertained (Zhu, 2015). Another process of starch isolation may be to process the tuber into flour by drying and milling and then extracting from the flour. Nimsung *et al.* (2007) extracted starch from the flour of unripe banana by treating the flour with 0.05N NaOH, blending the mixture, centrifuging and suspension in distilled water. The supernatant was decanted after sedimentation to remove impurities while sedimented starch was air-dried.

2.8 Starch Yield

Root and tuber crops are used as primary source of energy in the form of starch, which is the most abundant component in their dry matter. Dry matter content of starch sources is important by crop and cultivars because nutrition and energy calculations are based on amount and nature of its dry matter content. High dry matter contents will produce greater yield resulting in higher economic advantage. Yam starch has been found to accounts for about 60–80% of the dry matter of its tuber on dry basis (Otegbayo *et al.*, 2014). Ratio of starch extracted to original tuber weight is called the starch yield. This yield depends on factors such as structure and composition of the tubers (starch content in the original tuber), pre-harvest, harvest and post-harvest conditions, physiological state of tuber and efficiency of method of starch extraction. Emiola and Delarosa (1981) reported starch yield on dry basis for *D. alata* 84.7%, *D. cayenensis* 87.5%, *D. dumetorum* 88% and *D. esculenta* 86.1%. This showed *D. dumetorum* to have a higher starch yield than other species measured. Starch content in dried *D. dumetorum* flour has been reported to be 40.7-63.3% by Akinoso and Abiodun (2013). Other authors have reported varying observations: starch yield for six cocoyam cultivars ranged from 66.5-86.8% (Aboubakar *et al.,* 2008), new cocoyam 62.3% (Lawal, 2004), old cocoyam 55.1% and sweet potato 30% (Lim *et al*., 1994; Zhang and Oates, 1999). Much lower values of 10-25% (wet basis) were reported for *D. opposita* (Zhou *et al*., 2012), *D. rotundata* (Moorthy and Nair, 1989), *D. esculenta* and *D. alata* (Jayakody *et al.,* 2007). The starch yield is an important economic factor in selecting a botanical source of starch for commercial utilisation.

2.9 Molecular composition of starches

Purified starch granules are composed of two major types of alpha-glucan: amylose and amylopectin packaged in an organized manner within the granules. These components together make up approximately 98–99% of the starch dry weights (Tester *et al.,* 2004) while their ratio varies according to the botanical origin of the starch. Starch containing less than 15% amylose is referred to as waxy starch while those with range 20–35% are normal and high amylose starches are greater than 40% Perez and Bertoft, 2010). The amylose component of starch has relatively lower molecular weight compared with amylopectin which have larger and compacted molecules. Amylopectin is highly branched at the α-1, 6 position at about 10nm interval by small glucose chains along the molecular axis (Alcazay-Alay and Meireles, 2015). A helical starch growth ring structure is then formed from the sequencing of the alternating semi-crystalline amylose and amylopectin molecules (Jenkins *et al.,* 1993). The relative proportions of amylose and amylopectin depends on starch source and to a large extent determine the targeted functionality of the starch. Starch may also contain other minor constituents among which are protein, lipids, phosphorus, ash and other minerals. Tuber and root starches have been reported to contain less lipid and protein compared with cereal starches (Acker, 1982). These secondary constituents have profound effects on functional and physicochemical properties of starches and also affect their susceptibility to physical and chemical modification (Hoover, 2001)

2.10 Amylose and amylopectin component of starches

Starch are composed mainly of minor linear polymer, amylose, consisting of α-1, 4 linked D-glucopyranosol residues which contains up to 6000 glucose units and average range of molecular weight of $1x10^5$-$1x10^6$ and amylopectin a branched α-1,4 and 1, 6 linked polymer containing as much as a million glucose units which are not randomly distributed in clusters (Fig 2.3) (Hoover, 2001). Amylopectin are much larger than amylose with molecular weight range of $1x10^7$-$1x10^9$ (Ral *et al.,* 2008). The ratio of the two polysaccharides varies according to the botanical origin of the starch. These two components form a semi-crystalline structure in the starch granules, which consist of crystalline lamellae (ordered, tightly packed parallel glucan chains) and amorphous lamellae (less – ordered regions) (Oates, 1997). The actual structure and organization of the amylopectin is vaguely known till date but two major hypotheses exist: the cluster model and the building block backbone model (Vamadevan *et al,* 2013; Zhu, 2015). Relative proportions of amylose and amylopectin and their arrangement within the solid starch granules determine the physicochemical and functional properties of the starch. Amylose content has been postulated to appear to be the major factor controlling almost all physicochemical properties of rice starch due to its influence on pasting, gelatinization, retrogradation, syneresis and other functional properties (Wani *et al.,* 2012). Amylose contents in starch may be influenced by environmental and agronomic practices, genotype and other endogenous starch components. A variety of methods have been used to quantify amylose contents of tuber starches: Amani *et al.* (2004) evaluated amylose contents using calorimetric methods (DSC) while the iodine binding-colorimetric method was used by Otegbayo *et al.* (2014). Rolland-Sabate *et al.* (2003) employed the chromatographic method for amylose determination all of which gave varying results.

Amylose and amylopectin contents of starch also vary by biological origin and cultivar. Amylose contents are usually about 10-30% while amylopectin make up for the balance (Lawal, 2005). Moorthy (2002) and Tian *et al.* (1991) reported amylose content values of 13.6-23.8% for cassava, 20-25% for sweetpotato, and 3-43% for cocoyam starches based on varietal differences while higher values were reported for canna (31.7%) and ginger (26.5%) starches than in cassava (19.8%), arrowroot (20.8%) and sweetpotato (22.6%) starches (Peroni *et al*., 2006). Several *Dioscorea* starches have also been investigated and reported to contain varying contents of amylose. These include *D. alata* 21.7% (Otegbayo *et al*., 2014), *D. dumetorum* 12.3% (Farhat *et al*., 1999), *D. cayanensis* 26.5% (Riley *et al*., 2004), *D. rotundata* 25.2-28.8% (Amani *et al*., 2004) and *D. bulbifera* 12.2-14.3% (Jiang *et al*., 2012).

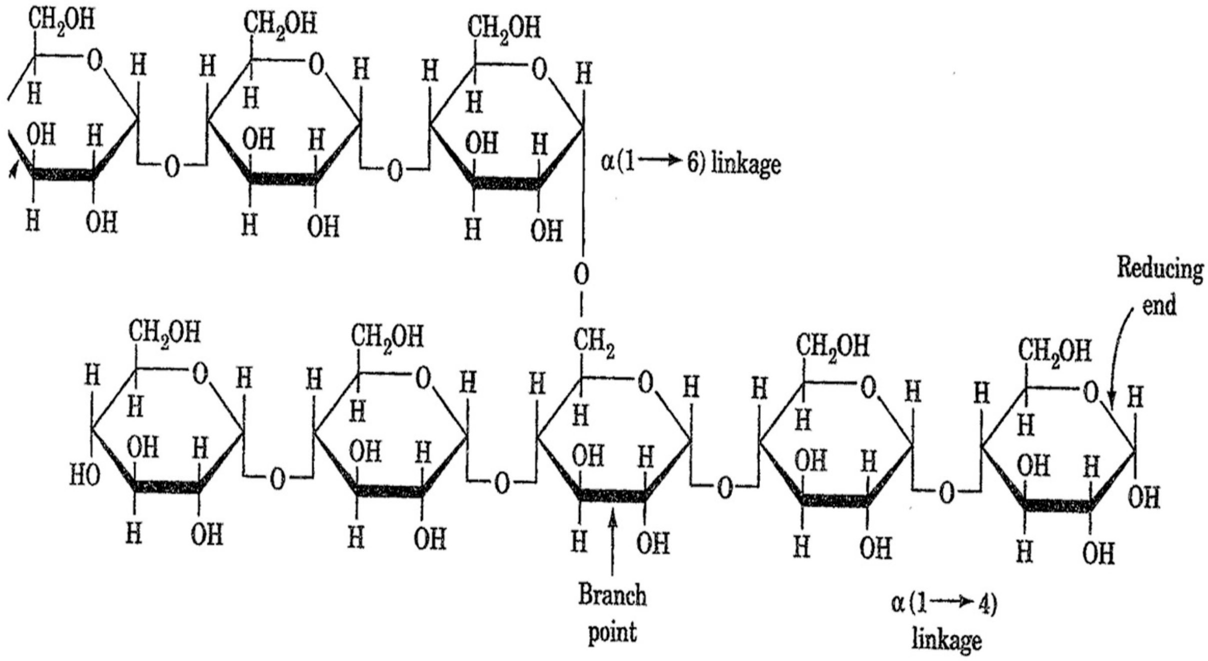


Figure 2.3. Structure of amylose and amylopectin chains (Adapted from Tester and Karkalas, 2002)

2.11 Starch granule morphology

Starches isolated from different botanical origin have characteristic granule structure, shape and sizes which are indicative of their unique properties, functionalities and applicability. A wide variety of granule morphologies are replete in literature in which the granules may be identified individually or associated in clusters. Distinct different particle size distribution and range have been recorded for several starch sources (Tester *et al*., 2004). Granule size diameter range of less than 1µm to 100µm and shapes like round, ellipsoidal, angular, truncated, polygonal, hexagonal, oval, spherical etc. have been reported (Zhu, 2015). Cereal crops generally have smaller granules compared to root and tuber crops (Vamadevan and Bertoft, 2015). Several methods have been employed in determination of starch granule morphology which include light microscopy (Otegbayo *et al.,* 2014), scanning electron microscopy (Jayakody *et al.,* 2007), and laser light diffraction based methods (Farhat *et al.,* 1999). Sizes and shapes that had been reported earlier include *D. dumetorum* having size range of 3.1-5.0µm with rounded shape as studied by Farhat *et al*., (1999) in the characterization of starches from West African yams (Table 2.3). Cassava starch granules were reported to have much larger sizes with range of 1.8-27.8µm and rounded shape (Eggleston *et. al.,* 1993). Mishra and Rai (2006) found that potato starch had sizes 14.3-53.6µm and displayed oval/flat shapes while those of tapioca starch granules were found to have smaller average size range of 3.6-14.3µm and were mostly spherical/truncated in shape. Corn starch granules were 7.1-25µm with polyhedral shapes (Mishra and Rai, 2006), *D. nipponica,* 9.5-32.3µm oval/sausage granule shape (Yuan *et al.*, 2007), Banana, 39µm lenticular shaped (Bello-Perez *et al.,* 2000), new cocoyam, 15-40µm round and polygonal (Lawal, 2004), *D. cayenensis* and *D. rotundata*, 28.5-30.6µm round/oval shape (Emiola and Delarosa, 1981). Scanning Electron Microscopy (SEM) studies of *Dioscorea alata* also revealed variation in granule sizes and shapes as studied by Riley *et al*. (2004) (8-38µm) and Amani *et al*. (2004) (18.6-29.3µm) showing that season and geographical origin influences starch granule morphology. Granule morphology has been shown to affect some functional properties of starches. Small granule sizes of cocoyam starches could make them useful as fillers in biodegradable plastics and aerosols (Moorthy, 2002) while small granule sizes also resulted in increased solubility and water absorption capacities of Malawian cocoyam starches (Mweta, 2009). Increased swelling power, (Tang *et al*., 2002), increased enzyme susceptibility (Fukai *et al*., 1994) and faster retrogradation (Vasanthan and Bhatty, 1996) have been associated with small starch granules than larger ones.

Table 2.3. Morphological characteristics of some crops starch granules

Crop/cultivar	Size range (µm)	Shape	Reference
Cassava	5-25	Flaked-shape, irregular	Falade and Akingbala (2010); Jane *et al.* (1994)
Potato	<110	Oval, irregular	Singh *et al.* (2003)
Sweet potato	5-25	Polygonal	Jane *et al.* (1994)
Corn	11.5	Angular	Lopez *et al.* (2010); Singh *et al.* (2003)
Wheat	<10	Spherical, ellipsoidal	Zhang *et al.* (2013)
New cocoyam	15-40	Round, polygonal	Lawal, (2004), Falade and Okafor (2013)
Old cocoyam	3-30	Round, polygonal	Moorthy (1994)
D. cayenensis	10-50	Ellipsoidal, polyhedral	Farhat *et al.* (1999)
D. rotundata	28-47	Oval, round, triangular, polygonal, elongated, irregular	Otegbayo *et al.* (2014)
D. alata	30-45	Oval, truncated spade	Jayakody *et al.* (2007)
D. dumetorum	2.2-3.6	polygonal	Akinoso and Abiodun (2013)
Banana	32-60	Elongated, oval, irregular, round, polygonal	Nimsung *et.al.* (2007)

2.12 Crystallinity of starch granules

Starch chains in native starch granules are usually present in micellar forms which are the basis of their crystalline structure (Sefa-Dedeh and Sackey, 2002). This crystalline nature is attributed to the interaction of well-ordered short chain fraction of amylopectin which are arranged in double helices and packed in small crystallites within the granules with each other and water. The linear amylose molecules on the other hand, are apparently present in amorphous state and distributed between the amylopectin crystals in the starch granules. The radial arrangement of the starch molecule displaying birefringence with the "Maltese cross" can be seen under a polarizing light microscope (Chen, 2003). The packing arrangement of helices give rise to the different crystalline patterns usually observed from different botanical starch sources. These crystalline patterns are as a result of position of different peaks while level of crystallinity is analysed by separating and integrating area under diffraction peaks (Mweta, 2009).

The two main types of crystal arrangement that have been identified are designated as A (found mostly in cereal starches) or B type (found in root and tubers and other high amylose starches) polymorph. A third arrangement designated as C-type is actually a mixture of A and B polymorphs as is found in legume starches (Lawal, 2005). Absolute crystallinity range of 15-45% has been recorded for native starches with type-A starches having values of 33- 44% and B-type having much lower values at 15-28% (Tian *et al*., 1991). Jakayody *et al*. (2007) found percentage crystallinity of 43 % for *Dioscorea alata* while 37% was found for *Dioscorea dumetorum* (Amani *et al*., 2004). The study done by Lawal (2005) found strong diffraction peaks at 15. 9, 17.2, 18.6 and 25.0 for native Xanthosoma sagittifolium starch assigned to the A type polymorph. Hydrothermal modifications (annealing and heat-moisture treatments at 18, 21, 24 and 27%) did not make significant changes to these peaks. The nature and level of crystallinity changes in starch may be investigated and characterized using methods like wide or small angle X-ray diffractometry and solid state Nuclear Magnetic Resonance (NMR) (Lawal, 2005; Amani *et al.,* 2004; Farhat *et al*., 1999; Jakakody *et al*., 2007; Zhou *et al*., 2013).

2.13 Granule birefringence of starches

Birefringence is an intrinsic optical property exhibited usually by crystalline substances including all starch granules in their native form. It is the ability of a substance (starch in this case) to split light into two plane polarizing components (double refraction of light) when the velocity of light in the starch is not equivalent in all directions, resulting in different refractive indices for light polarized in different planes (IFIS, 2005; Hinds Instruments, 2013). This property form patterns that is directly dependent on the crystalline structure through the radial arrangement of amylopectin molecules and their chains to form 90° angles with the reduced ends in the direction of the starch granule center. Starch often experience loss of birefringence due to deformation, disorganization or disordering of crystalline region which can be associated with gelatinization or modification effects (Liu *et al*, 1991, BeMiller and Whistler, 2009).

2.14 Glass transition in starches

This involves a reversible sudden transition of an amorphous polymer from a glassy condition to a flexible condition when it is heated to a specific temperature range (glass transition temperature) (IFIS, 2005). Glass transition occurs due to a change in the arrangement of the starch molecules from a coiled and motionless state to one where they move freely. Value for glass transition temperature varies according to the starch botanical origin and this temperature range is relatively small for each source.

2.15 Gelatinization in starches

This is an important functional property of starch that affects its application in different processes (Mweta, 2009). Raw starch granules are relatively insoluble in aqueous medium at ambient temperatures. Gelatinization is an endothermic reaction involving phase transition in which an aqueous medium acts as a plasticizer (Vamadevan and Bertoft, 2015). This transition phase process involves disruption of the molecular order within starch granules as a result of heating in water occurring over a range of temperature (IFIS, 2005). During this process in which the double helices in the intermolecular hydrogen bonds within the starch granules are unlocked and broken down is affected by a number of factors which include botanical origin of starch, granule size, structure and distribution, presence of minor components like lipids, lipid-amylose complexes, protein and phosphorus (Singh *et al.*, 2010), the starch-water ratio and heating rate (Amenorpe, 2010). Gelatinization temperature is characteristic of a given starch genotype, providing a qualitative measure of its crystalline structure. Some alterations accompanying the gelatinization process include imbibition of water by granules, irreversible swelling of the starch granules, progressive granule collapse, loss of birefringence, leaching of amylose into the surrounding aqueous medium and reduced or disordering crystallinity. The temperature range over which these alterations start to occur is the gelatinization temperature (Mweta, 2009). Prolonged heating of the starch granules eventually lead to total disruption and collapse of the granules. Gelatinization is therefore said to be complete when the crystalline structure of the amylopectin keeping the frame of the granule also breaks down and dissolves (Amenorpe, 2010). Starches from various sources have been known to gelatinize at different temperatures due to differences in degree of associative bonding within the raw starch granules. Since many industrial food systems and processes involving starch as ingredients undergo gelatinization, this process therefore substantially contributes to processing costs in terms of energy requirement. Cooking, textural and digestive properties of food products containing starch may also be significantly affected by gelatinization (Sichina, 2000). The thermal properties of starch-water formulations may be characterized instrumentally using the Differential Scanning Calorimetry method (DSC). The onset (T_o), peak (T_p) and conclusion (T_c) temperatures as well as the enthalpy change accompanying gelatinization (ΔH) may be monitored while detecting the critical transitions involved. The results obtained from DSC analysis may be useful in the development of resistant starches (RS) in processed foods as a source of possible nutritionally significant dietary fibre (Gruchala and Pomeranz, 1993).

2.16 Swelling and solubility of starches

Swelling and solubility are properties of starches that provide evidence of the non-covalent bonds existing within their molecules (Mweta, 2009) and may therefore allow for comparism of the relative bond strength at specific temperatures (Moorthy, 2002). These phenomena reflect the gelatinization behavior of starch granules (Zhu, 2015) causing a weakening in granule cohesion, irreversible increase in volume, swelling, increase in paste viscosity (Grysztin *et al*., 2014), leaching and solubilization of some components into solution. Swelling and solubility may be determined by heating a mixture of starch in excess water in a test tube at temperatures of 50-90^{o}C for about 30 minutes with intermittent shaking. The mixture is then cooled and centrifuged to separate supernatant. The swollen starch weight is recorded as a relative function of the initial starch weight. Several factors may affect the swelling and solubility patterns of starch (Ratnayake *et al.*, 2002). Chemical composition of starch including amylose-amylopectin contents, lipids and phosphate contents, granule size, temperature, starch concentration and environmental factors influence these parameters. The relative proportions of amylose and amylopectin determine interactions of the starch polymeric chains within the amorphous and crystalline granules (Zhang *et al*, 2005). Amylose has been found to act as diluent and inhibitor to swelling (Singh *et al*, 2003). A wide range of swelling and solubility values have been reported among starches from various origins (Lawal, 2004; Amani *et al,* 2004; Singh *et al*, 2003; Mweta, 2009; Zhu, 2015). The starch from yam appears to have lower swelling power (Otegbayo *et al*, 2014) than the one from potatoes (Iheagwara, 2013) with swelling power generally increasing with increasing temperature (Gebre-Mariam and Schmidt, 1998, Adebowale and Lawal, 2002).

Modification method also affects swelling and solubility patterns of starches (Simsek *et al.*, 2012). Oxidation and acid thinning were found to markedly decrease swelling of new cocoyam (*Xanthosoma sagitifollium*) starch at all temperatures between 55-95^{o}C while acetylation gave the opposite result, reducing swelling and increasing solubilities (Lawal, 2004). This trend has been attributed to the hydrolysis of glycosidic linkage by the hydroxonium ion (H_3O^+) and its preferential attack on the amorphous rather than the crystalline region of the granules. This results in an increased relative crystallinity and a restriction to swelling by the stiff amylopectin network of the crystalline region. High swelling starches may find utilization in industrial food applications that require improved viscosity as thickeners and binders or in pharmaceutical formulations for tablets and capsules as disintegrants (Okunlola and Odeku, 2009). High swelling power may however be undesirable for starch in products like complementary foods where thick gruel constitute a negative quality attribute (Otegbayo *et al*, 2014).

2.17 Rheological properties of starches

Rheology involves the study of behavior of visco-elastic materials with intermediate properties between ideal solids and ideal liquids. In food systems, it is the study of relation between forces exerted on a food material and the resulting deformation per time (IFIS, 2005). Rheology therefore provides scientific basis for subjective measurements like mouthfeel, spreadability and pourability. Rheological properties relates to concepts such as elasticity, viscosity, shear, thixotropy, stretch and rigidity. Starch generally exhibit distinct viscosity behaviors with changes in temperature, concentration and shear rate (Nurul *et al.*, 1999).

2.17.1 The flow and dynamic oscillatory analysis of starch

Starch suspensions have been analysed using dynamic rheometer which assesses the dynamic moduli during time dependent temperature and frequency sweep testing (Moorthy *et al.*, 2008; N'da Kouame *et al.*, 2011). Parameters measured include the storage dynamic modulus (G′), which is the energy stored in materials and recovered per cycle and loss modulus (G″) which is energy dissipated or lost per cycle of sinusoidal deformation (Alcazar-Alay and Meireles, 2015). The ratio G″/G′ is a parameter indicating physical behavior of systems and is designated as Tan δ. High values of G″/G′ (>1) indicate liquid-like behavior while low values indicate solid-like (<1) behavior (BeMiller and Whistler, 2009). Flow analysis involves measuring the viscosity changes accompanying various shear stress ranges that a starch gel undergoes.

2.17.2 Gel resistance in starch pastes

This is determined using a texture analyser, in which the parameter peak force [N] defines the resistance of the three-dimensional network of starch paste (Ulbrich *et al.,* 2015). Texture profile analysis of cowpea starch gel showed exceptionally higher values for hardness, gumminess, chewiness and initial modulus than corn and potato starch gels (Won *et al.,* 2000). Resistant starch has been shown to facilitate the formation of rigid network structure and also increase dietary fibre content of non-waxy rice starch (Yu and Shin, 2015). Other factors that may affect the dynamic viscoelasticity and formation of a closely-packed gel structure which possess high shear resistance in gelatinized starch granules include amylose contents and chain length distribution (Lu *et al.,* 2009).

2.17.3 Pasting characteristics of starches

The pasting property of starch is an important factor in the functionality and end product quality of starch products. It involves heating and cooling of starch–water mixture under constant mechanical shearing forces through a temperature range of 50-95^{o}C (Alcazar-Alay and Meireles, 20215). This is done on a programmed cycle while viscosity development during the heating and cooling process is measured instrumentally using a Rapid visco-analyser (RVA) or Brabender viscoamylograph. It is the phenomenon following gelatinization in starch dissolution and is the increase in viscosity associated with other changes that accompany heating aqueous starch suspension above a critical temperature. It involves swelling of starch granules, exudation of molecular amylose components and disruption of the granules, making them susceptible to thermal or mechanical breakdown (Zhu, 2015). The RVA is a rotational viscometer that has variable heating, cooling and shears capabilities. The potential relationship between structural features of starch molecules and their effects on starch functional properties is reflected by their unique pasting profiles. Values of the pasting parameters depend to a large extent on the amount of water and heat in the system, interactions among other starch components and starch granule size. Pasting determines properties of foods like viscosity, texture and moisture retention. Paste viscosity is therefore a significantly important factor in the potential industrial application of starch (Gryszkin *et al.,* 2014). Parameters determined from the pasting curve of a Rapid Visco Analyser (RVA) include peak viscosity, setback, trough, breakdown and final viscosities, pasting temperature and time to reach peak viscosity as recorded on the programmed cycle. A time- temperature regime is used to monitor viscosity development of starch-water mixture being heated under mechanical shear stress condition. An idle temperature of 50 ^{o}C for 1 minute is observed, the mixture is then heated from 50 ^{o}C to 95 ^{o}C in 3 minutes, 45 seconds, then held at 95 ^{o}C for 2 minutes 30 seconds after which subsequently cooled to 50 ^{o}C over a 3 minutes 45 seconds period, followed by a period of 2 minutes where the temperature is controlled at 50 ^{o}C (Alcazar-Alay and Meireles, 2015). The pasting temperature is the minimum temperature requirement for cooking a given starch sample and is significantly important in terms of energy costs for industrial processes. Peak viscosity gives an indication of the ability of a starch sample to slowly and progressively swell on heating to form a paste. It occurs at the equilibrium between granule swelling and granule rupture/disruption. While granule swelling increases viscosity of starch paste, granule rupture and disruption reduces swelling. During the period of holding starch mixture at high temperature (95^{o}C for 2.5 minutes) and subjecting it to high shear stress of rapid constant and continuous mixing, a breakdown in viscosity or shear thinning may occur; called the trough (Higley *et al.*, 2003). The ability of the starch mixture to remain undisrupted during this period is called the holding strength. This ability is also significantly important in industrial processing of starch. When cooked starch is cooled, gel formation occur leading to re-association between molecules of the amylases. As a result of the kinetic effect of this cooling, there is increase in viscosity of the starch mixture. This final viscosity is important in predicting and determining the final textural and sensory quality of starch based products. In a local food, pounded yam, the final viscosity is an invaluable property for determining its hardness and elasticity (Otegbayo, 2004). Consequently, the re-association or re-ordering of starch molecules after cooling (to 50 ^{o}C) results in a tendency of the starch to retrograde or setback. A more cohesive paste has been associated with high setback value and may find application in a domestic product like pounded yam where high setback, viscosity and high paste stability is required at low temperatures (Otegbayo *et al*., 2014). Ezekiel *et al.*

(2010) found pasting time and temperature to increase after storage of potato tubers but peak viscosity was lowered.

2.18 Retrogradation of starch

Retrogradation is a major functional property of starch that greatly affects quality, nutritional and sensory value of starchy foods (Wang *et al*., 2015). It is a process which occurs when disaggregated amylose and amylopectin chains in a gelatinized (disordered) starch paste re-associates to form a more ordered structure and under optimal conditions, may recrystallize (IFIS, 2005). It is also a molecular interaction produced after gelatinization and cooling of cooked starch. It may produce significant changes in the mechanical properties of starch products which consequently affects sensory appreciation. This process may be a detrimental or desirable quality in many starchy food products. For sensory/consumer acceptance, product reliability and storage quality, retrogradation has been implicated for example in the staling of bread, syneresis of gel and hardness but for some textural, nutritional and digestibility properties, retrogradation has been found desirable as resistant starch source (Park *et al.,* 2009).

Many methods have used to characterize starch retrogradation during storage and to investigate the changes that occur. Methods of monitoring retrogradation may be thermal using differential scanning Calorimetry (DSC) or differential thermal analysis (DTA) (Wang and Copeland, 2013) or may be spectroscopic using Fourier-Transform Infra-red spectroscopy FTIR (Flores-Morales *et al*., 2012; Lian *et al.*, 2013). Rheological tests mainly by RVA (Chen *et al*., 2015) monitor the physical changes like viscosity that occur in a product or gel as a result of retrogradation. Mechanical testing or instrumental texture analysis have also been employed in retrogradation measurements (Wang *et al.,* 2015).

Molecular techniques that study shifts in crystallinity, wide or small angle X-ray diffraction methods have also been employed. Tang and Copeland (2007) studied the microscopic imaging of the surface morphology of starch granules and retrograded starch using scanning electron microscope while physical methods like syneresis have also been used to monitor rate and extent of starch retrogradation (Wang *et al*., 2007). These methods are diverse because the process of starch retrogradation is a complex one that involves series of molecular and physical transformations. Factors influencing starch retrogradation are diverse. They include water content of products, storage temperature and time, presence of additives in the system that alters the rate and extent of retrogradation by competing with starch for water or by interfering with re-association of starch chains or other components of the food product. Starch retrogradation may then be controlled by the use of additives that change water activity in starch-water systems (Wang *et al.,* 2015). Some of these additives may be salts, lipids, proteins or other carbohydrates since starch is usually in combination with other polymeric ingredients to form different phases in the food processing industry. Protein interaction with starch was observed to cause emulsification effects (Alcazar-Alay and Meireles, 2015).

2.19 Syneresis/Freeze-thaw stability of starches

When a gel is allowed to stand, contraction of the gel, and the resulting exudation of liquid from it is called syneresis (IFIS, 2005). Starch gel syneresis is a parameter that represents the volume of water separated from formed gel under storage at varying conditions: room temperature, refrigeration or freezing conditions (Doue *et al.,* 2014). This phenomenon depends on a combination of specific and non-specific interactions: amylose and amylopectin components of a starch matrix, concentration of starch, thermal history, number of freeze-thaw cycles and centrifugation conditions through which the starch had gone through (Zhu, 2015). Syneresis therefore shows the stability of starch paste with temperature variation particularly during storage (Doue *et al*., 2014). Cassava starch paste had been reported to exhibit higher freeze-thaw stability than cocoyam starch paste with percentage water loss increasing with increasing number of days of freeze-thaw cycle until maximum exudate was achieved (Nwokocha *et al.,* 2009; Mweta, 2009). This showed that phase separation increased with increasing number of cycles. Lower freeze-thaw stability has been associated with higher retrogradation tendencies (Ciacco and D’Appolonia, 1977) and higher amylose contents since amylose is considered to be primarily responsible for the short-term retrogradation process through parallel re-alignment of dissolved amylose molecules (Chen, 2003). Control of syneresis is a key factor for optimizing many industrial food processes like increasing curd yield, improving cheese quality and also for predicting yoghurt storage quality.

2.20 Water and oil absorption capacities of starches

Starches often possess hydrophilic and lipophilic tendencies or capacity to imbibe water/oil as an important functional property. Water/oil absorption capacity is the ability of starch to associate with water/oil under conditions where such solvent is limited (Singh and Singh, 2001). It is calculated as the ratio of water/oil absorbed by starch to mass of the dry starch. This property is temperature dependent (Mweta, 2009) and varies with botanical origin, amylose/amylopectin ration of a given starch, presence of other hydrophilic or hydrophobic substances in the starch, granule particle size and shape and chain length distribution. It is also influenced by the extent of hydrogen and covalent bond association within the granules. These inter-granular binding forces are usually weakened by increase in temperature (Lawal and Adebowale, 2005). Larger starch granule sizes have been associated with high water absorption capacity (Mweta, 2009) while an inverse relation has been observed with amylose contents (Akalu *et al.,* 1998). Oil and water absorption capacities are important in enhancing food sensory properties (flavor encapsulation and retention, mouth-feel, palatability, consistency), enzymatic activity and in extending product shelf-life (Lawal and Adebowale, 2004) as in dough preparation. Oil absorption capacity reflects the emulsifying capability of a starch product formulation. Protein has been identified as the major chemical component affecting the oil absorption capacity of rice starch (Falade and Christopher, 2015). These hydrophilic or lipophilic behaviors are usually affected when functional groups are introduced into starch structure through modification.

2.21 Gelation of starch

This is a process of gel formation by coagulation of sols or aggregation of particles. A gel may be formed in a variety of ways according to the type of material involved. In the case of a polymer molecule like starch, gelation is caused by formation of network of intermolecular crosslinking and re-association of amylose molecules to one another and to the branched amylopectin molecules in the collapsed granule during heating or cooling (Otegbayo *et al.,* 2014). Aggregation of particles may be induced by a variety of stimuli including changes in pH or ionic strength. The phenomenon is also called gelling. A starch with high gelation capacity will have a low least gelation concentration, which is determined as the concentration at which gelled starch in an inverted tube start to slip or fall (Lawal, 2004). High gelling starches are often used in processes that require high thickening power and improved binding (Pharmaceuticals, paper, adhesive industries) while low gelling starches may be useful in processes that require low dietary bulk, reduced viscosity and elasticity like complimentary or weaning foods. Waxy starches (very low in amylose contents) have been found to produce weak gels.

2.22 Paste clarity/ light transmittance of gelatinized starch

Light transmittance, paste clarity, turbidity or opacity is a term used to describe the visual characterization of refraction and reflection of light through an aqueous starch paste. It is an important functional property that varies with starch source. Gelatinization makes starch granules to swell as molecules dissociate causing light to be able to pass through (transmission) without being reflected. This transmitted light is refracted in an inverse order with the degree of swelling (Craig *et al.,* 1989). Granular remnant or impurities in the swollen starch can also cause an inhomogeneous refraction effect leading to reduced level of transmittance by absorption and reflection (Craig *et al.,* 1989). Factors contributing to starch paste clarity include amylose/amylopectin concentrations, presence of impurities, starch granular morphology, wavelength of transmission, presence of additives (salts, lipids, sugar etc.), the nature of solvent, storage days, retrogradation and modification (Tetchi *et al.,* 2007a). The effects of these factors have been reported elsewhere (Lawal, 2004; Nwokocha *et al.,* 2009 and Ciacco and D'Appolonia, 1977). The realignment of leached amylose in retrograded starch results in reduced clarity as observed by Nwokocha *et al*. (2009). Clarity of starch has much relevance in food and textile applications. In bakery and confectionery products, fruit pie fillings are required to be transparent while salad dressings are preferred opaque (Craig *et al.,* 1989). These effects are derived from the nature of associative bonds within the molecular chains in the granules, the resultant granular integrity and optical homogeneity after starch pasting (Craig *et al*., 1989).

2.23 Fourier Transformed Infra-Red Spectroscopy (FT-IR) of starches

This is a mathematical technique that is used to evaluate structural differences in materials from the typical spectrum or interferogram it gives after Fourier transformation (Aboubakar *et al.,* 2008). An interferogram is the frequency range obtained from samples of materials after polychromatic irradiations. The system measure the range of wavelength in the infra-red region that are absorbed or emitted by a solid, liquid or gaseous material (Van Soest *et al*., 1995). Functional groups in materials may then be identified by the corresponding wavelength values and intensity of the peaks with the FT-IR standards.

In starch analysis, this spectroscopic procedure provides four distinct regions that describe the mid-infra-red spectrum of the range 4000cm^{-1} to 400cm^{-1}. The crystalline properties of starch have been described by the bands found at 1047cm^{-1} while bands at 1022cm^{-1} describe amorphous properties. The ratio of these two bands strongly indicates the degree of starch order (Van Soest *et al.,* 1995). The region where a group frequency occurs determines its nature and consequent characteristics. The alkane stretching (O-H, C-H and N-H) has been found to occur at the 4000-2500cm^{-1} region, the triple bond stretching at 2500-2000cm^{-1}, double bonds or carbonyl stretching (C=C or C=O) at 2000-1500cm^{-1} and the fingerprint region at 1500-600cm^{-1}. Fourier transformed Infra-red spectroscopy is applied in industrial food and pharmaceutical processes where high degree of purity is required. It has also found applicability in traceability, polymer analysis, ascertaining purity, product safety and quality assessment and control. Sacithraa *et al.* (2013) evaluated the potential of FT-IR in identifying starches in industrial environment. It can therefore be employed to provide a molecular fingerprinting of particular samples and also to monitor retrogradation in starch products (Van Soest *et al*., 1994; Goodfellow and Wilson, 1990). FTIR has been used to detect starch adulteration in onion powder separately and in combination with Near-Infrared spectroscopy (Lohumi *et al.,* 2014).

2.24 Colour properties of starch

Colour is a visual attribute of materials that reflect, emit or transmit light (Nemtanu, 2008). Colour perception occurs as interplay of light source, object and observer in three dimensions. Polyphenolic compounds, pigmentations and impurities in starch may be carried over into final products, impacting on the commercial acceptability and quality of such products (Gani *et al*., 2010). These colours are imparted because of non-enzymatic browning that occur due to interactions of sugars and protein with increased temperature or diffusion of pigments during preliminary processing (Falade and Christopher, 2015). The CIE tristimulus L*, a* and b*color scale is a standard approximate uniform scale by which colour values can be measured and compared (Hunter lab manual, 2001). The CIE LCH is a mathematically derived polar representation of the CIE L*, a*and b*rectangular coordinate system that describes colour of materials in terms of lightness, chroma and hue (Nemtanu, 2008). In a 3-dimensional perspective, L* values varies from 0 to 100 indicating lightness range from black to white, a* values range from red to green with positive a* as red, negative a* green and 0 the neutral point. Yellowness is indicated by positive b*, blue is the negative b* and 0 the neutral point. Chroma or saturation measures how dull or vivid an object colour is while hue (0-360^{o}) is characteristic of the dominant colour. Falade and Olugbuyi (2010) found the system to provide an objective means of evaluating the color characteristics of plantain pulp and powders as it is affected by drying methods and stage of maturity. Total color difference (ΔE*) between a test sample and a reference standard sample may be a measure of commercial acceptability of products and has been found useful in quality control and adjustment of formulation. It is therefore a vital component of visual quality and a guide to determining the suitability of starch for processing (Brennan, 2006). It may be used as a single number for taking a pass or fail decision in quality control and for accepting or rejecting a batch of sample. Falade and Ayetigbo (2015) reported increased CIE L* and b* and reduced CIE a* values for peeled cultivars of *Dioscorea spp* over the unpeeled cultivars. Native starch of *Dioscorea dumetorum* was also reported to possess higher CIE L* than the starches from *D. cayenensis, D. rotundata* and *D. alata.* In another study, high browning discolouration was associated with high CIE b* and high colour intensity in plantain cultivars and cooking banana flours (Falade and Oyeyinka, 2015).

2.25 Bulk density of starches

The bulk density of a powdered product relates to the spatial arrangement of particles in the powder bed, the intermolecular void volume and density of the powder (WHO, 2012). These properties are measures of relative density used in quality control, transportation, preparation, handling processing (in mixing sorting, packaging operations), storage and analyses of starch. Ashogbon (2014) associated bulk density with degree of coarsiveness of starch. Bulk density is determined as weight per overall unit volume of a loose material (powders, soil). It is used particularly for porous substances where density is affected by pore volume, particle geometry, and surface properties and can be increased by presence of pore fluid (IFIS, 2005). Bulk density of a material can be altered by mechanically tapping containers of a particulate material to interfere with flow and its ability to settle. Compressibility index ((loose volume-packed volume)/loose volume)*100), Porosity and Hausner ratio (loose volume-packed volume) may be used to evaluate bulking or packing of starch products (WHO, 2012).

2.26 Dispersibility of starches

The measure of the degree of reconstitution in a liquid medium or rehydration capacity of a starch material or its ability to form dispersions (a substance being suspended in another substance) is its dispersibility (Ashogbon, 2014). Falade and Olugbuyi (2010) found reconstitution to be a function of time and reported it to be affected by presence of additives, drying method and stage of maturity.

2.27 Wettability of starches

This is a physical property relating to the ability of a solid to absorb a liquid as it spreads over the surface of the solid. It provides information on surface interactive forces of a material and indicates the speed of affinity for a liquid medium (lipophilic or hydrophilic). Its importance in food polymer processing like starch have been elucidated by Bialopiotrowicz (2003) where attempt was made to relate starch content with contact angle. Mucoadhesive properties induced by processing (gelatinization, drying, mixing operations) form a gel barrier against water and other solvent uptake, thereby affecting permeability and solubility (Bialopiotrowicz, 2003). Interfacial properties of starch materials may be affected by temperature of processing and modification (Wiacek, 2015). The application of starch in new food product development, starch coatings, pharmaceutical formulations, packaging material development, paper and textile industries depends on its hydrophilic/hydrophobic character which is determined by its polarity (Wiacek, 2015). This offers functional variability to many food products (Abbas *et al*., 2010).

2.28 Limitations of native starches

Due to the wide range of demanding processing conditions that starch and starch products undergo in industrial preparations, many native starches have been found to be limited in functional attributes and unable to withstand these processing conditions. They are mostly unstable with changes in temperature, pH and shear forces, have strong tendency for decomposition and retrogradation while others have their starch granules inert, insoluble in water at room temperature and highly resistant to enzymatic hydrolysis (Alcazar-Alay and Meireles, 2015). Low shear resistance, thermal resistance, thermal decomposition and high tendency towards retrogradation limit the use of native starches in many industrial food applications (Berski *et al.*, 2011; Singh *et al.*, 2007). Starches generally have their inherent properties altered when heated in aqueous medium. Many structure-function characteristics of native starches have been found to be process intolerant as gelatinisation, pasting and retrogradation strongly depend on the changes that accompany the heating process (Eliasson, 2004). The characteristic properties contributed by starches to the food product in which they are contained are also determined by these changes. Starches are therefore modified to alter these physicochemical properties to improve upon the limitations of native starch while enhancing its versatility to satisfy consumer demands (Kavlani *et al*., 2012) and create an expanded range of functionality for food and non-food applications.

This makes native starches more suitable for a variety of different applications. Properties of native starches solely depend on their botanical source. Starches from various botanical origins have been modified by different methods to achieve different outcomes. Results of such modification are well documented (Perez *et al.*, 2012; Odeku *et al.*, 2008; Odeku *et al.*, 2009a; Odeku *et al.*, 2009b, Okunlola and Akingbala, 2013, Zhang *et al.*, 2012; Jayakody *et al.*, 2009; Lawal, 2005; Lawal, 2004; Jiang *et al.*, 2014; Huang *et al.*, 2006). Ultrasound modified maize starch produced films with better transparency, improved moisture resistance and stronger structure compared to the native starch (Shah *et al.,* 2016) while annealing resulted in a significant reduction in CIE L* and b* colour values for *Dioscorea spp.* starches (Falade and Ayetigbo, 2015). Eating quality of deep-fried food products have been improved by oxidizing native starches and retrogradation tendency of native starches have been reduced by oxidation and acid hydrolysis (Zavareze *et al.,* 2012; Atichokudomchai *et al.,* 2004).

2.29 Starch Modification

Starch has been modified from the native form to enhance its positive attributes or develop specific properties such as solubility, texture, adhesion and tolerance to heating temperatures for specific applications in industrial processes (Alcazar-Alay and Meireles, 2015). This aids to provide desirable functional attributes and offer economic alternative to other hydrocolloid ingredients like gums and mucilage which are often unreliable in quality and availability (Tharanathan, 2005).

2.29.1 Physical modification of starches

Increased awareness about need for renewable and environmentally friendly resources has necessitated the use of physically modified starch sources (Huang *et al.*, 2006). This is a type of modification that does not involve the use of any chemical or biological agent and does not result in gelatinization of the starch, damage to granular integrity, or loss of birefringence (Abbas *et al.,* 2010). It is the preferred method of modification when starch is meant for human consumption. It is considered to be relatively simple, cheap and safe (Lawal, 2005). Physical modification may involve the utilization of different combinations of temperature, moisture, pressure, shear and/or irradiation to achieve the required effects. These effects have been the subject of extensive investigations. The granular structure of the resulting starch is changed to produce a starch with smaller crystallites and improved solubility. Methods of physically modifying starch include pregelatinization, hydrothermal methods (annealing and heat-moisture treatments), a variety of non-thermal methods (glow discharge plasma method, microwave treatments, ultrasonic methods, ultra-high pressure methods, electric pulse, grinding, extrusion, retrogradation methods, osmotic pressure treatments, freezing and thermal inhibition treatments). These methods have been studied and reported to give different effects on functional, morphological, rheological and physicochemical properties of the native starches (Lawal, 2005; Adebowale *et al.*, 2009; Omojola, 2013; Chung *et al.*, 2010; Hoover and Vasanthan, 1994; Eerlingen and Delcour, 1995; Biliaderis *et al.*, 1999; Buckow *et al.*, 2007; Lim *et al.*, 2002).

2.29.1.1 Heat moisture treatments (HMT) of starches

This is a mode of treatment where starch is subjected to temperatures above the glass transition and gelatinization temperature(100^{o}C) with the moisture content adjusted to <30% and for extended period of time (>16hours) (Hoover and Vasanthan, 1994; Lawal, 2005). The observed effects of HMT are directly dependent on starch botanical origin, and treatments conditions (pH, moisture content, temperature, duration). In previous works, the effects of heat-moisture treatment of starch from different sources are well documented. Adebowale *et al.* (2009) studied the properties of native African yam bean starch and compared observations after heat-moisture and annealing treatments. They reported a reduction in swelling capacities and solubility with increasing level of heat-moisture treatments. Water absorption capacity was found to increase while oil absorption capacity decreased with a reduced tendency for retrogradation. Similar observations were reported by Olayinka *et al.* (2008) where heat moisture treatments also enhanced the gel formation and strength of white sorghum starch and by the works of Feroz and Abid (2009) in which modified taro starch had reduced swelling and solubility as a function of pH. This is a desirable characteristic in products where starch is utilized as thickener (sauces, soups and gravies) and in instant pudding, pie filling, soups and cake frostings where rapid solubilization of pre-gelatinized starch is important (Feroz and Abid, 2009). These observations were also corroborated by the reports of Lawal (2005) which concluded that heat-moisture treatments of new cocoyam markedly reduced swelling capacity, solubility, tendency for setback and oil absorption capacity but increased its water absorption capacity and light transmittance as storage days increased. Possible explanation for this phenomena may be the re-arrangement in the crystalline and amorphous order of the starch granules which occurs with the heat-moisture treatment and intermolecular interactions between the starch chains as is confirmed by the increased crystallinity (in the order

Native<HMT<Annealed) reported by Adebowale *et al.* (2009). Increased solubility and thermal stability with a reduction in starch paste clarity and swelling capacity have been reported for starches from heat-moisture treated cassava, arrowroot and sweet potato (Jyothi *et al.,* 2010). Similar effect on paste properties of rice starch and flour was reported by Puncha-Arnon and Uttapap (2013) for 70, 75 and 80% (w/v) starches treated 100^{o}C for 16 hours while Hoover (2010) showed that a change in crystalline structure and paste properties accompany HMT. At pH 5.6 and 6.5, potato starch adjusted to 20, 25 and 30% moisture content and heated at 120^{o}C for 3 hours showed decreased swelling capacity and amylose leaching (Kim and Huber, 2013).

2.29.1.2 Annealing of starches

Annealing is the treatment of starch granules in excess aqueous medium (<65%) or at intermediate water content (40-50% w/w) at temperatures below gelatinization but above the glass transition temperature (Adebowale *et al.*, 2005b). The objective of this treatment is to improve the molecular mobility of starch without triggering gelatinization (Alcazay-Alay and Meireles, 2015). Morphological characteristics have been shown to influence response to annealing by starch from different source elucidating the effect of genotype on annealing of starch (Jayakody *et al.*, 2009). Reductions in granule swelling and susceptibility to acid hydrolysis have been reported after annealing treatments of *Dioscorea alata* starch (Jayakody *et al.*, 2009). Although Jayakody and Hoover (2008) reported a dearth of information on effect of annealing on granule morphology especially of root and tuber starches, Falade and Ayetigbo (2015) reported reduced granule density and swelling powers for 33% (w/v) yam starch suspension after annealing at 50^{o}C for 24 hours. 40% (w/v) polylactic acid-commercial corn starch mixture was observed to cause an increase in the crystallinity associated with process temperature, thermal stability and mechanical properties after suspension was annealed at 50, 60, 80, 100 and 120^{o}C (Lv *et al.*, 2015). Polylactic acid has been used as a key component of many bio-degradable nanoparticles, possessing excellent encapsulation properties and as a delivery system for bioactive compounds (Weiss *et al.*, 2006).

Earlier, intermolecular interactions have been advanced as the possible reason for reduction of gelatinization temperature range observed after annealing in some starches as observed by differential scanning calorimetry parameters (Chiu and Solarek, 2009). However, it has been concluded that the arrangement and packing of double helix and crystals by the cluster and building block structure of amylopectin were facilitated by annealing treatments resulting in a more highly ordered structure (Vamadevan *et al.*, 2013). Yadav *et al.* (2013) reported a reduction in swelling capacity, solubility and viscosity of water chestnut starch.

2.29.1.3 Freezing in starch modification

Freezing may be referred to as a physical method of starch modification because reversible structure disorder occurs at freezing temperatures. It has been reported as an effective way of modifying potato starch by freezing water inside or outside the starch granules (Kavlani *et al.*, 2012). Freezing is often applied in food preservation, drying and lyophilization of starchy foods (Kavlani *et al.*, 2012) and as sample preparation procedure in granule morphology investigation by scanning electron microscopy or thermal electron microscopy. The effect of freezing on starch gel and its textural characteristics are well documented. Freezing hastens retrogradation in starch sols investigated but contrary observations were noted in pre-gelatinized starch where tendency to retrograde was reduced after freezing (Tomasik and Zaranyika, 1995). Freezing has also been reported to cause some changes in nutritional properties and digestibility of de-branched rice starch (Guraya *et al.*, 2001).

2.29.1.4 Ultra high pressure/steam treatment of starches

Starch granules may be non-thermally gelatinized by treating with ultra-high pressures over a critical pressure levels. This induces restricted amylose leaching on the starch while maintaining its granular structure (Katopo *et al.*, 2002). A reversible hydrolysis of the granule amorphous region then occurs and the crystalline order is disrupted causing an increase in hydrophilic tendencies of the crystalline region and resultant granule swelling. Crystalline structure of UHP treated starch granules have been observed to transit from A-patttern to B-type pattern (Hibi *et al.*, 1993). Steam pressure treatment of *Dioscorea spp* has also been found to reduce soluble amylose content, viscosity, swelling, paste stability and clarity (Moorthy, 1999).

2.29.1.5 Thermal Inhibition treatment of starches

When starch is dehydrated at temperatures above 100^{o}C for a period of time, the starch becomes inhibited and anhydrous with moisture contents less than 1%. The paste so produced possesses increased resistance to viscosity breakdown and have a cohesive texture (Chiu *et al.*, 1998). Lim *et al.* (2002) used ionic gums (Xanthan, CMC, sodium alginates) as crosslinking agents to form a graft co-polymer with the starch by formation of ester.

2.29.1.6 Osmotic pressure treatments of starches

Treatment of starch-water mixture with a high salt solution has been shown to induce osmosis in which a homogenous starch suspension with uniform heat distribution is obtained (Pukkahuta *et al.*, 2007). Gelatinization temperature was noted to significantly increase while crystalline patterns changed from B to A in potato starch after OP treatments. On economics of scale, large scale production of modified starch using this method has been shown to be possible compared to hydrothermal treatments of starch (Pukkahuta *et al.*, 2007). Similar methods have been applied in the production of nano-emulsions (Lin *et al.*, 2011).

2.29.1.7 Glow discharge Plasma treatment of starches

Glow discharge plasma treatments have been extensively used in material modifications (Coburn, 1991). It is a physical method of starch modification accompanied by little or no thermal degradation and no environmental concerns (Zou *et al.*, 2003). High energy electrons and highly active species are induced at ambient temperatures to cause excitation of starch functional groups. This results in a crosslinked product similar to the chemically modified crosslinked starch (Zou *et al.*, 2003).

2.29.1.8 Gelatinization and other methods of physical modification of starches (Extrusion, spray, roll, grinding, cryomilling)

Many other methods have been used to achieve gelatinization of starch granules. Cryomilling in a liquid nitrogen bath (63-77.2 K) at different time frame had been used to physically modify rice starch. The structure and properties of the modified starch were evaluated. It resulted in a loss of crystallinity that reduced starch pasting temperature, increased its water absorption capacity, and by fragmentation of starch (probably the amylopectin fraction) that reduced all viscosity parameters significantly while increasing its solubility (Devi *et al.*, 2009). Spray drying has been used to modify starches with excellent properties (Chiu and Solarek, 2009). Alves and others (1999) reported that extrusion gave a pre-gelatinized starch with range of properties including gel-forming capacity, cold water viscosity, and retrogradation when extrusion conditions were altered. Gelatinization generally leads to a re-arrangement of intra and inter-molecular hydrogen bonding between water and starch molecules to achieve a disruption of the molecular order within the granules. These changes are evidenced by an irreversible granule swelling, loss of birefringence, amylose leaching and loss of organized granule structure (Kavlani *et al.*, 2012).

2.29.1.9 Blended/composite starches

A range of properties of starch can be created by blending starches from different botanical origin. Textural, thermal, and morphological properties of starch blends of yam (*Dioscorea alata*), corn and cassava were studied. Blending of these starches at a certain ratio reduced the exudate in yam and corn starch gels, and cohesiveness of cassava starch gel (Karam *et al.*, 2005, 2006).

2.29.2 Chemical modification of starches

Starches used in industrial food and non-food applications are mainly modified using chemicals. This is for the development or enhancement of various required properties for specific applications through the introduction of functional groups within the starch molecules (Kavlani *et al.*, 2012). Reasons for chemical modification may include increased paste clarity, reduced retrogradation tendencies, syneresis or cold storage stability (freeze-thaw stability) and improved paste consistency (Singh *et al.*, 2007). Properties imparted in chemically modified starches are dependent on factors such as botanical origin of starch, presence of catalyst, reactant/reagent type and concentration, pH, reaction time, type and extent of substitution, size and structure of starch granules (Singh, 2008). The scope of application of starch in food and non-food industrial processes is widened by chemical modification.

2.29.2.1 Acid thinning/hydrolysis of starches

Acid hydrolysis is an important chemical modification method that can significantly change the structural and functional properties of starch without disrupting its granular morphology by decomposition (Wang and Copeland, 2015). It has been used to produce a range of different functional and physicochemical characteristics in starch. It is extensively used in the industrial preparation of glucose syrup from starch (Dufresne *et al*, 2014) and in production of extruded cereals and snacks (Kramer, 2009). The starch is usually hydrolyzed by treating with a mineral acid at temperatures below gelatinization. Time of treatment depend on desired viscosity and extent of hydrolysis. Hydroxonium ion attacks the glycosidic oxygen atom and hydrolyses the glycosidic linkage (Olu-Owolabi *et al.*, 2014). An acid acts on the surface of the starch granule first before it gradually enters the inner region to change the physicochemical properties of starch (Kavlani *et al.*, 2012). Acid thinning has been used to produce *Dioscorea opposita* starch with increased solubility, increased degree of crystallinity and reduced particle size. The reaction also changed polymorph of starch from the C pattern to A type (Yu *et al.*, 2009). This report was confirmed by the observations of Jiang *et.al.* (2011) where acid hydrolysis in alcohol (ethanol) solvent produced starch with changed polymorph from C to A, reduced granule size and also gave a high (>92%) starch yield than in the aqueous environment. Acid thinning of yam starch in alkaline environment and its effect on starch properties has been described (Jiang *et al.*, 2014). Different types of acid (HCl, HNO_3, H_2SO_4 and H_3PO_4) have been used to modify starch from different sources. The degradation and properties of starch obtained varied significantly as reported by Singh and Ali (2000).

2.29.2.2 Oxidation of starches

This is a method of starch modification by decomposition or de-polymerization to produce a range of structure and properties. It involves the reaction of starch with oxidizing agents like Sodium hypochlorite, Sodium periodate or ozone at specified concentration, temperature, pH and reaction duration. Ozone oxidation of *D. cayanensis* and *D.rotundata* starches introduced carbonyl and carboxyl groups (which has been reported to retards re-crystallization (Rutenberg and Solarek, 1984)) to produce starch with increased water solubility, amylose contents, cold paste viscosity and weight average molecular weight. The same treatment caused a reduction in gel strength, setback and number average molecular weight (Oladebeye *et al.*, 2013). 35% (w/w) sorghum starch suspension was oxidized with sodium hypochlorite using sodium hydroxide as catalyst at alkaline pH for 10 minutes. It produced decreased swelling capacity and viscosity of the paste obtained (Ali and Hasnain, 2014). The work of Jiang *et al.* (2011) has provided evidence that oxidation of *D.opposita* with sodium periodate produced a dialdehyde starch with reduced molecular weight, thermal stability and degree of crystallinity. Improvement in baking properties of oxidized sago starch as compared with the native samples has been reported (Tethool *et al.*, 2012).

2.29.2.3 Cross-linking of starches

Crosslinking or cross-ligation involve reacting starch sample with multifunctional reagents such that inter or intra-molecular linkages between the hydroxyl groups on the starch molecules are added at random locations. Covalent interconnection or reinforcement of the linear or branched chains increases its rigidity by forming a 3-dimensional network (Alcazar-Alay and Meireles, 2015). Crosslinking alters physical and thermal properties of starch with resultant effects depending on starch botanical source and the type of crosslinking agent. Important factors to consider in starch crosslinking include chemical composition of reagent, concentration, pH, reaction time and temperature. Chemical agents used may be sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), Epichlorohydrin (ECH) or phosphoryl chloride ($POCl_3$) (Woo and Seib, 2002) depending on the final product requirements. Crosslinking of *D. alata, D. rotundata, D. dumetorum and D. oppositifolia* starches in alkaline environment caused a disruption of the starch structures. Increased swelling power and solubility in cold water (22^{o}C) and decreased gelatinization parameters as studied by DSC was observed (Odeku and Picker-Freyer, 2009b). The 33% (w/w) commercial starches from wheat, corn, oat, banana, potato and rice were cross-linked using a mixture of STMP and STPP (99:1) at specified temperature (25-700C), pH (10.5-12.3) and duration (5-24 hours). Observations showed that the resistant starch produced (≤100% in all studied materials) was less soluble in water at 950C, and had increased gelatinization temperatures and enthalpies (Woo and Seib, 2002). Similar result was recently obtained by Kahraman *et al.* (2015) where higher concentrations of commercial corn and wheat starch increasingly produced resistant starch at higher pH values but at reduced duration and addition of 10% sodium sulphate. Starch modified by crosslinking is used in food applications like frozen products because of its stabilizing, thickening, clarity and retrogradation resistant properties. Its use in non-food industry as plastics has been documented (Lopez *et al.*, 2010). However, Jyothi *et al.* (2006) reported an increased syneresis and higher degree of retrogradation of cross-linked starch compared to the native and attributed this to ordered structure in starch paste.

2.29.2.4 Etherification and Esterification of starches

By substitution of the highly reactive hydrophilic hydroxyl group of starches with various hydrophobic functional groups, a wide range of starches with altered functionalities are created. The degree of substitution (DS) is defined as the number of hydroxyl group substituted per D-glucopyranosyl unit of a starch polymer (Yadav *et al.*, 2007). This results in carboxymethylation, acetylation, succinylation, hydroxypropylation, phosphorylation etc. (Kavlani *et al.*, 2012).

2.29.2.4.1 Carboxymethylation of starches

This method has been applied to produce starch with optimized DS. Lawal *et al.* (2008a) carried out single and multi-step modification of *Dioscorea spp* starches and monitored the structural changes. They found the resulting starch had reduced crystallinity with damaged granules, higher thermal stability and the DS increasing to 2.24 for the nine step modification as opposed to 0.98 obtained for the single step modification. These results were also corroborated by the work of Wang *et al*. (2009). Carboxymethylation reaction is carried out in an organic medium to prevent starch gelatinization. Cold water soluble starch is usually produced by carboxymethylation (Kavlani *et al.*, 2012). Sodium starch glycolate is an example of starch produced by this method that is been used in tablet formulation as a disintegrants in the pharmaceutical industry (Nattapulwat *et al.*, 2009). It is also used in the cosmetic, textile and paper industry as a printing and sizing agent.

2.29.2.4.2 Acetylation of starch

Acetylation is an esterification modification by the introduction of functional acetyl group (CH_3CO) to react with hydroxyl group in the branched chain of starch polymer to produce specific ester (Sweedman *et al.*, 2013). The reaction to prepare acetylated starch of any desired DS value can be controlled with high accuracy by adjusting the molar ratios of reagents (anhydrous acetic acid or vinyl acetate) and alkaline catalysts (NaOH, $Ca(OH)_2$, KOH or Na_2CO_3) used in the reaction mixture (Yadav *et al.*, 2007). The hydrophobic acetyl group substitutes the hydrophilic hydroxyl group of the glucose molecule. This method can be employed to provide simple and effective choice for food processors to target consumer needs and preferences. Acetylated starch has been shown to possess characteristics such as low gelatinization temperatures, increased swelling and solubility and improved storage stability (Liu and Corke, 1999). It has also been shown to limit crystallization and thereby stabilize starch sols by preventing the formation of hydrogen bonding between water molecules and hydroxyl group (Bentacur *et al.*, 1997). Lawal and Adebowale (2005) suggested that electrostatic repulsive forces on the molecules of acetylated starch were responsible for the restriction of these hydrogen bonds. Association of amylose molecules predisposes aqueous starch dispersion to increase in viscosity and gelation on cooling. These types of starches have been found to be useful in preventing cloudiness and retarding retrogradation in aqueous starch dispersions (Bentacur *et al.*, 1997). Acetylation of *D opposite* starch caused increase in thermal stability, reduced crystallization and lowered glass transition temperatures while causing a disruption in the starch granules (Zang *et al.,* 2008). FTIR analysis indicated changes in crystallinity of modified starches while SEM analysis showed indentation of acetylated starch granules (Yadav *et al.*, 2007). However, the reaction inversely influenced the digestibility of flours from potato and sweet potato. When compared with native starch, oat starch treated with anhydrous acetic acid using NaOH as catalyst produced a reduction in amylose contents, pasting temperature and viscosity at high temperatures. There was also rapid development of viscosity upon cooling (Berski *et al.*, 2011). The presence of hydrophobic acetyl groups, carbonyl and carboxyl groups in acetylated barley starches caused a partial disorganization and depolymerization of starch granules (El Halal *et al.,* 2015). Hydrothermal pretreatment of acetylated 65% w/v commercial corn starch suspension increased the swelling capacity of granules and peak viscosity but decreased the pasting temperatures (Chen *et al.*, 2014). Acetylated starches with low DS have been applied in flavor encapsulation, as stabilizers and as thickeners in food systems.

2.29.2.4.3 Hydroxypropylation of starches

This is a type of etherification reaction where starch is treated with highly reactive reagents like 1, 2 epoxypropane (propylene oxide) in the presence of alkaline catalyst to introduce hydroxypropyl group into the starch polymeric chain. The hydroxypropyl group disrupts inter- and intra-molecular hydrogen bonds thereby weakening the starch granular structure. This results in an increase in motional freedom of starch chains in the amorphous region (Kavlani *et al.,* 2012). The hydrophilic hydroxypropyl group reduced starch gelatinization and has been shown to reduce retrogradation by stearic inhibition of alignment of starch chains during aggregation or re-crystallization of potato starch (Perera and Hoover, 1999). Starch isolated from African finger millet (*Eleucine coracana*) was etherified with propylene oxide to produce its hydroxypropylated derivative by Lawal (2009). He observed no pronounced difference between the diffractograms of native starch and the modified derivatives; although, peak viscosity and swelling capacities were increased at temperatures 30-90^{0}C. Starch suspension turbidity and pasting temperatures were reduced. Lower values observed for setback was confirmed by DSC results that showed syneresis to be reasonably reduced after hydroxypropylation (Lawal, 2009).This is in agreement with the observations of Hoover *et al.* (1988) in which increased freeze-thaw stability and cold storage stability were observed for hydroxypropylated field pea starch. Hydroxypropylation of *Dioscorea spp.* starches enhanced free swelling and solubility while also increasing susceptibility of the starches to α-amylase enzyme of *Bacillus lichenoformis*. This has been attributed to disrupted granules and crystallinity order (Lawal *et al.,* 2008b; Odeku and Picker-Freyer, 2009). Paste clarity was observed to increase while retrogradation and gelatinization parameters as measured by DSC declined with storage time (Lawal *et al.,* 2009).

2.29.3 Enzyme modification of starches

Enzymatic modification involves hydrolysis of some part of starch into one with lower molecular weight using amylolytic enzymes (Miyazaki *et al*., 2005). Starch suspension is treated with hydrolyzing enzymes to produce functional derivative. This is the earliest type of modification employed in the production of glucose syrup or high fructose corn syrup. Currently, only hydrolyses (amylases) are used to modify starches (Chiu and Solarek, 2009). Enzymes may be sourced from amylomaltases (AM) that are isolated from eukarya, archea representatives or bacteria. *Thermus thermophiles* bacterium used to modify high amylose potato, maize and pea starch yielded derivatives with improved gel texture (Hansen *et al.,* 2008) while cyclomaltodextrinase (CDase; EC 3.2.1.54) from alkalophilic *Bacillus sp.* I-5 (CDase I-5) produced rice starch with low amylose contents, reduced digestibility (from 28.5% to 9%) and lowered retrogradation when stored at 4^{o}C for 7 days (Auh *et al.,* 2006). Viscosity reduction was observed when granular corn starch was treated with aqueous α-amylase (Kobayashi *et al.,* 1996). Resistant starch (RS) is defined as the sum of starch or the sum of starch degradation products that are not absorbed by the small intestine in healthy individuals (Champ *et al.,* 2003). Dietary fibres are a form of RS produced by starchy products with low digestibility. Taylor *et al.* (2015) reported reduced digestibility of starch modified by amylase enzyme hydrolysis. This was thought to be contributed to by the presence of amylo-lipid complexes formed in the starch. Resistant starch with low glycemix index was produced by modifying maize starch with maltogenic α-amylase+transglucosidase, β-amylase+transglucosidase, maltogenic α-amylase and β-amylase. The reduced rate of digestion observed was in the order 31%, 29%, 19.8% and 14.5% respectively for the enzymes. This reduction has been attributed to increase in starch branch density and crystalline structure (Ao *et al.,* 2007). These types of modified starches may find application in developing foods for diabetics, obese population, patients with cardiovascular issues and as therapeutic food supplements. Enzyme modification is useful for degradation of starch (saccharification) for production of sugar syrups and for conversion of residual dextrins to fermentable sugars during production of low calorie beer.

2.29.4 Genetic modification of starches

Hybrid breeding and genetic engineering offer the possibility of new base starches with varying properties that may show better performance in some applications than traditional native, chemically and/or physically modified starches with enhanced properties (Chiu and Solarek, 2009). It involves transgenic technology, mutation breeding, enzymatic alterations or the use of biotechnology to enhance natural genetic resource and develop desired traits in plants (Amenorpe, 2010). Gene alteration insertion, deletions or translocation may be employed to temporarily modify properties of plant materials but DNA and chromosome alterations result in permanent alterations. These techniques have been used to produce high amylose starch, amylose-free starch, starch with altered amylopectin structures and resistant starch as functional foods (Schwal *et al.*, 2000; Jobling *et al.*, 1999; Bird *et al.*, 2000). It can also be used to provide empirical data for crop improvement. The application of ionizing radiation (gamma and electron beam) is reported to generate free radicals that are capable of inducing molecular changes and fragmentation of starch (Grant and D’Appolonia, 1991; Sabularse *et al.*, 1991; Sokhey and Hanna, 1993). Development of unique properties from genetically modified starches led to desired functional properties such as reduction of viscosity and high water solubility (Bhat and Karim, 2009; Lee *et al*., 2003; Bao and Corke, 2002). Radiation modification has been found to be an environmentally friendly physical process, in contrast to chemical modification. It is economically viable, safe, and possesses several advantages over other conventional methods employed for modification and cross-linking of starch (Bhat and Karim, 2009).

2.29.5 Dual/double modification of starches

This is a type of modification whereby methods are combined to optimize the functionality of starch (Ashogbon and Akintayo, 2013). A chemical modification in the presence of specific physical environment is often used to create starch with novel properties. Crosslinking and phosphorylation of rice starch improved its freeze-thaw stability as observed by Kavlani *et al. (*2012). Starch of *Dioscorea alata* that has been de-branched was then subjected to heat-moisture treatments. The degree of granule crystallinity, melting temperatures and entalpty of gelatinization were found to increase. The resistant starch content of the resulting starch was also enhanced while starch became more stable to thermal flunctuations (Trinh *et al.,* 2013). Combination of hydroxypropylation and crosslinking modifications of *Dioscorea* starches was found to cause an increase in swelling powers, and a reduction of gelatinization parameters of the starches (Odeku and Picker-Freyer, 2009b). Combination of physical methods like ultrasound and microwave treatments of potato starch in neutral, alkaline and acidic water was observed to increase the degree of polymerization and reducing sugar production of the resulting starch (Hernoux *et al.,* 2013). Šubarić *et al.* (2012) found gelatinization temperature and retrogradation tendencies of wheat starch subjected to succinylation and acetylation to be lower than for native starch. The storage stability of starch paste was also found to be improved.

2.30 Industrial application of starches

Native and modified starches from various origins have been used in a wide range of food and non-food applications as macro-constituents (Zhu, 2015; Miyazaki *et al.*, 2006); the utility of which is based on the natural or synthesized functional characteristics. As food, starch is the most abundant, inexpensive and important digestible polysaccharide (Alcazar-Alay and Meireles, 2015) that is used to impart or modify functional, sensory, physical or chemical properties of industrial food and non-food products. Properties that may be imparted include moisture barrier or retention, gas exchange permeability, gelation, viscosity, texture, flavor encapsulation, cohesion, adhesion etc. Commercial starch may be obtained mainly from cereals (wheat, corn, sorghum, rice, barley, millet, oat etc.) and from root and tuber crops (Cassava, yam, cocoyam, and potato).

2.30.1 Food applications of starch

As fat susbstitute: Increased health awareness about the negative effects of overconsumption of some types of fat has necessitated the development of low fat foods or imitation fats. Fat as a food component contributes to the flavor, appearance, texture, and shelf life of food products (Mun *et al.*, 2009; Abbas *et al.*, 2010). Since these desirable quality attributes may be lost if fat is entirely removed in food product formulations, a combination of non-fat ingredients but with similar functional roles can be used to replace or imitate fats (Mun *et al*., 2009). Also, in the nutritional management of some physiological disorders, starch may be used as fat replacers in certain developed food products (Goff *et al.,* 2001; Takahashi *et al.,* 1999). Sajilata and Singhal (2005) demonstrated the use of maltodextrin, a starch based fat replacer in the production of low-fat butter spread/margarine, low fat mayonnaise, low fat milk type products and low -fat ice cream.

As source of resistant starch for improved nutritional claims and labeling: Resistant starch may be regarded as a functional fiber because it allows for high fiber nutritional claim and is considered the third type of dietary fiber because it delivers some benefits of insoluble and soluble fiber (Abbas *et al.*, 2010). It has many advantages compared to traditional sources of fiber due to its smaller crystallites which has been reported to have low water-holding capacity, small particle size and bland flavor (Sajilata and Singhal, 2005). Commercial resistant starch is a special high-amylose starch that has been modified by biochemical or physical processing to maximize its total dietary fiber content (Abbas *et al.,* 2010).

As composite flour ingredient in food products: Native *Dioscorea* starches have been used as substitute in composite wheat flour up to 30% to yield bread with acceptable sensory and textural quality (Nindjina *et al.,* 2011). Starch is generally used in bakery products as texture improvers, in icing sugars and as fillings and glazes. High amylose corn starch has been employed in the production of extruded and fried snacks to keep crispness and consistent color while preventing oil leakage to the snack. Native extruded *Dioscorea rotundata* starch was used to produce starch pasta with addition of brewers spent grain to yield product with high dietary fibre content (Sobukola *et al.,* 2013).

Flavour encapsulation/slow release: Oils, flavor and other micro-food components like vitamins and antioxidants use starches as carriers or vehicle for sustained release of their active components and additives. It is also used in emulsions and non-diary creamers.

Canning: Starches are incorporated in canned products to resist viscosity breakdown or as viscosity enhancer. It also acts as opacity agent, texturizer and filler in soups, sauce, pudding and gravies. Cross-linked starch has been applied in soup, sauce and bakery products (Gamonpilas *et al.,* 2013).

Frozen foods: Starch is used as ingredient to confer cold-storage stability property on frozen foods which may be soups, sauces, fillings and cream-based products

Production of alcohol and fermentation products: Ethanol and converted starch have been produced from native and dual modified starches (acid thinned and oxidized starch) (Shahidul *et al.,* 2013; van der Maarel and Leemhuis, 2013).

Glucose syrup, maltodextrins: These are starch products used as bulking agents (Herrero *et al.,* 2014) in ice-cream production (Homayouni *et al.,* 2008) and as intermediate products for other derivatives like fructose syrup (Liu *et al.,* 2007).

Edible films production: Renewable and biodegradable edible films with a wide range of colors, thickness, deformation and strength have been produced from native and modified *Dioscorea* starches, cellulose, chitosans and gums (Durango *et al.,* 2006; Perez *et al.,* 2012). Processing conditions are altered to impart thermoplasticity, oxidation barrier, moisture permeability, and gas exchange barrier or lipo-phobic properties on starch products

Confectionery products: Starches are used as molding powders for sweet, as thickening or gelling agents, as tenderizers and as sweeteners in breweries and distilleries.

2.30.2 Non-Food starch applications

Pharmaceutical industry: Starches are used in drug development technologies as excipients in dosage formulations. Starch is incorporated to impart properties like mechanical strength, stability, tablet disintegration, controlled release or plasma volume expansion to drugs. Starches are used as pill coatings, dusting agents, tablet binders or as dispersing agents. Daudt *et al.* (2014) demonstrated the use of cross-linked Pinhao starch as pharmaceutical excipient.

Textile industry: Starches are esterified, oxidized and are subject to various cross-linking agents to produce materials used in warp sizing, fabric finishing and printing (Shahidul *et al.*, 2013)

Paper mill: Starches are used to provide greater strength to tissues and paper towels, and they allow a greater use of recycled paper in liner board and cardboard. Applications include use for internal sizing, filler retention, surface sizing, paper coating (regular and color), carbonless paper stilt material, disposable diapers, feminine products, water soluble pouches for detergents and insecticides.

As biological plastics: The growing demand for biodegradability promises to provide additional volumes as starch is used in plastic films and sheets as well as in natural fibre formulations that will eventually replace plastic foams

Adhesive industry: Adhesives starches are acid or alkali treated, they are modified with oxidizing agents, salts and different alcohols. Functions of starch in these systems is as hot-melt glues, stamps, bookbinding, envelopes, labels (regular and waterproof), wood adhesives, laminations, pressure sensitive adhesives and as paper sacks (Satin, 2010).

Explosives Industry: Starch is used as a wide range binding agent and match-head binder

Construction Industry: Used as concrete block binder, asbestos, clay/limestone binder, fire-resistant wallboard, plywood/chipboard adhesive, gypsum board binder and paint fillers

Cosmetics Industry: Starch is incorporated in dusting powders, make-up, soap filler/extender and face creams

Miscellaneous uses: Starch is utilized in dry cell batteries, printed circuit boards, leather finishing, oil well drilling muds, ore flotation and sedimentation.

2.31 Demand, supply, utilisation and challenges of starch in Nigeria

As a country develops, so does her demand for high quality, highly functional, value-added starches. Globally, volume of starch and its derivatives sold in 2012 were estimated at a cost of $51.2 billion and are expected to reach $77.4 billion by 2018 indicating a compound annual growth rate (CAGR) of 7.1% between 2012 and 2018 (BBC research, 2013). Because of industrial technological advances, the starch derivative market is expected to grow extensively at a rate of 6.2% from 2014 to 2019 (World News Network, 2014). The annual demand for native and modified starches in food, pharmaceutical and other non-food utilizing industries exceeded 230,000 tonnes (FMARD, 2010)

In Nigeria, the major source of industrial starch is corn and potatoes which are entirely imported into the country as the world starch market is dominated by starch obtained from corn (> 80%). Recently, there have been some contributions from cassava as the only indigenous starch source. This results in a significant loss to foreign exchange, stifling of local production and reduced demand for local crops. Though Nigeria is the world's largest producer of major root and tuber crops (cassava, yam, cocoyam) (FAOSTAT, 2015) from which starch could be cheaply sourced, there has been little progress in development of commercial processed products like starch from them. This is due to the fact that these same crops serve as staple foods in varying proportion for the generality of the populace so attention need to be shifted to underutilized unconventional sources. The use of local source of starch provides economically feasible options for extending the spectrum of desired functional properties, which are needed for added-value food product development. New starches from non-conventional sources such as those isolated from roots and tubers like yam and cocoyam could provide options for extending the spectrum of desired functional properties, which are needed for added-value food product development (Perez-Pacheco *et al.*, 2014) without belaboring and putting pressure on more utilized staple like cassava.

2.32 Future trends of starch research

There is a promising prospect for the industrial application of native and modified starches sourced from roots and tuber crops because of their availability, cost, compatibility and environmentally friendly nature compared with synthetic polymers (Singh *et al.*, 2010). There is an envisaged utilization of underexploited native and modified starches in unexplored areas of industrial application especially as Nigeria is trying to diversify her economy from oil-based to other areas in which Agriculture, food processing and indigenous content development will play a major role. Excellent opportunities exist to grow and expand the starch base requirements by industries because of developments in nutrition, health and environmental needs. Changing consumer and functional needs has also to meet these needs due to increased consciousness of consumers for safer and cheaper foods. Value addition to starch will predispose it to greater utilization prospects. Daramola and Falade (2006) had suggested enhancement of agricultural value to expand the upstream and downstream opportunities for starch and starch adjuncts. Attention will then be shifted to processes that have starch as residue or by-products for economic and environment-sensitive utilization.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Sources of Materials

Cocoyam samples were collected from six accessions of *Colocasia esculenta* species. (NCe 001, NCe 002, NCe 003, NCe 004, NCe 005 and NCe 010) (Figure 3.2 (a-f)) and three of *Xanthosoma sagitiffolium* species (NXs 001, NXs 002 and NXs 003) (Figure 3.3 (a-c)) from the cocoyam programme of the National Root Crop Research Institute (NRCRI), Umudike, Nigeria. These are from the 2011/2012, 2012/2013 and 2013/2014 planting seasons harvest. Samples of white and yellow cultivars of trifoliate yams were purchased as fresh tubers from three farm markets in Egbeda area of Ibadan, Nigeria (Figure 3.1 a and b). All tubers were transported to the laboratory, washed, sorted and processed within 72 hours of harvest for further work.

3.2 Root dry matter

Tuber dry matter was determined gravimetrically (AOAC, 2000). Fresh tubers were washed and peeled using kitchen knives. Five (5g) grammes of sliced tuber was dried in a hot air oven (Gallenkamp model OV-160 size two BS, Cheshire, UK) at 105^{o}C for 24 hours until constant weight was achieved. Dry matter content (DM) was calculated by expressing the dry weight as a percentage of fresh tuber weight.

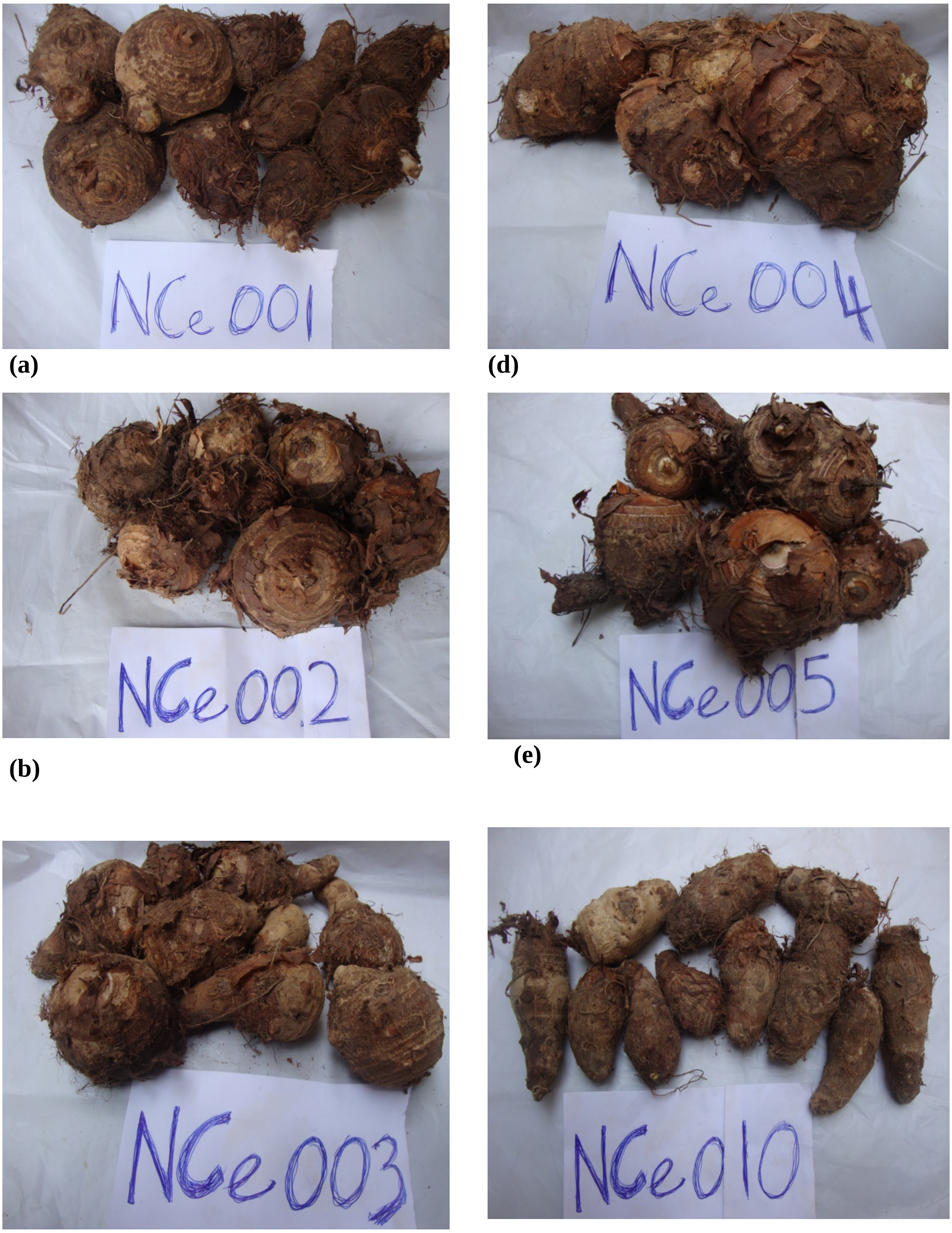
$$DM\ (\%) = (Dried\ weight/wet\ weight) *\ 100\%$$

3.3 Isolation of starch from cocoyam and bitter yam

Purified starch granules were extracted using a method described by Faulks *et al.* (1989) and modified for tubers by Farhat *et al*, (1999). The isolation process is outlined in Figure 3.4.

(a) (b)

Fig. 3.1. Yellow (a) and white (b) cultivars of bitter yam



(a) (d)

(b) (e)

(c) (f)

Figure 3.2 (a)-(f). *Colocasia esculenta* cultivars of cocoyam

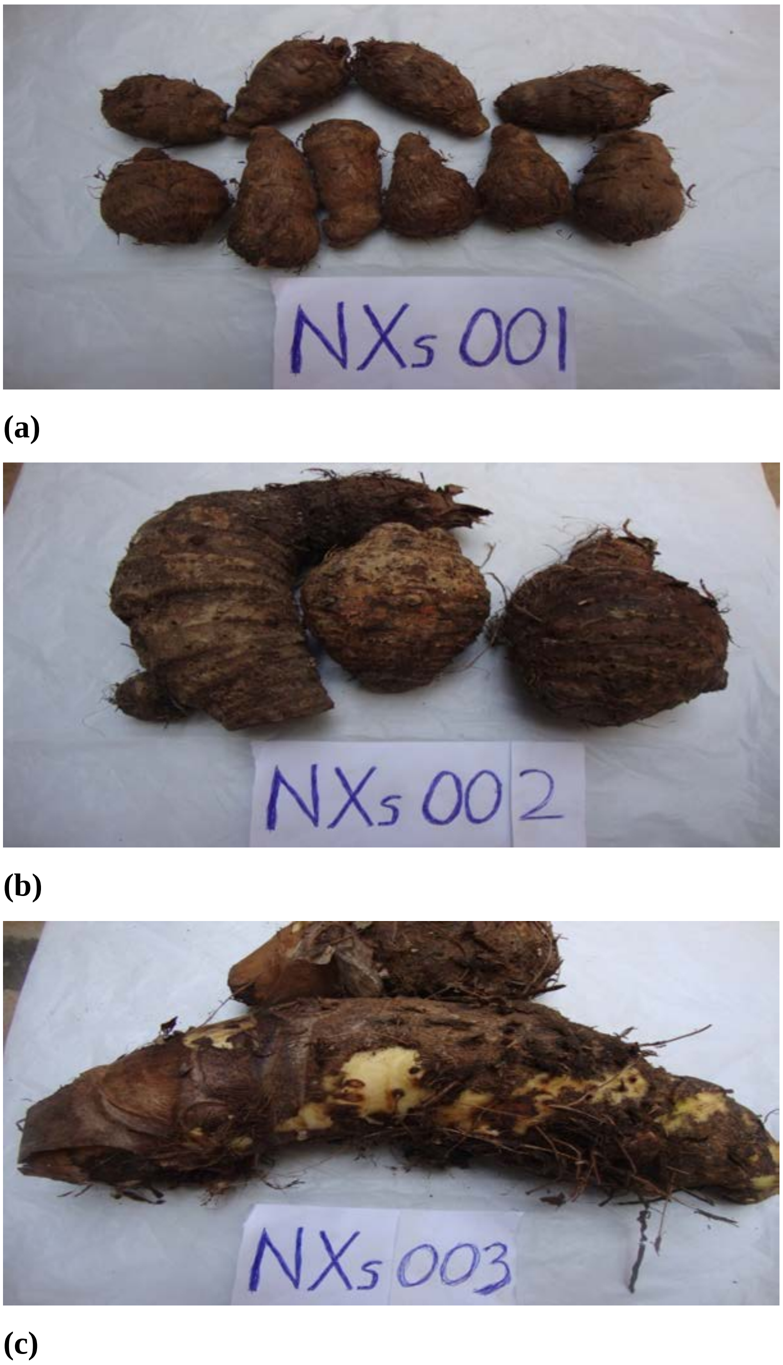


Figure 3.3 (a)-(c). *Xanthosoma sagittifolium* cultivars of cocoyam

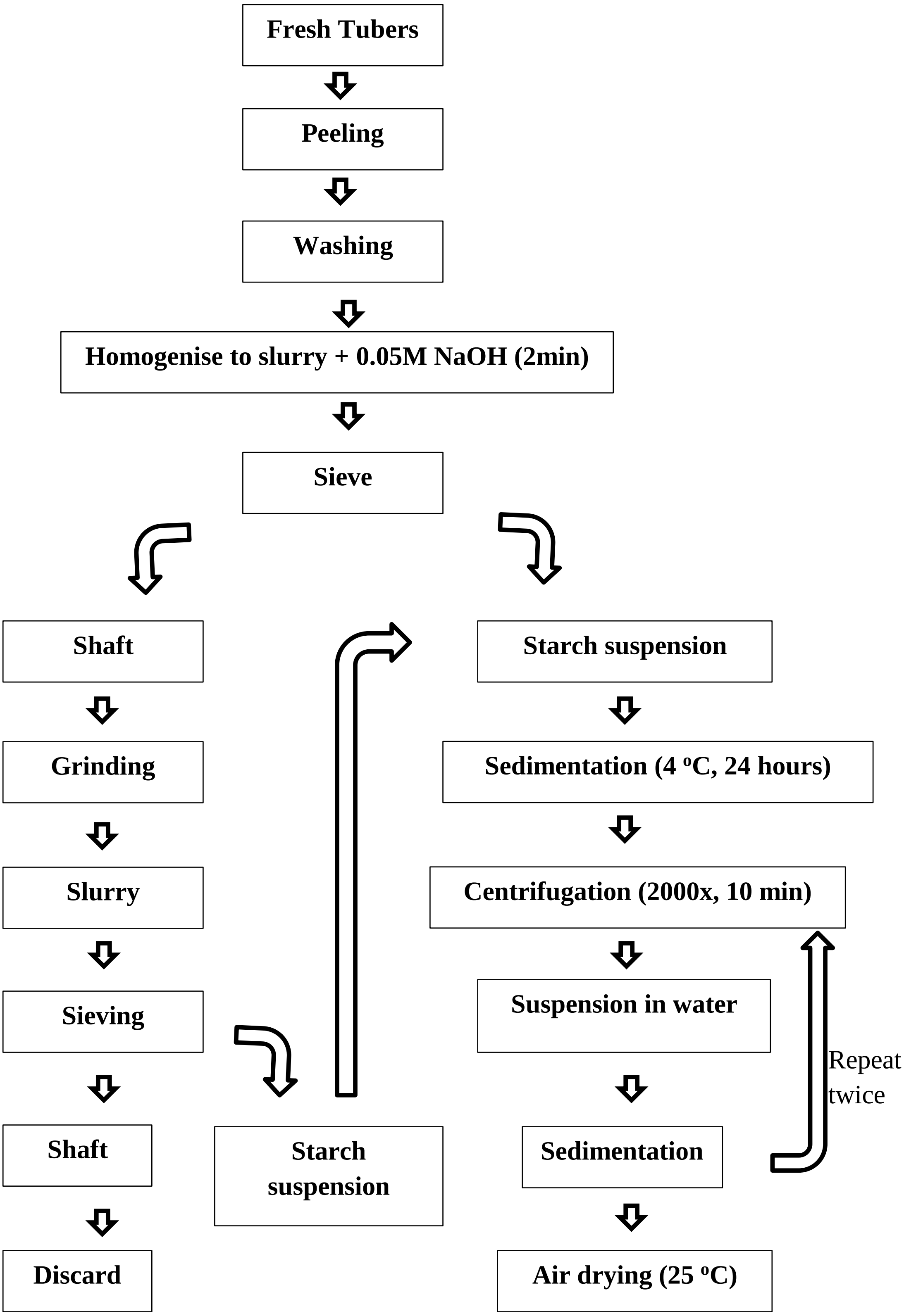


Figure 3.4. Isolation of starch from cocoyam and bitter yam tubers

3.4 Starch yield

This was determined by expressing the weight of starch isolated as a percentage of the weight of fresh tubers.

$$Yield\ (\%) = (W2/W1) * 100$$

Where W_2 = Weight of fresh tubers and
W_1 = Weight of dried starch isolated

3.5 Proximate composition of cocoyam and bitter yam starches

Native starch samples were analysed for moisture, ash, crude fat and crude protein contents using approved methods (AOAC, 1990). Carbohydrate was estimated by difference. Phosphorus content was also determined using AOAC (1990) method.

3.6 Starch modification

Modification of native cocoyam and bitter yam cultivar starches was done using physical and chemical methods. Heat-moisture treatments (at 18, 24 and 27% moisture levels) and annealing are the physical methods used while acid thinning was the chemical method employed. Modifications were carried out as follows:

3.6.1 Heat moisture treatment

The method of Franco *et al.* (1999) as described by Olayinka *et al.* (2008) was employed for heat-moisture conditioning. Moisture contents of the starches were adjusted to 18, 24 and 27% after determining the original moisture contents of the starches. This was done by spraying the native starch with appropriate amount of distilled water. The mixtures were well stirred and sealed in glass jars. They were then heated in a hot air oven dryer (Gallenkamp model OV-160 size two BS, Cheshire, UK) at 110^{o}C for 16 hours then subsequently cooled to 25^{o}C in open air. The jars were opened and starch samples air-dried to moisture content of about 10%.

3.6.2 Annealing

The starch samples were annealed using the method of Jacobs and Delcour (1998) by weighing 1 part starch into 2 part distilled water solution (w/v) in a sealed glass jar using a digital weighing balance (OHAUS Discovery DV 241C, Pine brook, NJ, USA). It was then transferred to a temperature regulated water bath. Temperature of water bath was set at

50^{o}C for 24 hours. The samples were then centrifuged (K241R, Centurion Scientific, Chichester, UK) at 2000 x g for 10 minutes to remove excess water and subsequently air dried at room temperature to 25^{o}C.

3.6.3 Acid thinning

The acid modification of native starches was performed using established method described elsewhere (Assen *et al*., 2011) with modifications. Four hundred (400) grammes of starch were hydrolyzed by suspending in 600 ml of 6% (w/v) HCl solution at 25^{o}C for 192 hours without stirring. The suspension was then neutralized with 10% (w/v) NaOH solution to terminate the reaction. The acid modified starch slurry was washed with distilled water five times to remove respective ions. The wet starch was dried in a hot air oven drier (Gallenkamp model OV-160 size two BS, Cheshire, UK) at 40^{o}C for 6 hours, cooled to 25^{o}C, sieved through a 125µm mesh and stored in High Density Poly Ethylene (HDPE) bags.

3.7 Colour Analysis

This was determined using colorimeter (Chromameter CR 410 Konica Minolta, Sensing Inc., Japan). The colorimeter operates on the CIE (Commission Internationale de l'Eclairage) tristimulus L^*, a^*, b^* colour scheme and was first standardized (L=93.24, a=00.96, b=-02.75) with a Business Xerox 80g/m2 white paper with 136 CIE whiteness D65 while commercial cassava starch was used as control (L=99.80 a=-0.72, b=04.33). About 3g of starch were put in a clean paper and the colour meter was placed on the sample by allowing the sensor to touch the sample. Several points on the samples were measured. The instrument display three-dimensional colour difference in uniform colour space (Lab) co-ordinates. Uniform colour space defines three directions, a light to dark direction, called L*, a red to green direction called a*, and a blue to yellow direction called b. Chroma or saturation (ΔC), colour intensity (ΔE) and hue angle (h) were calculated according to the following equations (Hunterlab, 2008).

$\Delta C = \sqrt{} (a^*)^2 + (b^*)^2$

$\Delta C = \sqrt{} (a^*)^2 + (b^*)^2$

$\Delta E = \sqrt{} (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2$

$\text{Hue angle} = \text{Tan}^{-1} b/a$

3.8 Microstructure of starch granules

Starch samples were observed using a polarized light microscope (Olympus BX 51, U-TV1X-2 Japan) with a quarter wave-plate. Samples were prepared by mixing 2–3 mg of finely powdered starch sample with a droplet of safranin solution (3 drops of safranin in 2ml sterile distilled water) and then observed under the microscope at 100 x, 40 x and 20 x magnifications. Similar procedure has been reported by Primo-Martin *et al.* (2007). The granule size was calculated as the average granule diameter that was estimated by measuring at least 10 randomly selected granules from microphotographs of each starch using Image analysis program, ImageJ® for granule size analysis.

3.9 Amylose content determination

The modified method of De La Cruz and Cush (2000) was used to evaluate amylose contents. Starch-iodine complex (with dark blue colour) is formed due to its high affinity for iodine. Sample (0.1g) was weighed into a test tube to which 1mL of 95% ethanol and 9 mL 1N NaOH are added, the test tube was covered and the content vortex mixed. The mixture was heated in a water bath at 100^{o}C for 10 minutes to gelatinize the starch, and then allowed to cool to 27±2^{o}C. An aliquot of 0.5mL was taken from a 10 part diluents of the extract to which 0.1 mL of acetic acid solution, and 0.2 mL of iodine solution was added. The volume was made up to 10ml with distilled water. The test mixture was left for 20 minutes for colour development (dark blue colour) after which it was vortexed and the absorbance read at 620 nm on a spectrophotometer (Spectronic 21D, Milton Roy, USA). Absorbance of standard corn amylose with known amylose concentration was used to estimate the amylose content in the sample as follows:

$$\begin{aligned}\%\text{Amylose of sample}\\ &= (\%\text{Amylose of standard x Absorbance of sample})\\ &\quad /\text{Absorbance of standard}\end{aligned}$$

3.10 Pasting characteristics of native and modified starches of cocoyam and bitter yam

The pasting profiles were studied using a Rapid Visco-Analyser (RVA super 4, Newport Scientific Pty. Ltd, NSW, Australia) as described by Farhat *et al.* (1989). A 2.5g of starch was mixed with 25g of distilled water to give a starch concentration of 90±2.5g/kg The time-temperature profile used was as follows: the mixture was held at 50°C for 1min, heated from 50 to 95°C in 3min 45s, then held at 95°C for 2 min 30s; the sample was subsequently cooled to 50°C over a 3min 45s period, followed by a period of 2min where the temperature was controlled at 50°C.

3.11 Starch swelling power and solubility index

Swelling power and solubility index were determined according to the method of Olayinka *et al.* (2008) with slight modifications. Starch sample of 0.2g was accurately weighed into a clear dried centrifuge tube and reweighed (W_1). The starch was dispersed in 10 mL of distilled water and tube stoppered. The resultant slurry was heated at 50, 60, 70, 80 and 90^{o}C differently for 30 minutes in a water bath to determine temperature effect. The mixtures were then cooled to 30±2 ^{o}C and centrifuged (K241R, Centurion Scientific, Chichester, UK) at 2000 x g for 10 minutes. The supernatant was decanted and residue obtained with the retained water reweighed (W_2).

$$\text{Swelling power of starch} = (\text{W2} - \text{W1})/\text{Initial weight of starch taken}$$

Aliquots (5 mL) of supernatant obtained after centrifugation was transferred into a pre-weighed petri-dish and dried in a hot air oven at 110^{o}C to constant weight. The residue obtained after drying the supernatant is the amount of starch solubilized in water and is calculated as g/100g starch on dry weight basis.

3.12 Bulk density and Porosity

Packed and loose bulk densities were determined using the method of Falade and Omojola (2008). 5g of starch powder (Ws) was measured and gently poured through a short stemmed glass funnel into a 25mL graduated cylinder. The loose volume occupied by the starch is taken as Vl. The graduated cylinder was gently tapped on a wooden surface at a height of 5 inches for 50 times until no further change in volume was observed. This volume (Vp) was taken as the packed volume

Loose bulk density (ρL) = weight of starch /loose starch volume, i.e. Ws/Vl

Packed bulk density (ρP) = weight of starch/ packed starch volume, i.e. Ws/Vp

Porosity is calculated as follows:

$$(Vl - Vp)/Vl$$

3.13 Water absorption capacity (WAC)/Oil absorption capacity (OAC)

This was determined using methods described by Beuchat (1977) with slight modification. One (1g) gramme of starch sample was weighed into 25 ml graduated centrifuge tubes and reweighed. Ten (10 mL) mililtres of distilled water was then added to the suspension, mixed thoroughly with a variwhilrl mixer for 30 seconds and then allowed to stand for 30 minutes at room temperature (30 ± 2 °C). The suspension was centrifuged at 3000 x g for 10 minutes. The volume of supernatant was noted and water absorbed by starch calculated as the difference between the initial water used and the volume of the supernatant obtained after centrifuging. The result was expressed as a gram of water absorbed per gram of sample on dry weight basis.

Same procedure was repeated for oil absorption capacity but water was replaced with Mamador vegetable oil by PZ Cussons (PZ Wilmar Limited, Nigeria).

3.14 Least gelation concentration

Least gelation concentration was determined according to the method described by Lawal (2004). Native or modified starches sample was mixed with distilled water to form 2-18% (w/v) were prepared in 5mL test tube. The starch suspensions were mixed with a vari-whirl mixer for 5 minutes. The test tubes were heated at 80^{o}C for 30 minutes in a water bath, followed by rapid cooling under running cold tap water. The test tubes were further cooled at 4^{o}C for 2 hours. Least gelation concentration was determined as that concentration when the sample from the inverted test tube did not slip or fall down

3.15 Fourier Transformed Infrared Spectroscopy

The method described by Aboubakar *et al.* (2008) was employed to obtain IR spectra of the native and modified starches using a Spectrum 100 FT-IR spectrometer (Spectrum BX Perkin Elmer, USA). Starch sample (0.2mg) was taken on a microspatula with about 200mg of KBr. It was mixed thoroughly in a mortar while grinding with the pestle. The mixture was placed in hydraulic press and pressed at 5000 psi for 60 seconds. The pellet was carefully removed from the die and placed in the FTIR sample holder. The pressed disc was nearly clear while translucent ones were ground and repressed before measurements were taken in transmittance mode from 4000 to 400 cm-1.

3.16 Paste Clarity/Light transmittance of starch gel

The paste clarity of starch was determined using the method of Bhandari and Singhal (2002) and modified by Iheagwara (2013). Two (2) % w/v aqueous dispersion of the starch sample (dry weight basis) was made into 10 mL cotton wool-plugged test tubes. The test tubes were vortex mixed and then heated at 100^0C in a water bath (with occasional stirring) for 30 minutes. The gelatinized starch was cooled to ambient temperature and the percentage transmittance (%) was determined at 650 nm against a water blank using a spectrophotometer (Spectronic 21D, Milton Roy, USA). The remaining samples were stored at 4°C for 4 weeks. A portion was thawed to 30^oC and transmittance again recorded at 650 nm each day for 4 days and then on a weekly basis for 4 weeks.

3.17 Freeze-Thaw stability of starch paste

Stability of starch samples to freezing was determined as described by Amani *et al*. (2004) with modifications. 5% w/v of paste sample was conditioned in a plastic tube by heating rapidly for 90 seconds to the gelatinization temperature with constant agitation and mixture was held for 30 minutes. 10g of gel was taken, cooled and further held at -20 °C for 18 hours after which it was thawed to 28^oC for 6 hours. It was then vortex mixed for 15 seconds and centrifuged at 3000 x g for 10 minutes. Amount of water separated was measured using a 10 mL syringe and expressed as % water separated. The remaining mixture was kept again at -20°C for 4 weeks. Freezing stabilities were performed every week by thawing the samples and measuring the percentage of water separated after each freeze-thaw cycle and centrifugation. The analysis was replicated.

$$\%\ \text{water separated} = (\text{weight of separated liquid}/\text{weight of gel used}) * 100$$

3.18 Starch thermal analysis

Gelatinization of the starch samples were analyzed according to a method described by Jayakody *et al* (2007) with slight modification using differential scanning calorimetry (DSC 6000 System PerkinElmer, MA, USA). It was calibrated with Indium Kit no: N5190762. 3.0mg (+/-0.01) starch samples were weighed in triplicates into DSC standard aluminum sample pan (kit no: N5340188) to be analyzed against empty reference pan. Distilled water was added to the starch sample using a transfer pipette to establish a starch: water ratio of 1:3. The pans were then hermetically sealed and the samples were left to stand for1 hour at room temperature for moisture equilibration. The sealed pans were purged with nitrogen gas at 10 ml per min and heated from 20^oC to 130^oC at a heating rate of 10^{o}C/min to gelatinize the starch samples. From the DSC thermograms, onset temperature (T_o), peak temperature (T_p), end temperature (T_e) and enthalpy of gelatinization (ΔH_{gel}) were analyzed using PerkinElmer (Pyris) software. Temperature range (R) and peak height index (PHI) were also calculated as T_p - T_o and as the ratio ΔHgel/ (T_p-T_o), respectively. The gelatinized starches were stored at 4^{o}C for a period of 4 days, after which the samples were equilibrated at room temperature for 1 hour, and rescanned in the DSC using the previous heating programme to measure the retrogradation transition temperatures and enthalpy (ΔHret).

3.19 Statistical Analysis

All analyses were carried out in triplicate (except as noted). Data were collected and expressed as means ± standard deviation and further subjected to a one-way analysis of variance using SAS (Statistical Analysis System Institute, Inc., 2008, Cary, NC) version 9.2 program of the complete randomized design to determine differences among the starch cultivars and modified derivatives at significance level P=0.05**.** Duncan multiple-range test was then used to separate the means.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Root dry matter and starch yield of cocoyam and bitter yam tubers

Mean values obtained for root dry matter and starch yield of bitter yam, *Colocasia* and *Xanthosoma* species of cocoyam in g/100 g fresh weight are shown in Table 4.1. Dry matter content of tubers of the *Colocasia* spp ranged from 26.24% (NCe005) to 35.48% (NCe003) while those of *Xanthosoma spp.* ranged from 32.42% (NXs002) to 37.00% (NXs003). Bitter yam tubers recorded higher dry matter values than the cocoyam cultivars with both yellow and white cultivars showing over 39% dry matter contents. The bitter yam cultivars recorded lower starch yield (61.59-64.26%) than the *Xanthosoma spp.* (67.90-73.56%). Agbor-Egbe and Treche (1995) reported that bitter yam has lower dry matter content than other *Dioscorea spp.* tubers. Afoakwa and Sefa-Dedeh (2001) also reported the dry matter content of yellow (23.83%) and white (22.15%) cultivars of bitter yam. These values are lower than the results obtained in this study. The difference may be attributed to differences in geographical origin, planting conditions, stage at harvest and storage days of tubers.

The main constituents of dry matter in a plant system are starch and cellulose (Tharanathan, 2005). The highest starch yield in the cocoyam cultivars studied was from the NXs002 while NCe003 of the *Colocasia spp.* gave the lowest. These results are within the range of values reported earlier by Sefa-Dedeh and Agyir-Sackay (2004) that the dry matter content of *Colocasia spp.* and *Xanthosoma spp.* varied from 27.94 to 40.70 and 22.6-45.54%, respectively. A lower starch yield of 62.3% was reported by Lawal (2004) for new cocoyam (*Xanthosoma spp.)* while Aboubakar *et al.* (2008) reported *Colocasia spp.* varieties from Cameroun to give a yield of 66.5-86.6%. The observed significant differences within the cocoyam cultivars and between cocoyam and bitter yam dry matter and starch yield could be due to variations in a number of factors like moisture contents, tuber tissue structure and composition, efficiency of isolation method, age of tubers at harvest or condition of the soil at harvest. Ebah-Djedji *et al.* (2012) reported that harvesting periods had significant effects on the starch yields and dry matter contents of cassava varieties.

Table 4.1. Root dry matter and starch yield of cocoyam and bitter yam cultivars (% per 100g fresh tuber)

Commodity	Cultivar	Dry matter	Starch content	Yield (%)
Cocoyam	NCe 001	28.73 ± 0.38^{f}	18.92 ± 0.31^{cd}	65.87 ± 1.96^{bcd}
	NCe 002	31.52 ± 0.84^{d}	18.32 ± 0.62^{d}	58.12 ± 0.42^{g}
	NCe 003	35.48 ± 0.61^{c}	18.35 ± 0.35^{d}	51.72 ± 0.11^{h}
	NCe 004	29.68 ± 0.51^{f}	16.21 ± 0.12^{e}	54.63 ± 0.52^{h}
	NCe 005	26.24 ± 0.49^{g}	15.97 ± 0.09^{e}	60.86 ± 1.50^{fg}
	NCe 010	31.05 ± 0.35^{e}	19.78 ± 0.74^{c}	63.70 ± 1.67^{def}
	NXS001	35.18 ± 0.87^{c}	23.88 ± 0.04^{b}	67.90 ± 1.78^{b}
	NXS002	32.42 ± 0.18^{d}	23.85 ± 0.36^{b}	73.56 ± 0.71^{a}
	NXS003	37.00 ± 0.14^{b}	24.80 ± 0.42^{a}	67.02 ± 0.89^{bc}
Bitter yam	White	39.11 ± 0.41^{a}	25.13 ± 0.17^{a}	64.26 ± 0.24^{cde}
Bitter yam	Yellow	39.55 ± 0.78^{a}	24.35 ± 0.49^{ab}	61.59 ± 2.47^{ef}

Means in columns not followed by same alphabet(s) are significantly different at 5%

The *Xanthosoma spp* had higher starch yield than the *Colocasia spp*. The starch content of tubers generally ranges from 50 to 80% of the dry weight (Farhat *et al.*, 1999). Consequently, the starches of the cocoyam and bitter yam cultivars could constitute cheap alternative sources of commercial starch due to their relatively high starch yields, compared to starch yield from cereal crops like rice (45.7-65%), corn (45-63%) and legumes (9.6-40%) (Ji *et al.*, 2004; Ashogbon and Akintayo, 2013; Sung and Stone, 2004; Wani *et al.*, 2016).

The starches of NCe001, NCe002, NCe003 and NCe004 cultivars were observed to present a difficulty in isolation as their starch granules did not sediment easily compared to the other cultivars even when allowed to stand for over 24 hours and at refrigerated temperatures. The *Colocasia* starches were also observed to have high mucilage contents. These observations were also reported by Aboubakar *et al* (2008). This could be responsible for the inability of the starch to settle because it is held within the mucilages' dense slimy network. Thus, the mixture had to be centrifuged, the contaminating layers scraped and washed severally to remove the slimy mucilage and isolate pure starch granules. This inability to settle is due to the very small granule sizes of the starches as confirmed by the light micrograph results and this could have contributed to the low starch yields recorded for the *Colocasia spp* starches. Bitter yam starches, though having small granules sizes as well, did not present the same isolation problems as the *Colocasia esculenta* starches because they were not mucilaginous. Similar isolation issues have been reported for taro corms (Jirarat *et al.*, 2007) and for *Anchomanes difformis* starch which also have very small granule sizes (Afolayan *et al.*, 2012).

4.2 Starch proximate composition

Proximate composition of the native starches (Table 4.2) showed presence of low levels of phosphorus, protein, fats and crude fibe but high levels of carbohydrates. In the cocoyam starches, carbohydrate levels varied significantly ($p<0.05$) from 81.82% in NCe010 starch to 85.26% in NCe004 while starches from the bitter yam cultivars varied from 82.12% (yellow) to 83.12% (white). Minor components of starch granules though significantly small in quantity, affect functional and physicochemical properties of starch. Phosphorus contents varied significantly within the cocoyam and bitter yam cultivars ranging from 0.065mg/g (NCe002) to 0.987mg/g (NCe010) in the *C. esculenta* starches, 0.021mg/g (NXs002) to 0.299mg/g (NXs003) in *X.sagittifolium* and 0.058mg/g (white) and 0.508mg/g (yellow) in the *D.dumetorum* starches.

Table 4.2. Proximate and phosphorus composition of native starches from cocoyam and bitter yam cultivars

	Phosphorus (mg/g)	Ash (%)	Crude Protein (%)	Fat (%)	Crude Fibre (%)	Moisture (%)	Carbohydrate (%)
Colocasia esculenta							
NCe001	0.315±0.00^{d}	1.08±0.03^{d}	0.24±0.00^{g}	0.49±0.58^{a}	2.47±0.02^{cd}	12.79±0.15^{ab}	82.94±0.49^{cd}
NCe002	0.065±0.00^{i}	2.29±0.00^{a}	0.35±0.00^{c}	0.16±0.00^{a}	2.70±0.07^{bc}	11.40±0.57^{d}	83.11±0.65^{bc}
NCe003	0.259±0.00^{f}	1.07±0.04^{d}	0.40±0.01^{b}	0.13±0.00^{a}	2.65±0.28^{bc}	12.6±0.07^{abc}	83.16±0.16^{bc}
NCe004	0.101±0.00^{h}	0.99±0.01^{e}	0.32±0.01^{d}	0.12±0.00^{a}	2.12±0.02^{e}	11.38±0.74^{d}	85.08±0.69^{a}
NCe005	0.832±0.00^{b}	2.33±0.02^{a}	0.26±0.01^{f}	0.10±0.00^{a}	2.37±0.01^{de}	12.0±0.04^{bcd}	82.91±0.00^{cd}
NCe010	0.987±0.00^{a}	2.12±0.01^{c}	0.26±0.00^{fg}	0.14±0.00^{a}	2.76±0.06^{b}	12.90±0.14^{a}	81.82±0.07^{e}
Xanthosoma sagittifolium							
NXs001	0.116±0.00^{g}	0.96±0.04^{ef}	0.29±0.00^{e}	0.15±0.00^{a}	3.03±0.10^{a}	10.32±0.04^{e}	85.26±0.09^{a}
NXs002	0.021±0.00^{k}	0.91±0.04^{f}	0.43±0.02^{a}	0.18±0.01^{a}	2.87±0.08a^{b}	11.74±0.23^{d}	83.88±0.07^{b}
NXs003	0.299±0.00^{e}	2.33±0.01^{a}	0.25±0.01^{fg}	0.17±0.00^{a}	2.25±0.07^{de}	11.88±0.18^{cd}	83.12±0.22^{bc}
Dioscorea dumetorum							
White	0.058±0.00^{j}	2.09±0.01^{c}	0.26±0.00^{f}	0.18±0.00^{a}	2.20±0.14^{de}	11.60±0.14^{d}	83.66±0.30^{bc}
Yellow	0.508±0.00^{c}	2.20±0.00^{b}	0.31±0.00^{de}	0.16±0.00^{a}	2.45±0.07^{cd}	12.75±0.35^{ab}	82.12±0.41^{de}

Means in columns not followed by same alphabet(s) are significantly different at 5% level ($P<0.05$).

Starch from NCe010 contained the highest amount of phosphorus while that from NXs002 contained the least with no particular trend observed. These values are slightly higher than the values reported for starches from *D. esculenta* (Jayakody *et al,* 2007), *D.rotundata* (Moorthy and Nair, 1989) and *D.alata* (Riley *et al.,* 2006) but comparable to the range reported by other workers (Mweta *et al.*, 2008; Perez *et al.,* 2011). The observed differences may be attributed to differences in method of starch isolation and crops genetics. Phosphorus levels have been reported to influence pasting and gelatinization characteristisc of starches (Alcazay-Alay and Meireles, 2015) and may be present in different forms linked by covalent bonds as phospholipids or phosphate esters within the starch granules. Fats contents varied between 0.10 and 0.49%, falling within the range earlier reported for tuber starches (Zhu, 2015) and were not significantly different within all the starches studied. Results indicated that the moisture contents of the starches are generally acceptable for safe storage while protein contents were also within the range previously reported for tuber starches (Amani *et al.,* 2004; Mweta *et al.*, 2008).

4.3 Colour parameters of native and modified cocoyam and bitter yam starches

The measured CIE tristimulus parameters (*L*, a*, b**) and calculated (*delta*chroma, hue and total colour difference were calculated for native cocoyam and bitter yam starches (Table 4.3 and 4.4) showed significant variations (P<0.05) with cultivar and modification methods. The CIE L* value varied between 64.32 (NCe003) and 94.99 (NCe010) for *Colocasia spp*, 77.06 (NXs002) and 91.45 (NXs003) for *Xanthosoma spp.,* and 85.02 (white) to 88.22 (yellow) for bitter yam starches. Lightness has been associated with level of purity of starches with values higher than 90 are considered acceptable (Boudries *et al,* 2009). Since starch is an ingredient in many processed products, colour of starch may be carried over to adversely affect visual quality and commercial acceptability of such coloured products. Therefore, the high lightness values of NCe005 (90.12), NCe010 (94.99) and NXs003 (91.45) were satisfactory for commercial application. Contrary to expectation, starch obtained from the yellow cultivar of bitter yam had higher lightness (88.22 to 85.02) and lower yellowness (6.44 to 7.31) values than starch from white cultivar. Effectiveness of starch isolation procedure and bleaching of the yellow colouration during drying may be adduced for this.

Table 4.3. Colour properties of native and modified cocoyam starches

Cultivar	Treatment	L*	a*	b*	ΔC	ΔE	Hue angle
NCe 001	Native	87.61±0.00^{abc}	1.00±0.01^{c}	3.20±0.00^{c}	-1.04±0.0^{c}	5.73±0.00^{de}	72.63±0.45^{g}
	Ann	89.13±0.02^{c}	0.69±0.01^{cd}	3.12±0.00^{d}	-1.20±0.0^{d}	4.16±0.02^{e}	77.60±0.20^{d}
	Acid	85.35±0.19^{c}	1.14±0.00^{de}	5.95±0.01^{ef}	1.66±0.01^{fg}	8.17±0.19^{f}	79.2±0.03^{ab}
	HMT18	84.39±0.02^{ab}	1.36±0.00^{g}	6.20±0.01^{d}	1.96±0.01^{e}	9.26±0.02^{ef}	77.63±0.03^{d}
	HMT24	68.50±0.01^{c}	2.64±0.01^{e}	10.40±0.00^{a}	6.34±0.0^{bc}	26.87±0.01^{e}	75.75±0.05^{d}
	HMT27	64.11±0.02^{c}	3.01±0.02^{e}	12.91±0.01^{a}	8.86±0.00^{a}	32.09±0.01^{d}	76.82±0.18^{c}
NCe002	Native	73.61±0.02^{de}	1.19±0.00^{b}	7.34±0.00^{a}	3.04±0.00^{a}	20.76±0.02^{b}	80.79±0.00^{c}
	Ann	68.06±0.04^{g}	1.92±0.00^{b}	6.85±0.01^{ab}	2.72±0.01^{ab}	26.68±0.04^{a}	74.34±0.02^{f}
	Acid	62.96±0.06^{h}	5.37±0.23^{a}	12.37±0.00^{a}	9.09±0.00^{a}	33.48±0.08^{a}	66.51±0.73^{d}
	HMT18	64.66±0.08^{f}	4.54±0.02^{a}	11.38±0.02^{a}	7.85±0.03^{a}	31.35±0.07^{a}	68.08±0.28^{h}
	HMT24	47.40±0.01^{fg}	5.88±0.01^{a}	10.90±0.01^{ab}	7.29±0.00^{a}	49.48±0.01^{ab}	59.81±0.04^{k}
	HMT27	44.96±0.00^{f}	6.44±0.01^{a}	10.27±0.00^{cd}	7.73±0.01^{b}	52.17±0.00^{a}	57.82±0.06^{j}
NCe003	Native	64.32±0.01^{e}	-1.49±0.01^{g}	6.67±0.01^{ab}	2.44±0.01^{ab}	30.57±0.01^{a}	77.43±0.03^{e}
	Ann	75.89±0.01^{e}	-0.06±0.00^{g}	6.10±0.00^{bc}	1.71±0.00^{bc}	18.08±0.01^{c}	89.44±0.00^{a}
	Acid	72.74±0.01^{g}	2.59±0.01^{b}	10.18±0.01^{b}	6.11±0.00^{b}	22.41±0.01^{b}	75.62±0.11^{bc}
	HMT18	66.24±0.06^{f}	3.11±0.01^{c}	10.49±0.01^{a}	6.54±0.01^{b}	29.30±0.06^{a}	73.49±0.02^{f}
	HMT24	49.66±0.01^{f}	4.66±0.01^{bc}	10.03±0.00^{ab}	6.67±0.00^{ab}	46.93±0.01^{b}	65.06±0.05^{i}
	HMT27	44.78±0.04^{f}	5.61±0.01^{b}	11.26±0.01^{b}	8.19±0.01^{b}	52.36±0.04^{a}	63.56±0.05^{h}
NCe004	Native	80.18±10.28^{bcd}	0.55±0.01^{de}	2.89±0.01^{c}	-1.45±0.01^{c}	13.74±10.21^{bcd}	79.18±0.04^{d}
	Ann	80.60±0.01^{d}	-0.11±0.00^{g}	3.65±0.00^{d}	-0.74±0.00^{d}	12.94±0.01^{d}	88.77±0.00^{a}
	Acid	74.65±0.06^{f}	1.86±0.01^{c}	8.29±0.01^{cd}	4.10±0.01^{cd}	19.90±0.05^{c}	77.36±0.04^{b}
	HMT18	74.39±0.04^{de}	1.57±0.01^{g}	6.76±0.02^{c}	2.54±0.02^{de}	19.89±0.04^{bc}	77.95±1.74^{cd}
	HMT24	53.82±1.76^{e}	3.94±0.01^{d}	8.97±0.08^{c}	5.40±0.07^{d}	42.29±1.75^{c}	66.22±0.08^{g}
	HMT27	52.18±0.01^{d}	4.65±0.02^{c}	10.08±0.01^{cd}	6.71±0.00^{c}	44.26±0.01^{c}	65.16±0.03^{g}
NCe005	Native	90.12±0.02^{ab}	0.71±0.01^{d}	2.58±0.01^{cd}	-1.72±0.00^{cd}	3.49±0.02^{de}	74.64±0.09^{f}
	Ann	72.90±0.07^{f}	2.06±0.01^{a}	6.82±0.00^{ab}	2.73±0.00^{ab}	21.54±0.07^{b}	73.17±0.08^{f}
	Acid	75.53±0.02^{f}	2.89±0.01^{b}	9.16±0.00^{bc}	5.21±0.00^{bc}	19.34±0.01^{c}	72.53±0.03^{c}
	HMT18	69.11±0.00^{ef}	3.54±0.03^{b}	8.65±0.00^{b}	4.95±0.01^{c}	26.02±0.00^{ab}	67.63±0.10^{h}
Cultivar	Treatment	L*	a*	b*	ΔC	ΔE	Hue angle

	HMT24	59.06 ± 0.01^{d}	4.74 ± 0.00^{b}	10.65 ± 0.00^{a}	7.26 ± 0.00^{a}	37.09 ± 0.01^{d}	66.06 ± 0.00^{h}
	HMT27	44.65 ± 0.01^{f}	5.72 ± 0.02^{b}	10.57 ± 0.02^{c}	7.62 ± 0.01^{b}	52.44 ± 0.01^{a}	61.62 ± 0.03^{i}
NCe010	Native	94.99 ± 0.04^{a}	0.43 ± 0.01^{ef}	2.57 ± 0.01^{cd}	-1.79 ± 0.01^{cd}	3.34 ± 0.03^{e}	80.64 ± 0.10^{c}
	Ann	93.37 ± 0.01^{a}	0.29 ± 0.00^{f}	3.12 ± 0.00^{d}	-1.26 ± 0.00^{d}	1.79 ± 0.01^{g}	84.70 ± 0.00^{b}
	Acid	90.49 ± 0.00^{a}	0.43 ± 0.01^{f}	3.08 ± 0.00^{g}	-1.28 ± 0.00^{h}	2.82 ± 0.00^{h}	82.11 ± 0.10^{a}
	HMT18	87.92 ± 0.01^{ab}	0.68 ± 0.01^{i}	4.74 ± 0.01^{e}	0.40 ± 0.01^{f}	5.22 ± 0.01^{f}	81.89 ± 0.08^{a}
	HMT24	76.36 ± 0.01^{a}	1.89 ± 0.01^{g}	7.83 ± 0.01^{d}	3.67 ± 0.01^{e}	18.02 ± 0.00^{h}	76.50 ± 0.01^{c}
	HMT27	75.35 ± 0.01^{a}	1.21 ± 0.01^{i}	5.35 ± 0.01^{g}	1.09 ± 0.01^{f}	18.70 ± 0.01^{g}	77.27 ± 0.13^{b}
NXs001	Native	89.87 ± 0.05^{ab}	0.57 ± 0.01^{de}	2.88 ± 0.00^{c}	-1.46 ± 0.00^{c}	3.51 ± 0.04^{de}	78.76 ± 0.07^{d}
	Ann	89.53 ± 0.03^{c}	0.45 ± 0.00^{e}	3.18 ± 0.01^{d}	-1.18 ± 0.01^{d}	3.67 ± 0.03^{e}	81.93 ± 0.06^{c}
	Acid	84.44 ± 0.02^{cd}	1.06 ± 0.02^{e}	5.43 ± 0.01^{f}	1.14 ± 0.01^{g}	9.02 ± 0.02^{ef}	78.95 ± 0.17^{ab}
	HMT18	86.82 ± 0.05^{ab}	1.08 ± 0.00^{h}	4.24 ± 0.01^{ef}	-0.02 ± 0.01^{fg}	6.46 ± 0.05^{f}	75.70 ± 0.04^{e}
	HMT24	76.42 ± 0.01^{a}	2.08 ± 0.01^{f}	7.82 ± 0.00^{d}	3.70 ± 0.00^{e}	17.98 ± 0.01^{h}	74.95 ± 0.02^{f}
	HMT27	75.00 ± 0.01^{a}	1.34 ± 0.01^{h}	3.46 ± 0.01^{h}	-0.68 ± 0.01^{g}	19.08 ± 0.01^{g}	68.78 ± 0.03^{e}
NXs002	Native	77.06 ± 0.02^{cd}	1.73 ± 0.00^{a}	6.32 ± 0.01^{b}	2.16 ± 0.01^{b}	17.02 ± 0.02^{bc}	74.61 ± 0.03^{f}
	Ann	71.77 ± 0.13^{f}	1.81 ± 0.01^{b}	7.20 ± 0.02^{a}	3.03 ± 0.02^{a}	22.76 ± 0.13^{b}	75.92 ± 0.13^{e}
	Acid	90.12 ± 0.02^{a}	1.36 ± 0.00^{de}	5.56 ± 0.01^{f}	1.33 ± 0.01^{g}	3.58 ± 0.01^{h}	76.25 ± 0.08^{bc}
	HMT18	69.87 ± 0.04^{ef}	2.61 ± 0.14^{d}	7.45 ± 0.02^{c}	3.50 ± 0.02^{d}	24.90 ± 0.04^{ab}	70.74 ± 0.06^{g}
	HMT24	45.69 ± 0.04^{g}	4.59 ± 0.02^{c}	9.48 ± 0.01^{bc}	6.14 ± 0.01^{bc}	51.09 ± 0.04^{a}	64.13 ± 0.07^{j}
	HMT27	49.26 ± 0.10^{e}	4.21 ± 0.02^{d}	9.51 ± 0.01^{e}	6.01 ± 0.00^{d}	47.24 ± 0.10^{b}	66.12 ± 0.07^{f}
NXs003	Native	91.45 ± 0.03^{a}	0.29 ± 0.00^{f}	2.06 ± 0.01^{d}	-2.32 ± 0.01^{d}	2.77 ± 0.03^{e}	82.02 ± 0.03^{b}
	Ann	91.55 ± 0.06^{b}	0.40 ± 0.01^{ef}	3.29 ± 0.00^{d}	-1.08 ± 0.00^{d}	1.89 ± 0.05^{f}	83.16 ± 0.11^{c}
	Acid	87.48 ± 0.02^{b}	0.55 ± 0.01^{f}	4.03 ± 0.01^{g}	-0.33 ± 0.01^{h}	5.64 ± 0.02^{g}	82.14 ± 0.10^{a}
	HMT18	88.93 ± 0.01^{a}	0.75 ± 0.00^{i}	3.39 ± 0.01^{f}	-0.92 ± 0.01^{g}	2.30 ± 0.01^{f}	77.54 ± 0.07^{d}
	HMT24	71.99 ± 0.02^{bc}	2.06 ± 0.01^{f}	8.05 ± 0.00^{d}	3.92 ± 0.00^{e}	22.66 ± 0.02^{fg}	75.58 ± 0.09^{e}
	HMT27	73.47 ± 0.00^{ab}	1.77 ± 0.01^{g}	7.34 ± 0.00^{f}	3.16 ± 0.00^{e}	2.97 ± 0.00^{fg}	76.50 ± 0.11^{d}

Means in columns not followed by same alphabet(s) (by modification) are significantly different at 5% level (P<0.05).

Table 4.4. Colour properties of native and modified bitter yam starches

Cultivar	Treatment	L*	a*	b*	ΔC	ΔE	Hue angle
White	Native	85.02±3.95^{abc}	0.54±0.23^{e}	7.31±0.49^{a}	2.94±0.49^{a}	8.88±3.84^{cde}	85.39±1.62^{a}
	Ann	90.20±1.48^{bc}	0.79±0.20^{c}	6.66±1.51^{abc}	2.32±1.52^{abc}	3.88±1.72^{e}	82.89±0.77^{c}
	Acid	82.26±1.94^{e}	1.24±0.38^{de}	7.02±1.73^{de}	2.76±1.62^{ef}	11.68±2.05^{d}	79.25±6.20^{ab}
	HMT18	81.80±5.34^{bc}	1.94±0.29^{f}	10.75±0.83^{a}	6.53±0.87^{b}	13.88±4.69^{de}	79.78±0.69^{b}
	HMT24	75.41±6.12^{ab}	1.80±0.18^{g}	9.94±1.01^{bc}	5.71±1.03^{cd}	19.64±5.75^{gh}	79.76±0.09^{a}
	HMT27	71.47±5.52^{b}	1.79±0.21^{g}	9.95±0.99^{de}	5.72±1.01^{d}	23.64±5.25^{f}	79.78±0.21^{a}
Yellow							
	Native	88.22±17.75^{ab}	1.09±0.20^{bc}	6.44±1.31^{b}	2.14±1.33^{b}	12.73±15.9^{cde}	80.36±0.32^{c}
	Ann	94.22±3.33^{a}	0.61±0.18^{d}	5.70±1.22^{c}	1.35±1.20^{c}	3.26±2.65^{g}	83.13±2.68^{c}
	Acid	83.78±2.34^{d}	1.47±0.47^{d}	8.01±1.82^{cd}	3.76±1.83^{de}	10.48±2.55^{de}	79.32±3.04^{ab}
	HMT18	77.22±12.4^{cd}	2.17±0.34^{e}	10.99±1.65^{a}	6.81±1.68^{b}	19.49±10.79^{cd}	78.82±0.17^{bc}
	HMT24	71.55±3.44^{c}	2.14±0.17^{f}	10.62±0.73^{a}	6.44±0.75^{b}	23.74±3.17^{ef}	78.67±0.14^{b}
	HMT27	66.96±0.78^{c}	2.29±0.05^{f}	10.17±0.17^{cd}	6.03±0.18^{d}	28.42±0.74^{e}	77.29±0.00^{b}

Means in columns not followed by same alphabet(s) (by modification) are significantly different at 5% level ($P<0.05$).

However, all the native starches showed low CIE *a** values ranging between -1.49 to 1.73. The NCe003 starch showed a shift toward green (negative *a**) while all others tended toward red (positive *a**).

During homogenization of the fresh roots in the starch isolation process, NCe002 and NCe003 were observed to present green and purple colouration respectively when the root tissues were exposed to atmospheric oxygen. This may be as a result of actions of inherent oxidative enzymes like polyphenol oxidase and peroxidase which have been identified to induce major browning effects in cocoyam (Alline *et al.*, 2016). Some of these colours were probably carried over into the starch as evidenced also by the slightly high CIE *b** values reported for the native starches (2.06-7.34). Calculated *delta*chroma (ΔC) values ranged from -2.32 in NXs003 to 3.04 in NCe002 with significant differences among the starches and the method of modification. A negative shift in the chromatic space for NCe001, NCe004, NCe005, NCe010 and NXs003 was observed indicating that these samples were less saturated or chromatic in comparism with the commercial cassava starch used as control. This also indicates a lower tolerance for *a** and *b** values in quality control. . However, hue angle values were in the range of 72.63-85.39^o while total colour difference, ΔE^* ranged from 2.77 (NXs003) to 30.57 (NCe003) for all native starches. Colour in starch is imparted due to the presence of constituent polyphenolic compounds, ascorbic acid and carotene (Falade and Ayetigbo, 2015) which have significant effect on the quality and therefore commercial acceptability of final product. High lightness and low chroma values are desirable in starch of high commercial quality (Gani *et al.*, 2010). Native starches from cocoyam and bitter yam cultivars showed significantly different variations with modification methods.

Annealing generally caused an increase in lightness and hue angle values with decreasing values of *a**, *b**, *delta*chroma and total colour difference. This effect was more evident especially in NCe003, NCe001 and the bitter yam starches. Annealing treatments resulted in a significant shift of *L** from 64.32 to 75.89, *b** from 6.67 to 6.10, ΔC from 2.44 to 1.71, hue from 77.43 to 89.44 and ΔE from 30.57 to 18.08 in NCe003 starch. This shows an obvious improvement in colour quality parameter for the annealed starch. Similar trend observed for the bitter yam yellow cultivar starch caused an increase in lightness from 88.22 to 94.22, *a** reduced from 1.09 to 0.61, *b** from 6.44 to 5.70, ΔC from 2.14 to 1.35, ΔE from 12.73 to 3.26 and hue increased from 80.36 to 83.13. These observations agree with results obtained for potato starch films after annealing treatments (Zavareze *et al*, 2012) where values of total colour difference and *a** were significantly lowered by the treatment but contrary to that of Falade and Ayetigbo (2015) where annealing, acid hydrolysis and citric acid modification of native white bitter yam starch resulted in reduction of *L**, *a** and *b** values. Degradation of the oxidized polyphenolic starch components during equilibration of granules with the aqueous environment encountered during the annealing process could be responsible for these changes. Acid hydrolysis also produced significant improvements in the colour properties of NXs002 and NCe003 starches as indicated by higher lightness values (from 64.32 to 72.74 for NCe003) though not as high as annealing treatment (75.89).

Lawal (2004) reported decrease in ash, fats, protein and amylose contents of acid-thinned new cocoyam starch. It implies a degradation of these heterogeneous colour components due to acid hydrolysis and could therefore be adduced as the reason for colour improvements in these samples. However, yellowness (*b**) and redness (*a**) indices were found to generally increase except for the NXs002, NCe010 and the white bitter yam starches. The decreased colour purity of these acid-thinned starches may have been influenced by the extended treatment time for the acid hydrolysis (192 hours) indicated by the increased saturation. Similar trend was found for acid-hydrolysed *Araucaria angustifolia* seed starch where a significant increase in *a** and *b** values was reported (Goncalves *et al.*, 2014). Hue angle values were found to be in the first quadrant (reddish-yellow region) of the major colour component corresponding to angle $<90^o$. Hue angle of modified starches varied from 57.82^o to 89.44^o.

Heat-moisture treatments at 18, 24 and 27% moisture levels were found to negatively and significantly affect all the colour parameters with increasing moisture contents (Table 4.3). Generally, the lightness and hue angle reduced while yellowness, redness, deltachroma and total colour difference increased as the moisture content increased. This can be attributed to possible occurrence of Maillard reaction between reducing sugars in the starch and residual amino group in the starch protein fraction favoured by presence of moisture and also to possible partial cooking occurring in the heat-moisture treated starches during modification. Variation in material structure or composition could be reflected through colour perception (Nemtanu, 2008). The objective colour evaluation system of the Commission Internationale de l’Eclairage (CIE) provides a standard scale that defines a 3-dimensional tolerancing space for industrial colour quality control and formula adjustment by the relative difference between a standard and the sample under evaluation as a measure of commercial acceptability (Hunter Laboratory Manual, 2001).

4.4 Cocoyam and bitter yam starches granule microstructure

Starch granule shapes and sizes in this study varied significantly with crop and cultivar but not with modification. Starches are grouped into large, medium, small or very small size ranges according to a classification range developed by Lindeboom *et al.* (2004) in which large granules have sizes larger than 25µm, medium 10-25 µm, small 5-10 µm and very small granules having sizes less than 5 µm. The average granule sizes of starches under study estimated by taking average of 10 determinations of granule diameter gave a range of sizes in the order: NCe010> NXs002 >NCe005 >NXs003 >NXs001 >NCe001 >yellow bitter yam >white bitter yam >NCe002 >NCe003 >NCe004. The NCe010, NXs002 and NCe005 starches fall within the medium granule range (15.5, 13.1, 10.0 µm respectively) with the NCe010 having the largest granule sizes while NXs001 (7.8 µm) and NXs003 (9.2 µm) are small, and NCe001 (3.9 µm), NCe002 (2.5 µm), NCe003 (1.9 µm), NCe004 (1.2 µm), yellow (2.7 µm) and white (2.0 µm) cultivars of bitter yam are grouped in the very small category (Table 4.5). There were no large granules found among the starches from cocoyam and bitter yam cultivars investigated in this study. The native and modified NCe003 (Figure 4.3(i-vi)) and NCe004 (Figure 4.4 (i-vi)) starches were similar in size and were generally round and angular in shape. The modifications did not exert any significant effect on the starch granule size except for some level of clumping and aggregation of the granules observed with increasing level of moisture in the heat-moisture treated starches. Heat-moisture treatment did not produce any significant alteration of size and shape in the starches, an observation similar to results obtained for cassava (Abraham, 1993), cocoyam (Lawal, 2005), wheat and oats starches (Hoover and Vasathan, 1994).

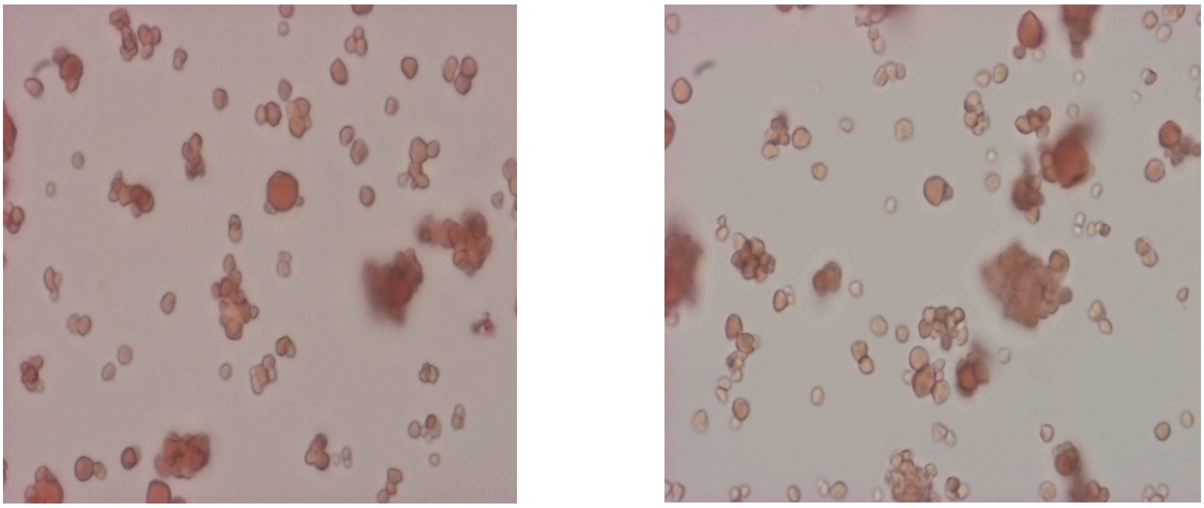
Starch granule morphology is due to the ratio and arrangement of amylose and amylopectin to produce concentric rings of amorphous and crystalline regions (Palma-Rodriguez *et al.*, 2012). Granule sizes have been found to have significant effect on starch functionality (Otegbayo *et al.*, 2014) while differences in starch granule shapes which do not affect functionality have been known to be mainly influenced by the environment of growth (Moss, 1976). Starches with large granules were more easily isolated than those with smaller granules as observed in this study. This could be due to the fact that smaller granules were trapped within the network of other starch components (mucilage, fibre and fats) and so do not sediment readily.

Table 4.5. Average granule sizes (µm) and shapes of native and modified cocoyam starches

Cultivar	Native (µm)	Annealed (µm	Acid (µm)	HMT18 (µm)	HMT24 (µm)	HMT27 (µm)	Shapes
NCe001	3.5±1.03^{ef}	3.62±0.63^{ef}	3.54±0.67^{ef}	3.31±0.27^{ef}	3.24±1.00^{ef}	3.27±1.01^{ef}	Angular, round, clustered, broken
NCe002	2.46±0.08^{f}	2.01±0.43^{f}	1.86±0.09^{g}	1.97±0.40^{g}	1.73±1.04^{g}	1.78±0.70^{g}	Angular, round, aggregated, flattened
NCe003	1.95±0.10^{g}	1.62±0.5^{g}	1.79±0.62^{g}	2.13±1.00^{f}	2.12±0.33^{f}	2.78±0.62^{f}	Rounded, clustered
NCe004	1.17±0.43^{g}	1.87±1.00^{g}	1.88±0.20^{g}	1.73±1.03^{g}	2.42±0.69^{f}	2.43±1.06^{f}	Round,
NCe005	10.01±3.11^{c}	9.80±2.54^{d}	9.87±1.08^{d}	11.85±2.03^{b}	11.15±2.93^{c}	11.85±2.30^{b}	Polygonal, round, angular, broken, fragmented and flattened
NCe010	15.51±2.40^{a}	14.42±1.98^{ab}	14.63±1.44^{ab}	14.21±4.31^{ab}	14.03±2.43^{ab}	_	Polygonal, round, angular, broken, fragmented and flattened
NXs001	7.77±1.90^{de}	7.87±1.81d^{e}	7.75±1.22^{de}	6.24±1.71^{e}	6.37±2.02^{e}	_	Pentagonal, polygonal and clustered
NXs002	13.06±3.62^{b}	11.05±3.98^{c}	9.44±2.00^{d}	10.67±2.06^{c}	10.56±1.45^{c}	_	Round and angular
NXs003	9.22±1.87^{d}	8.59±1.77^{d}	8.91±1.76d	9.12±2.44^{d}	8.52±1.34d	_	Round and angular
Yellow	2.70±0.54^{f}	2.65±0.53^{f}	2.72±1.00^{f}	2.70±1.32^{f}	2.70±1.11^{f}	2.81±0.61^{f}	Angular, irregular, rounded
White	2.00±0.10^{f}	2.02±1.12^{f}	1.99±0.31^{g}	2.30±0.55^{f}	2.00±0.32^{f}	2.00±0.36^{f}	Angular, irregular, rounded

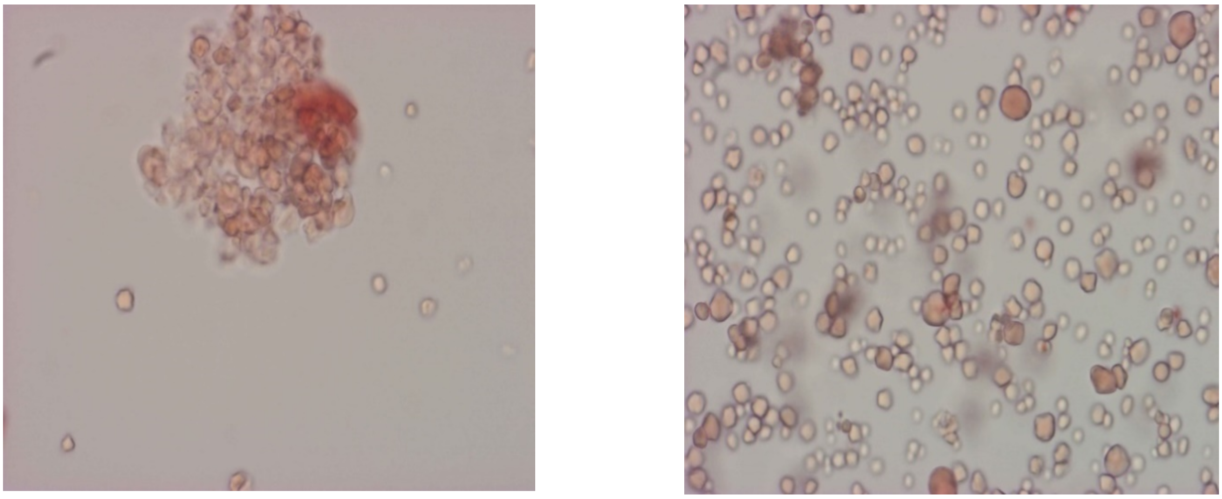
Means in columns not followed by same alphabet(s) are significantly different at 5% level ($P \leq 0.05$).
Data expressed as means (of 10 determinations) ±SD

Starches with small granules may therefore be utilized in applications that require smooth texture as stabilizers and fat replacers. Otegbayo *et al.* (2014) reported native *Dioscorea dumetorum* starch in the small size range (7-10µm) with pentagonal and hexagonal architecture while similar result was obtained by Sefa-Dedeh and Agyir-Sackey (2002) for *Colocasia spp.* Falade and Ayetigbo (2015) reported a range of 2.5-7.5µm with random, irregular and polyhedral shapes for native and modified white bitter yam starch. These values are higher than those in this study. However, Farhat *et al.,* (1999) and Rasper and Coursey (1967) reported size ranges of 3-5µm and 1-3µm, respectively, with rounded structures; closer to the range presently observed. The different shapes reported for *Dioscorea dumetorum* starches by different authors could be as a result of the very small sizes of the starch granules making it difficult to evaluate their exact surface features except at very high magnifications. *Xanthosoma sagittifolium* starches were reported to be oval-kidney or roughly spherical shaped with small sizes (Sefa-Dedeh and Agyir-Sackey, 2002). In this study, NCe001 native starch granule sizes showed no significant variation with modification, presenting angular features (Table 4.5 and Figure 4.1 (i-vi)). *Colocasia spp.* starches were generally angular, rounded or polygonal while the *Xanthosoma spp.* were pentagonal, angular and rounded in shape. Bitter yam starches were also observed to be round or angular in feature. Heat-moisture treatments caused aggregation, clustering or flattening of some starch granules of NCe001 starch at 18 and 24% moisture levels. (Figure 4.1 (i, ii and iii)). This may be attributed to the effect of high temperature of the modification treatments. Similar granule aggregation with hydrothermal modification was obvious in NXs001 (Figure 4.7 (i)), white bitter yam (Figure 4.11 (i-iii)), NCe010 (Figure 4.6 (i and ii)) and NCe005 (Figure 4.5 (i-iii)). Some forms of fragmentation and fissures were observed in the acid-hydrolyzed starches evidenced by increased number of small granules in the micrograph of NCe005, NCe003 and NXs003 compared with the native starches. There was no significant difference between the native and annealed starches of NCe001 (Figure 4.1 (v and vi)).



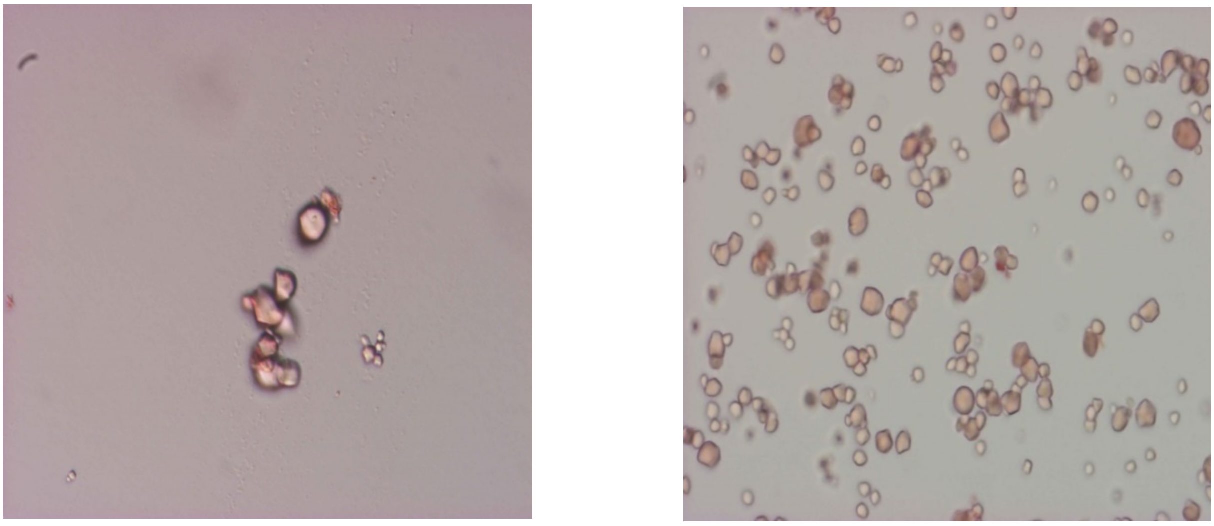
(i) NCe001 (HMT18)

(iv) NCe001 (Acid)



(ii) NCe001 (HMT24)

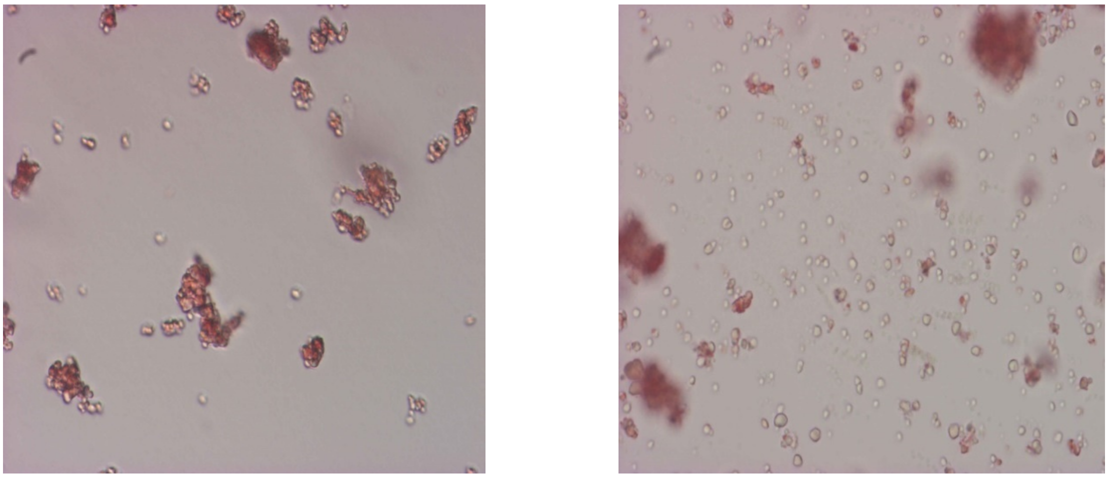
(v) NCe001 (Annealed)



(iii) NCe001 (HMT27)

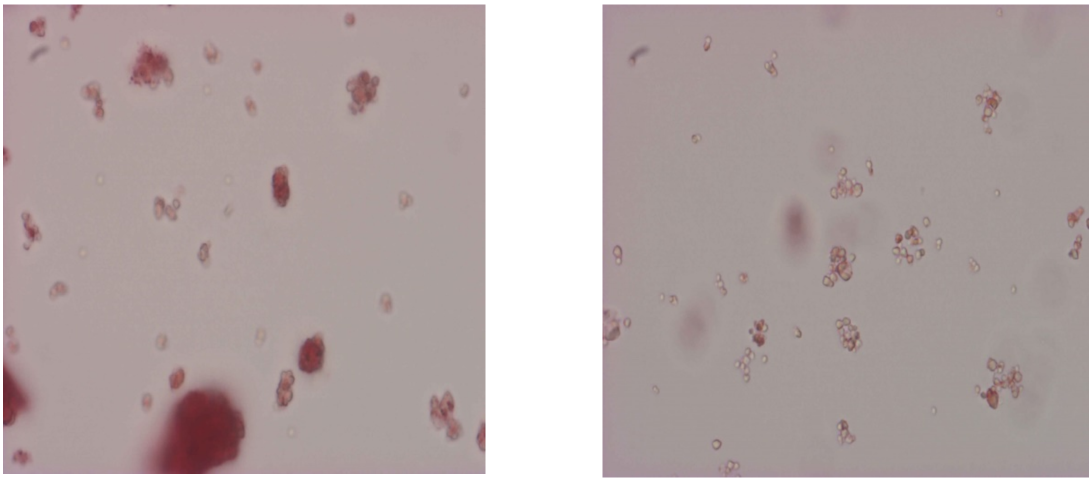
(vi) NCe001 (Native)

Figure 4.1. Light micrograph of NCe001 native and modified cocoyam starches **(X40)**



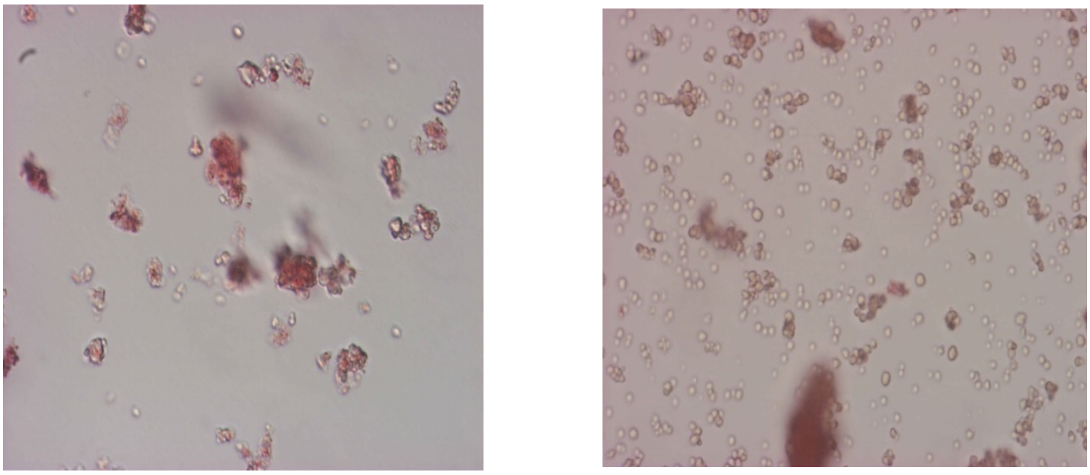
(i) NCe 002 (HMT18)

(iv) NCe 002 (Acid)



(ii) NCe 002 (HMT 24)

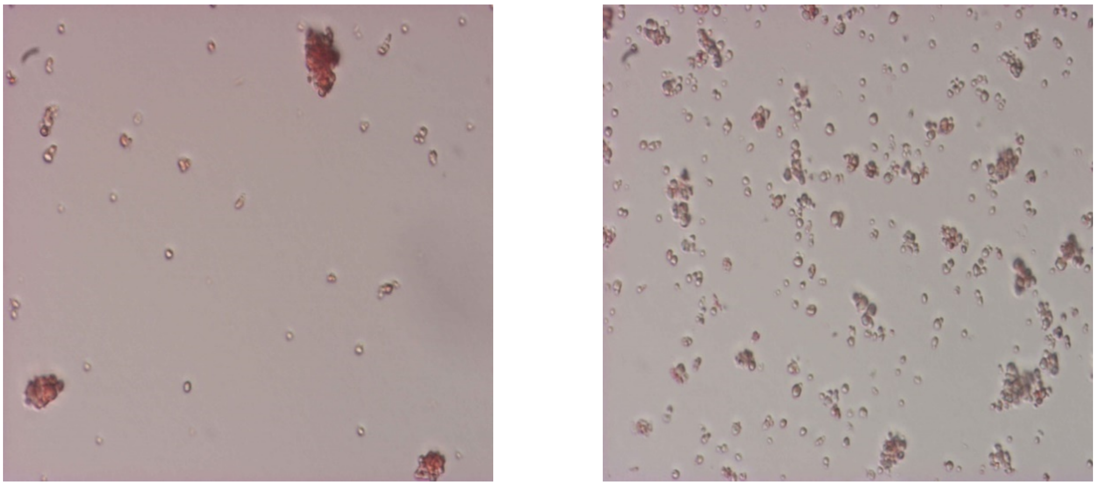
(v) NCe 002 (Annealed)



(iii) NCe 002 (HMT 27)

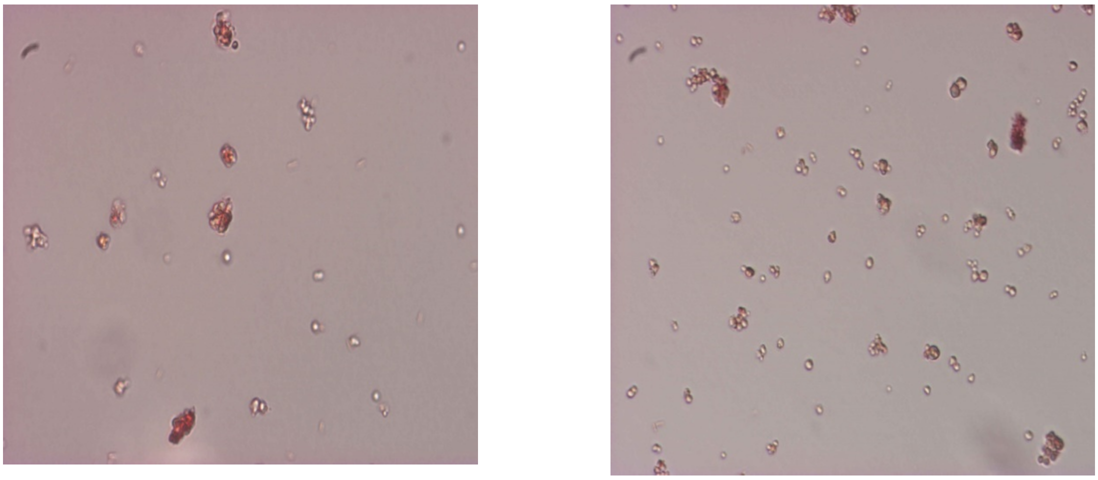
(vi) NCe 002 (Native)

Figure 4.2. Light micrograph of NCe002 native and modified cocoyam starches **(X40)**



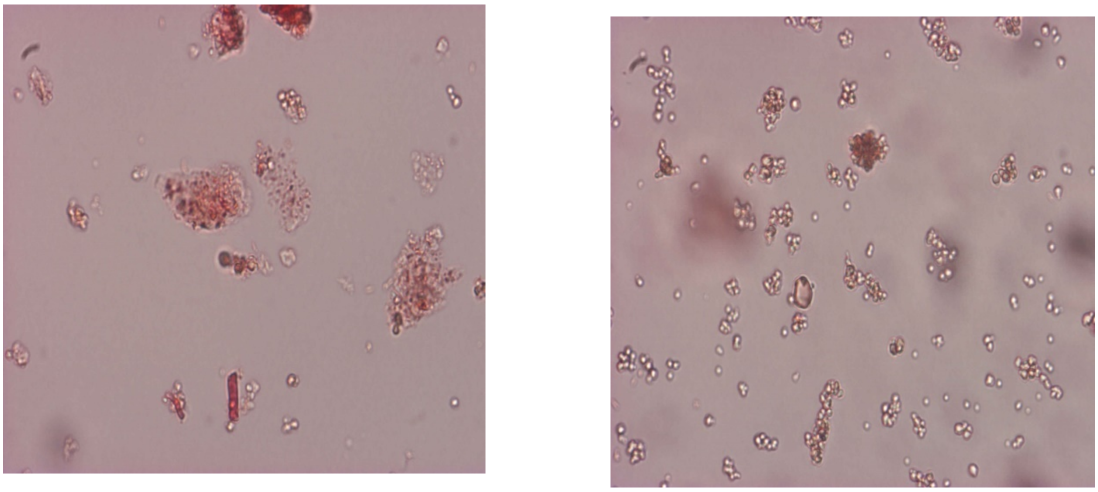
(i) NCe 003 (HMT 18)

(iv) NCe 003 (Acid)



(ii) NCe 003 (HMT 24)

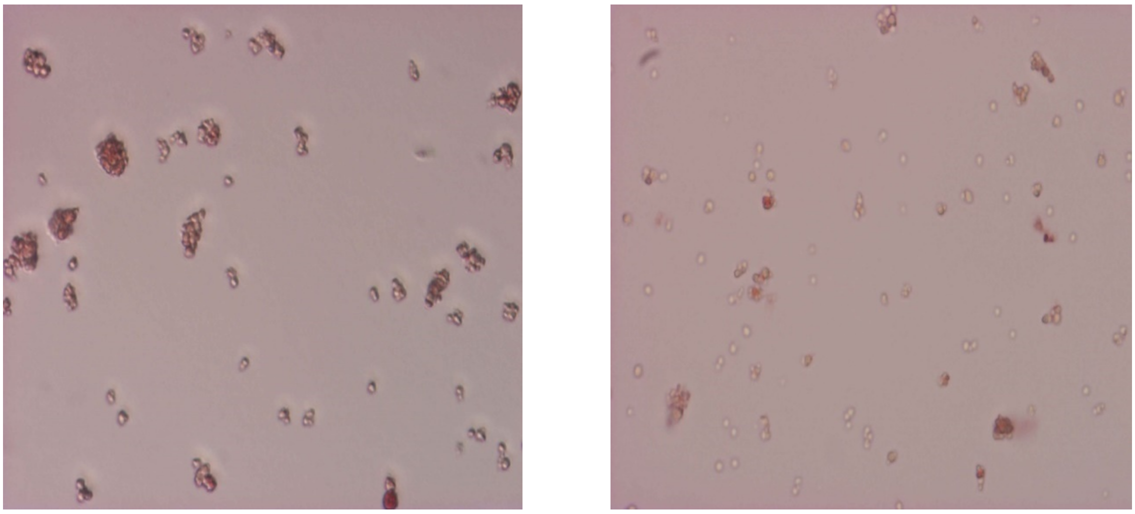
(v) NCe 003 (Annealed)



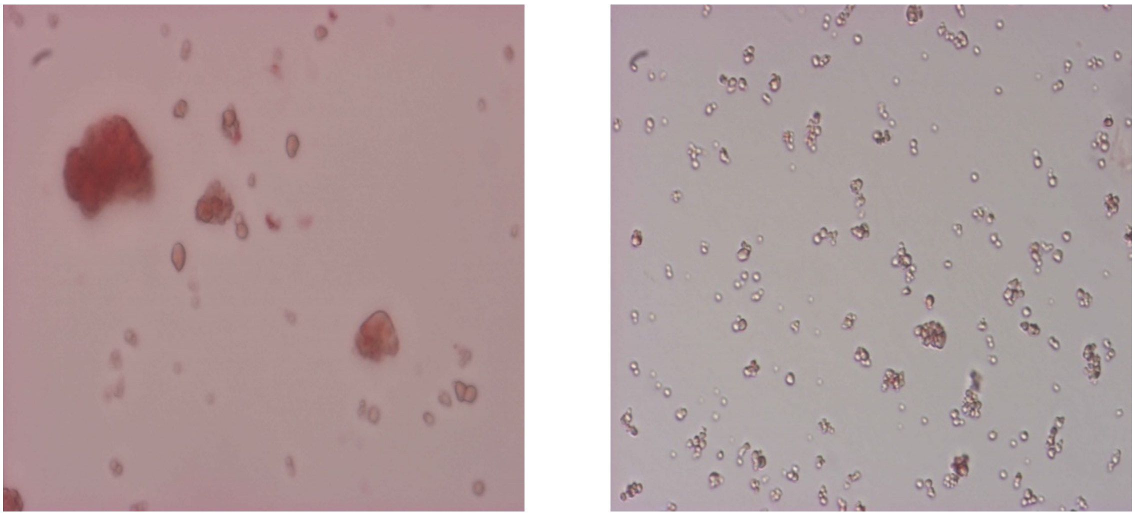
(iii) NCe 003 (HMT 27)

(vi) NCe 003 (Native)

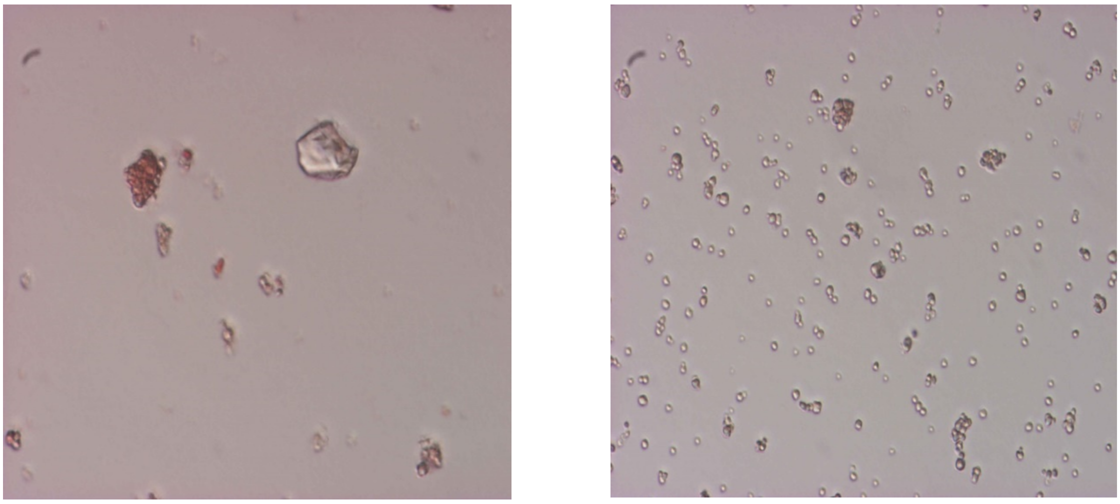
Figure 4.3. Light micrograph of NCe003 native and modified cocoyam starches **(X40)**



(i) NCe 004 (HMT 18) (iv) NCe 004 (Acid)

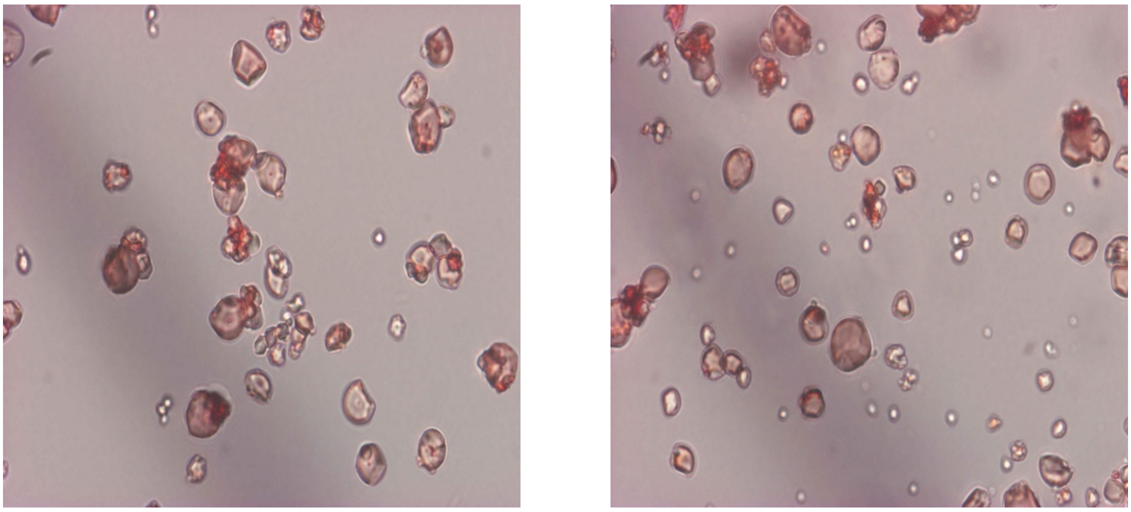


(ii) NCe 004 (HMT 24) (v) NCe 004 (Annealed)



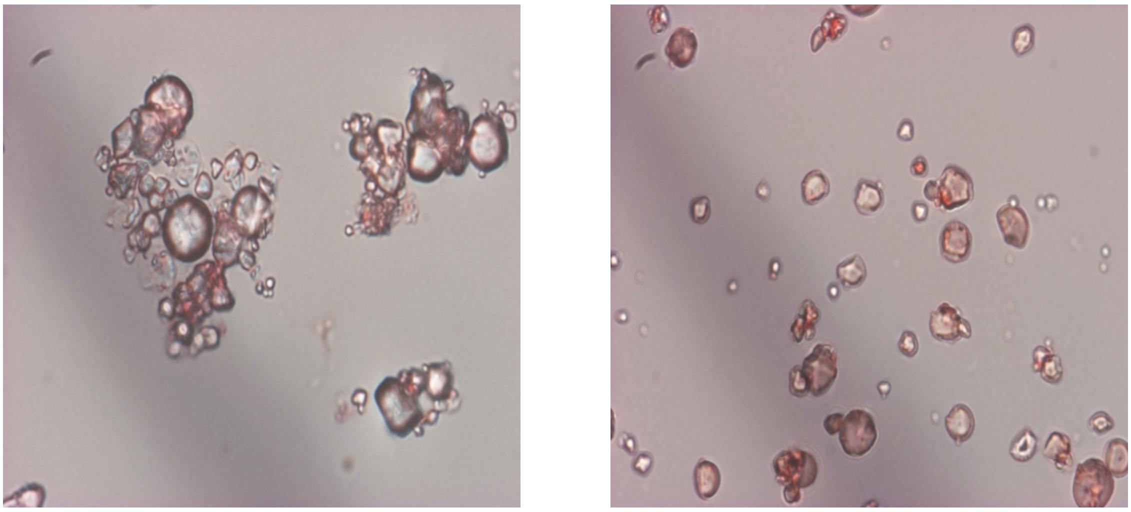
(iii) NCe 004 (HMT 27) (vi) NCe 004 (Native)

Figure 4.4. Light micrograph of NCe004 native and modified cocoyam starches **(X40)**



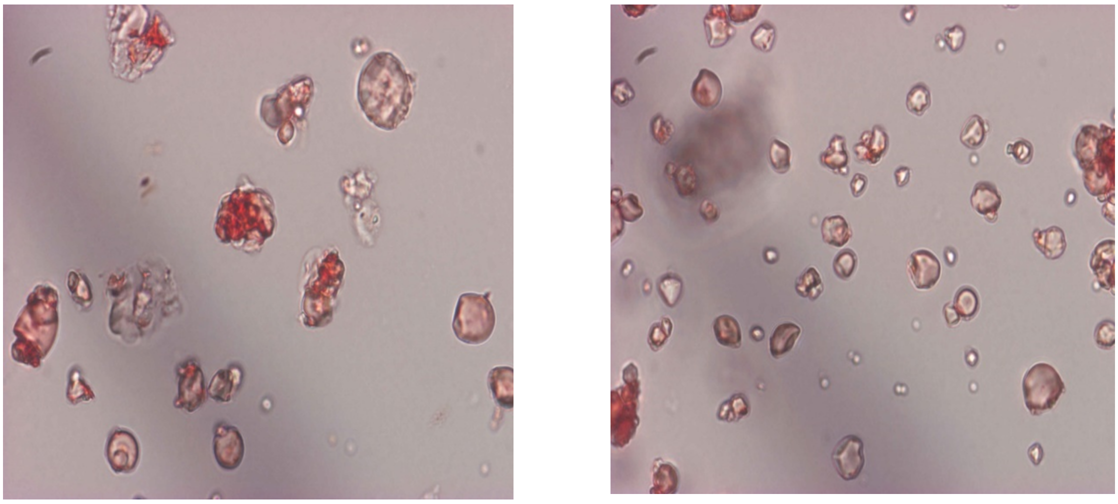
(i) NCe 005 (HMT 18)

(iv) NCe 005 (Acid)



(ii) NCe 005 (HMT 24)

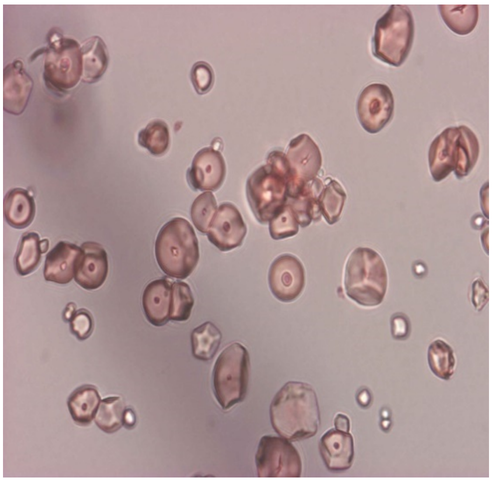
(v) NCe 005 (Annealed)



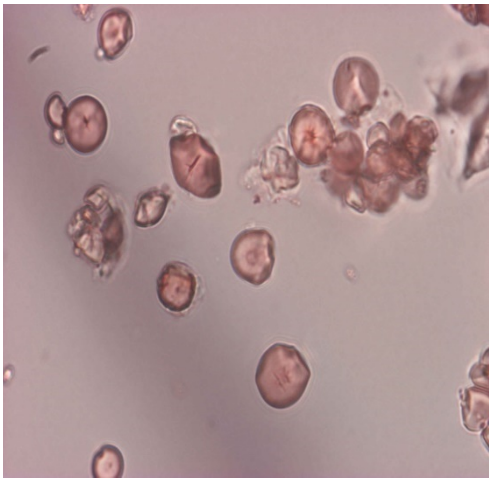
(iii) NCe 005 (HMT 27)

(vi) NCe 005 (Native)

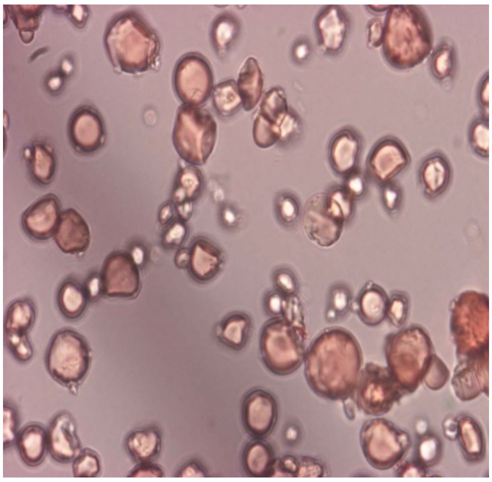
Figure 4.5. Light micrograph of NCe005 native and modified cocoyam starches **(X40)**



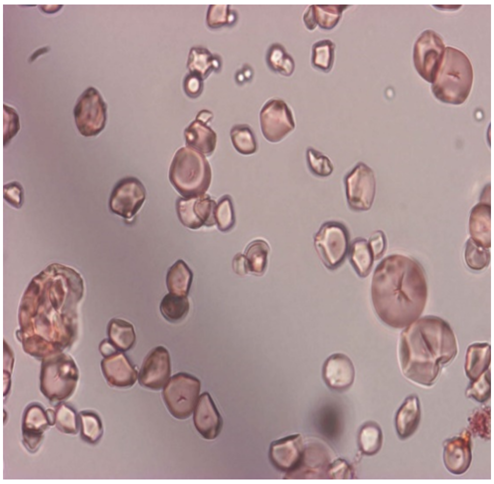
(i) NCe 010 (HMT 18)



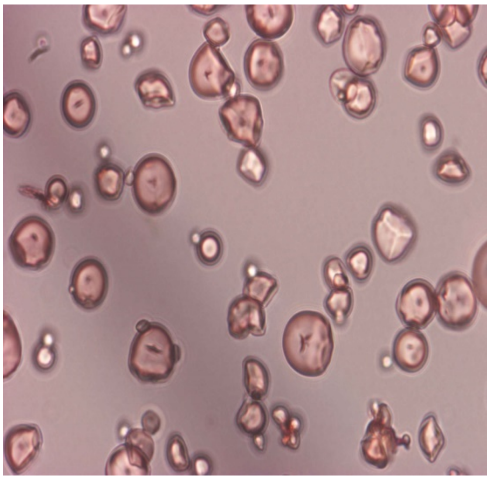
(ii) NCe 010 (HMT 24)



(iii) NCe 010 (Acid)

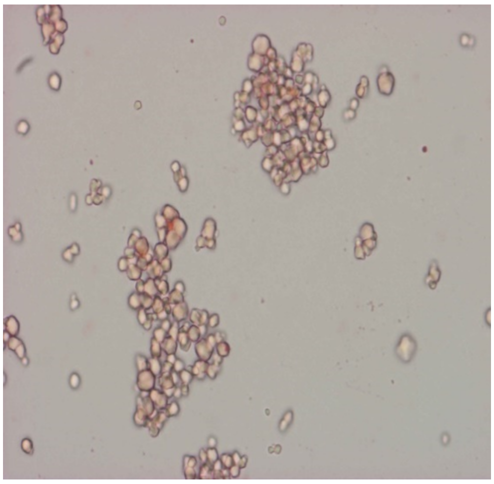


(iv) NCe 010 (Annealed)

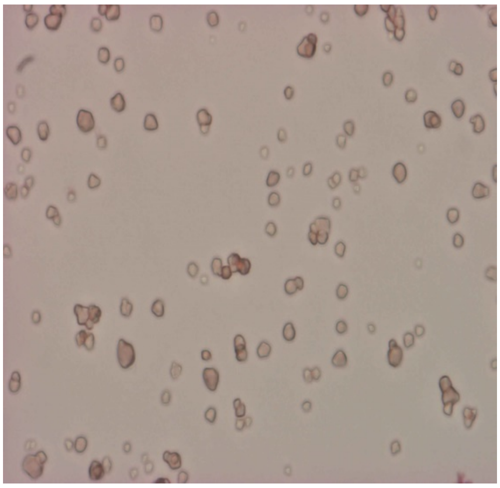


(v) NCe 010 (Native)

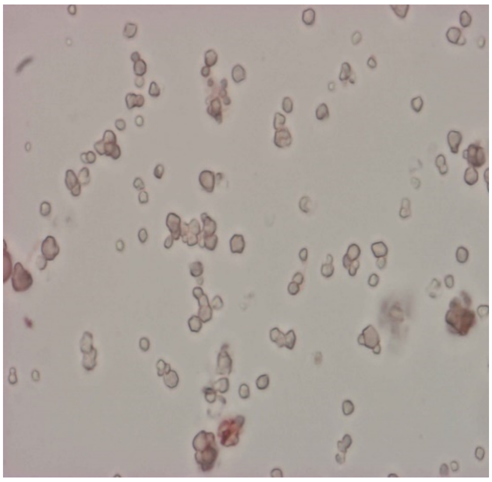
Figure 4.6. Light micrograph of NCe010 native and modified cocoyam starches **(X40)**



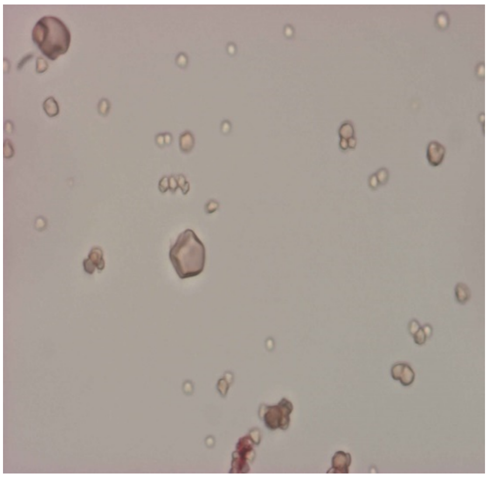
(i) NXs 001 (HMT 18)



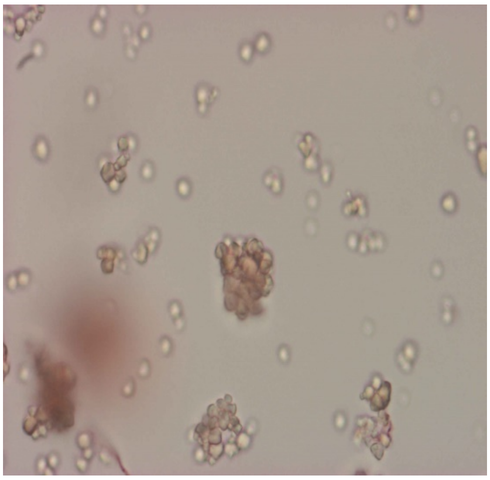
(iv) NXs 001 (Annealed)



(ii) NXs 001 (HMT 24)

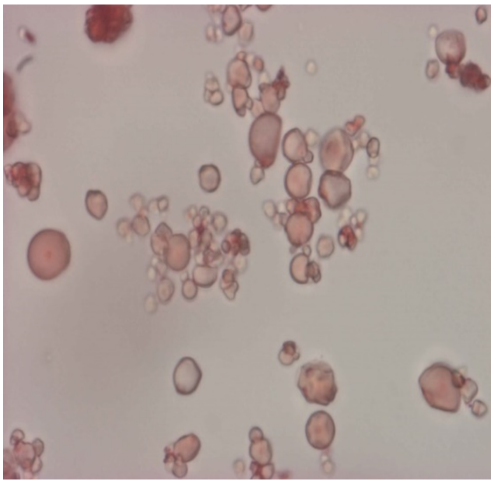


(v) NXs 001 (Native)

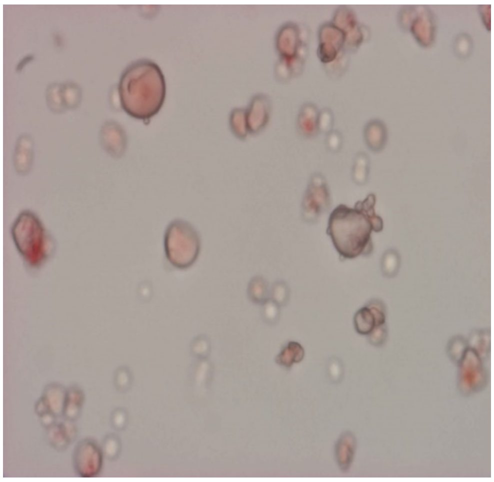


(iii) NXs 001 (Acid)

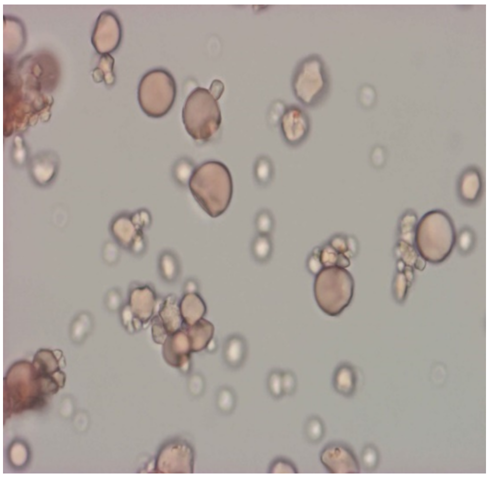
Figure 4.7. Light micrograph of NXs001 native and modified cocoyam starches **(X40)**



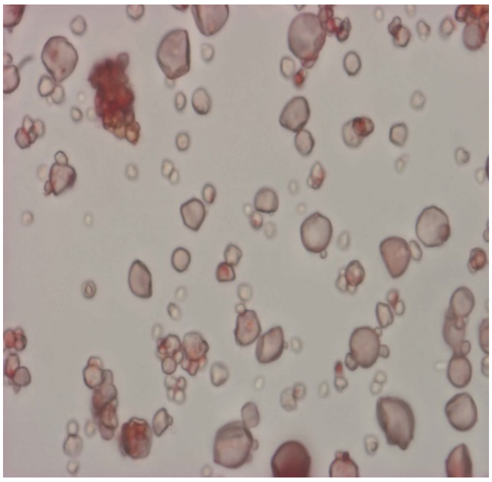
(i) NXs 002 (HMT 18)



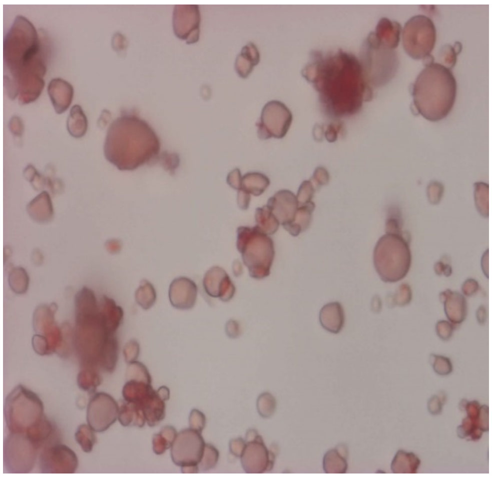
(ii) NXs 002 (HMT 24)



(iii) NXs 002 (Acid)

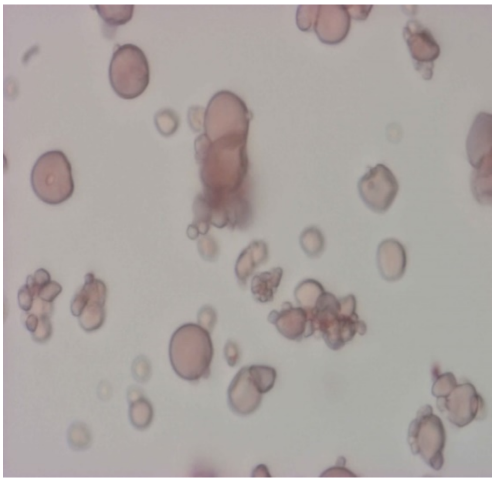


(iv) NXs 002 (Annealed)

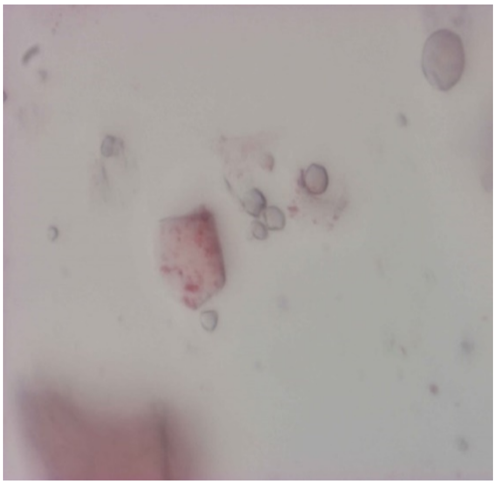


(v) NXs 002 (Native)

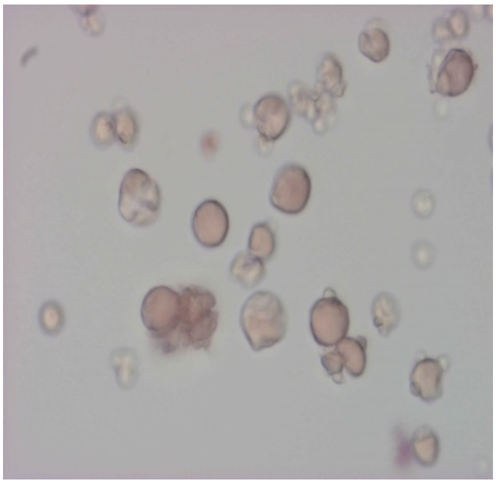
Figure 4.8. Light micrograph of NCe002 native and modified cocoyam starches **(X40)**



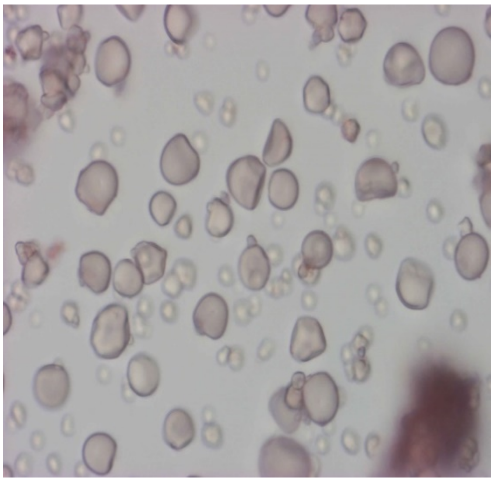
(i) NXs 003 (HMT 18)



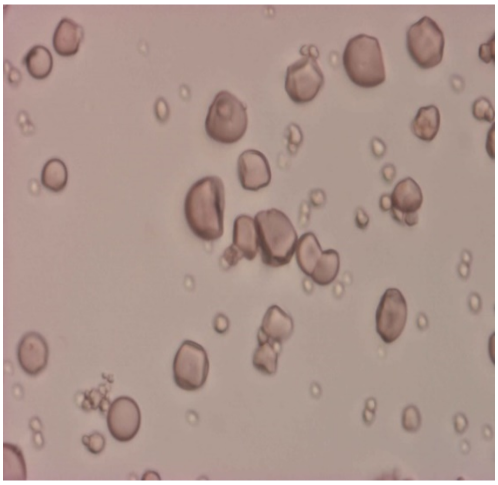
(ii) NXs 003 (HMT 24)



(iii) NXs 003 (Acid)

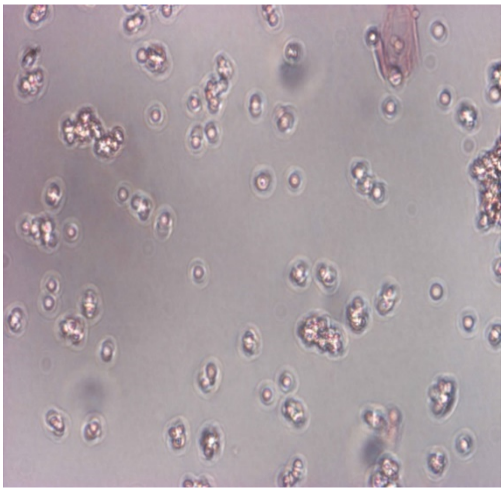


(iv) NXs 003 (Annealed)

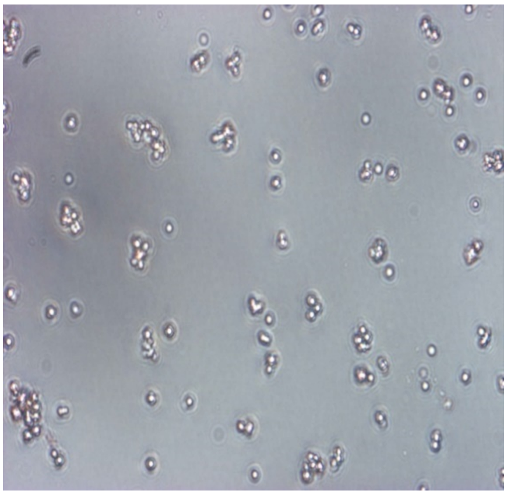


(v) NXs 003 (Native)

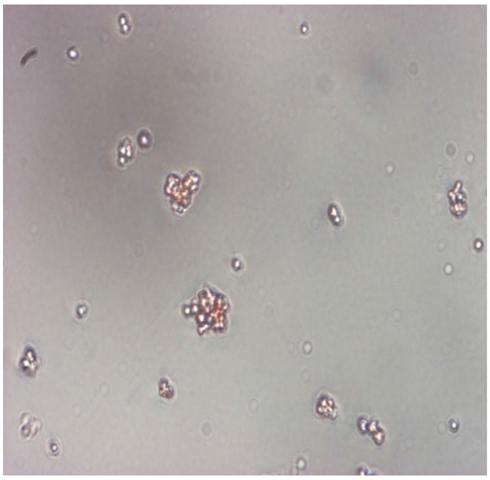
Figure 4.9. Light micrograph of NCe003 native and modified cocoyam starches **(X40)**



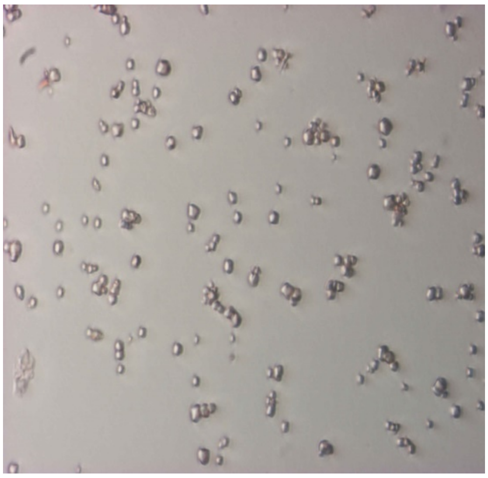
(i) *D. dumetorum* Yellow (HMT18)



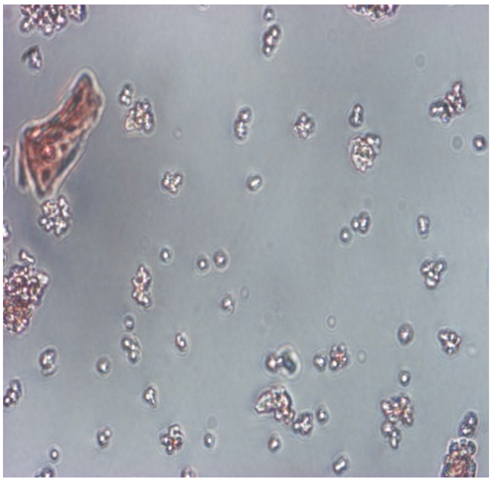
(iv) *D. dumetorum*Yellow (Acid)



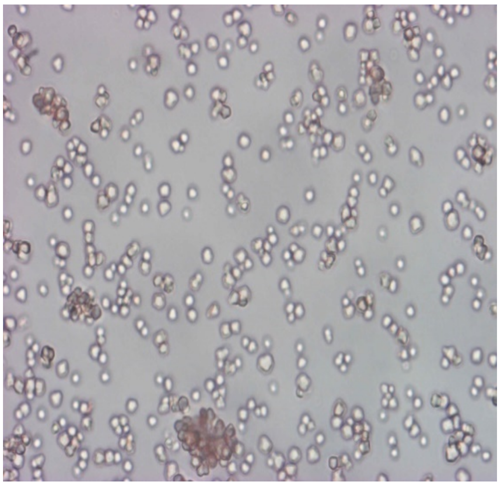
(ii) *D. dumetorum* Yellow (HMT24)



(v) *D.dumetorum*Yellow(Annealed)

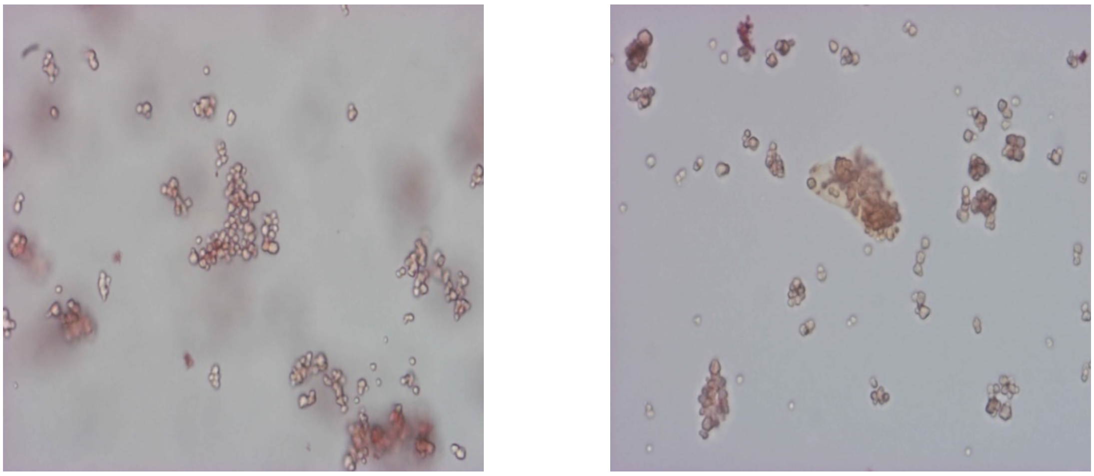


(iii) *D.dumetorum*Yellow (HMT27)



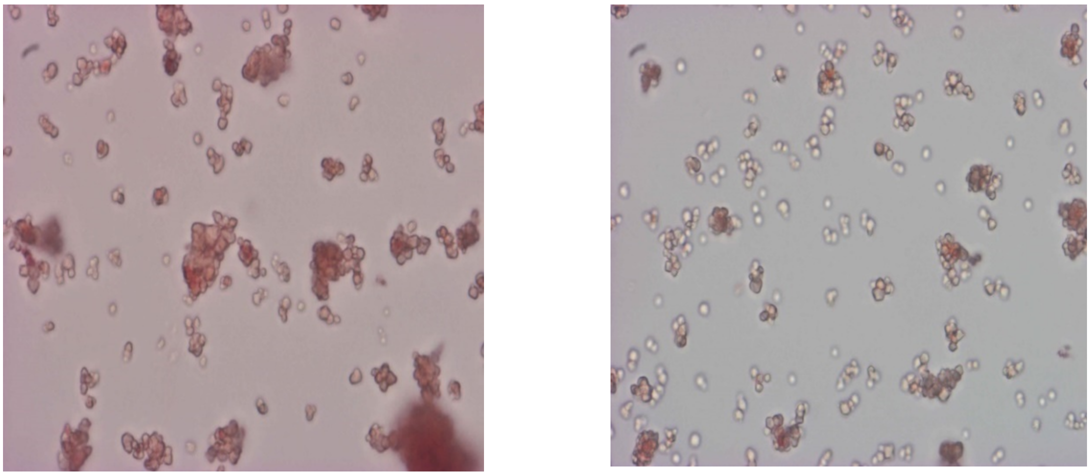
(vi) *D.dumetorum* Yellow (Native)

Figure 4.10. Light micrograph of Yellow cultivar of native and modified bitter yam starches **(X40)**



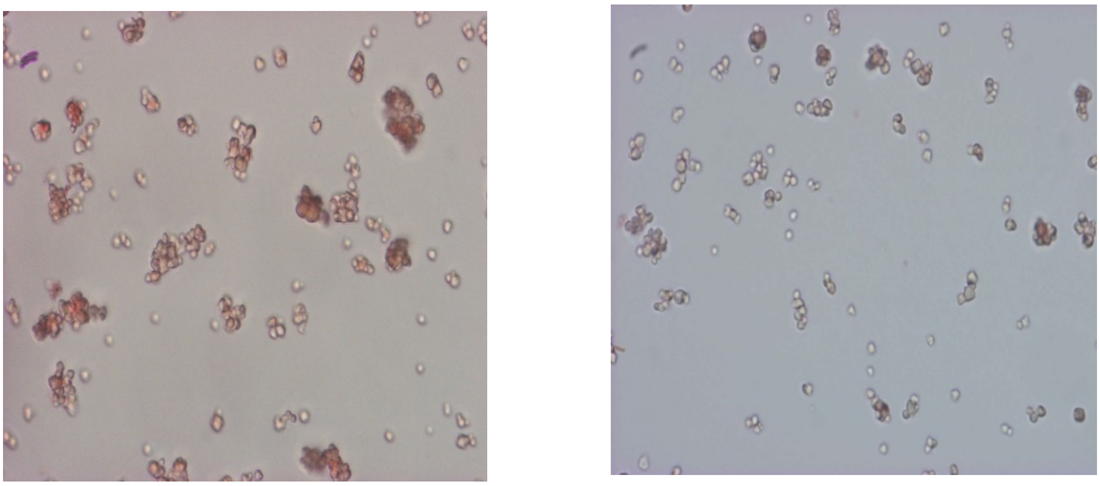
(i) *D.dumetorum* White (HMT18)

(iv) *D.dumetorum* White (Acid)



(ii) *D.dumetorum* White (HMT24)

(v) *D.dumetorum* White (Annealed)



(iii) *D.dumetorum* White (HMT27)

(vi) *D.dumetorum* White (Native)

Figure 4.11. Light micrograph of white cultivar of native and modified bitter yam starches **(X40)**

4.5 Amylose contents of native and modified cocoyam and bitter yam starches

Relative proportions of amylose and amylopectin contents of starch are important factors that affect almost all starch physicochemical properties. Amylose contents have been shown to affect gelatinization, retrogradation and pasting parameters of different wheat starches (Sasaki *et al.,* 2000) and starches from other sources (Czuchajowska *et. al.*, 1998; Fredriksson *et. al.,* 1998; Yuryev *et. al.,* 1998). Significant differences (P<0.05) were observed in the amylose contents of native cocoyam and bitter yam cultivar as shown in Figures 4.12-4.14. The amylose contents of the *Colocasia spp* starches ranged from 10.11 to 24.71% (Figure 4.12) and that of the *Xanthosoma spp* from 18.21 to 37.08% (Figure 4.13). The *Xanthosoma* spp showed considerably higher levels of amylose. Similar observation of higher amylose contents in *Xanthosoma sagittifolium* than *Colocasia esculenta* has been reported earlier by Perez *et al,* (2005). The variation in amylose content was narrow within the *Colocasia spp.* starches with no significant difference among the NCe001, NCe002 and NCe003 cultivars. These results agree with the findings of Mweta *et al.* (2009) who reported Malawian cocoyam amylose contents of 10.6-21.0%. Different amylose contents have been reported as 26.7% (Tetchi *et al*., 2007b), 33.3% (Nwokocha *et al*., 2009), 18-22% (Jane *et al*, 1992) and 14.7-30.8% (Aboubakar *et al*, 2008) elsewhere for cocoyam cultivars. These variations could be attributed to differences in genotype, methods of determination, climatic condition and planting location. In this study, the lowest amylose content was recorded for the white cultivar of bitter yam (8.69%) while the highest was found in NXs002 (37.08%). The starches could be grouped together based on amylose contents. The amylose content of NCe005, NXs003 and yellow bitter yam were not significantly different. Also, NCe010 and NXs001 starches were not significantly different in amylose contents. The variation of amylose content within the same botanical source could be due to differences in genotypic origin and culture conditions (Gao *et al.,* 2014).

The overall quality, functional and nutritional characteristics of starch-containing foods are dependent on changes that starches undergo during processing, modification and storage conditions. Hydrothermal modifications at 18, 24 and 27% moisture levels resulted in progressive decrease of amylose contents with increasing moisture contents in the NCe002, NCe010, NXs001, NXs002, NXs003 and both cultivars of the bitter yam starches (Figure 4.15), suggesting a specie-specific pattern among the heat-moisture modified *Xanthosoma sagitifollium* and *Dioscorea dumetorum* starches. The reduction may be attributed to effect

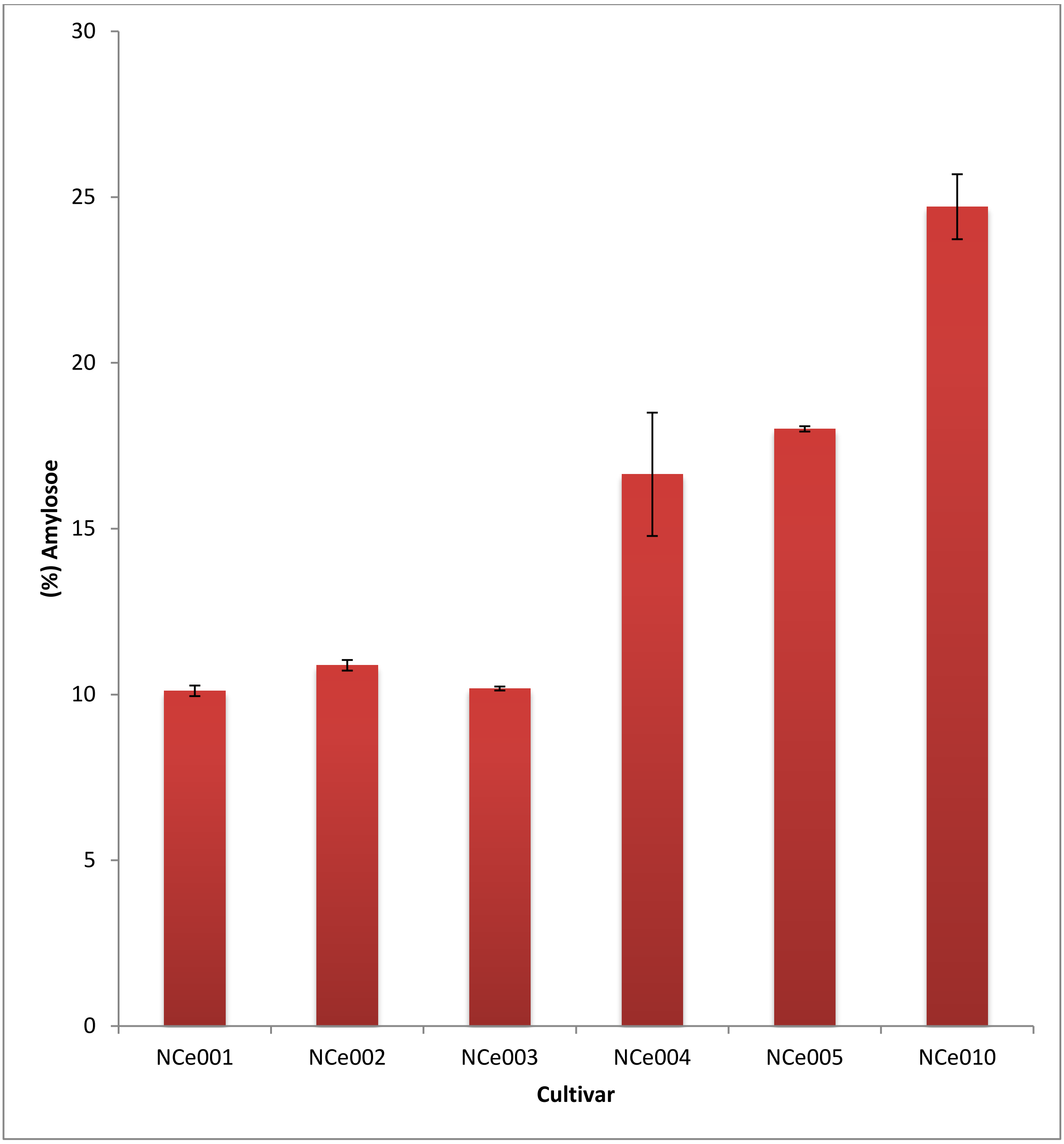


Figure 4.12. Amylose contents of native *Colocasia esculenta* starches

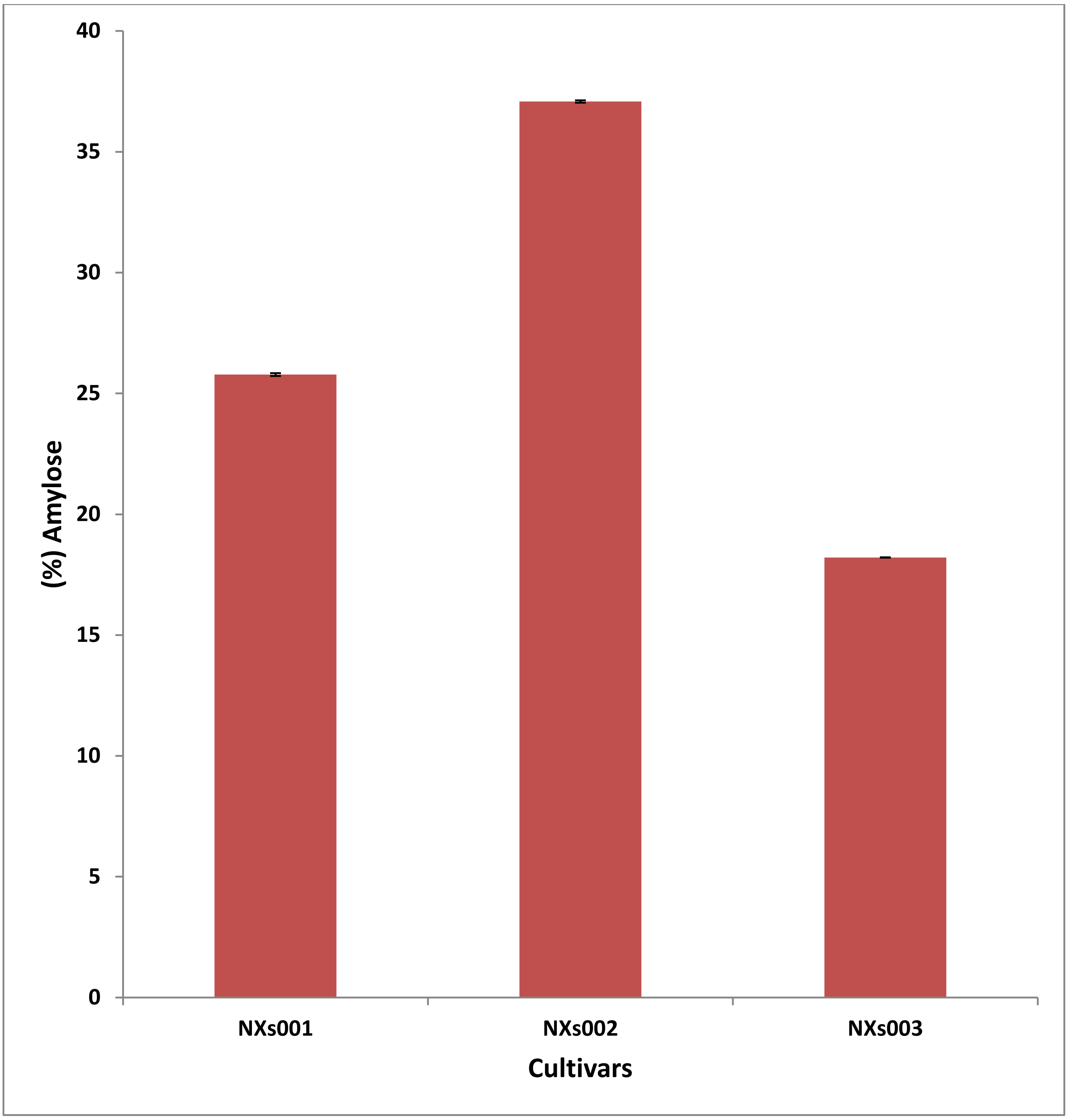


Figure 4.13. Amylose contents of native *Xanthosoma sagittifolium* starches

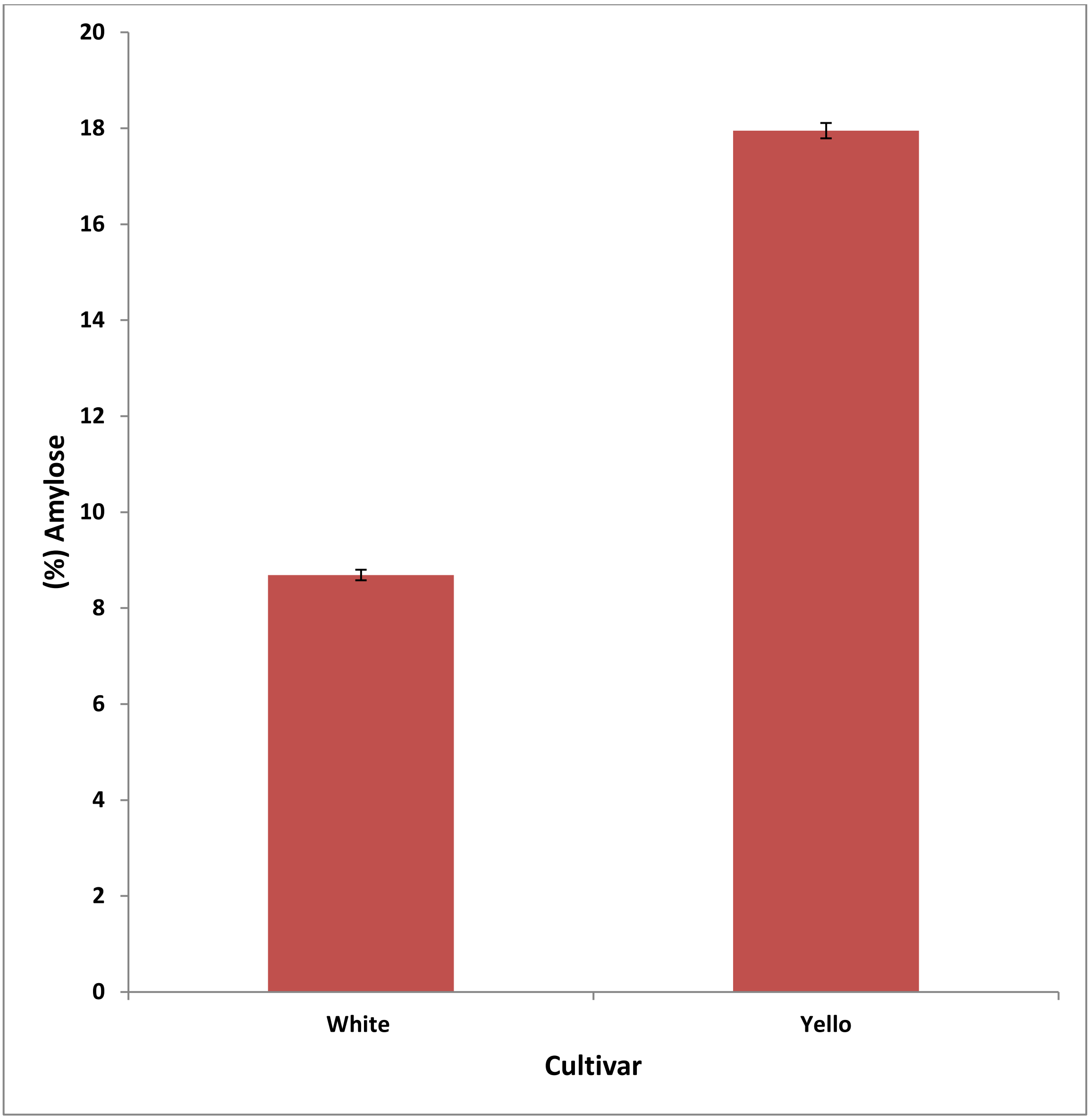


Figure 4.14. Amylose contents of native *Dioscorea dumetorum* starches

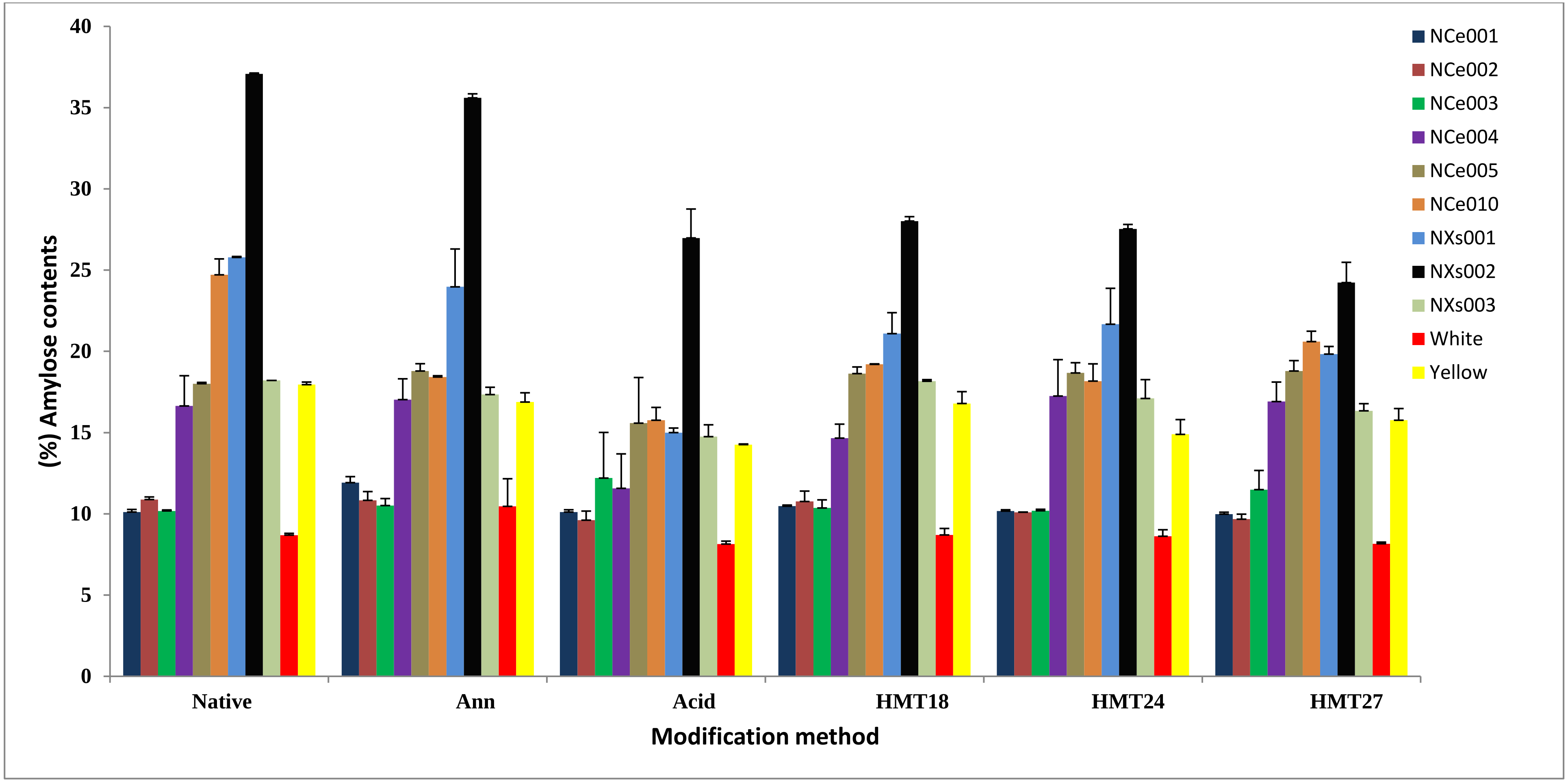


Figure 4.15. Effect of modification on amylose contents of native starches of cocoyam and bitter yam cultivars

of amylose leaching accompanying gelatinization conditions the starches encountered during the modification treatment. The leached amylose may have bound with lipid fractions in the starch to form amylo-lipid complexes which would lead to a reduced estimation of amylose contents. The results obtained for acid hydrolyzed starch appeared to be not specie-specific for *Colocasia spp.* as NCe001, NCe003, NCe004 and NCe005 amylose contents increased from 10.11 to 11.92, 10.18 to 10.10.51, 16.64 to 17.03 and 18.01 to 18.79, respectively, while NCe002 decreased from 10.88 to 10.83. All of the *Xanthosoma spp* had their amylose contents significantly lowered by acid-thinning. The branched nature of amylose fraction in starch makes the branched points in the amorphous region more accessible to hydrolyzing agents like acids. Size of the disordered amorphous core at the reducing end of the lightly branched long glucan chain of starch granules have been related to the amylose contents of starch (Wang *et al.*, 2015). As evident in Figure 4.15, annealing generally caused significant ($P<0.05$) reduction in amylose contents in all cocoyam and bitter yam cultivars except in the NCe003 starch in which amylose remain unchained. This reduction of amylose contents reflect influence of amylose leaching as a result of the annealing treatment. This is different from the results obtained by Kohyama and Sasaki (2006) in which annealing (at 20^o and 50^oC) caused amylose contents to remain unchanged. It has been postulated that amylose chain mobility could increase due to annealing; resulting in the formation of double helices arising from interactions between amylose–amylose and/or amylose–amylopectin chains (Jacobs *et al.*, 1998; Hoover and Vasanthan, 1994).

4.6 Pasting properties of cocoyam and bitter yam starches

Pasting parameters of native and modified cocoyam and bitter yam starches are presented in Tables 4.6 and 4.7 while the pasting patterns are shown in Figure 4.16-4.18. The intrinsic characteristics of a particular starch sample determine the shape and size of its pasting curve through which the gelatinization process of the starch is quantified by monitoring the changes in its viscosity and other accompanying changes. Peak viscosity of native *Colocasia spp.*, *Xanthosoma spp* and bitter yam starches vary between 202.50-332.80RVU, 187.92-327.46RVU and 183.63-366.70RVU, respectively. The highest peak viscosity recorded was noted in the starch from white cultivar of bitter yam. This is an indication of the viscous load likely to be exerted on a blending or mixing cooker during processing of products having starches as components in their formulations. The native bitter yam cultivar starches were found to significantly differ in pasting parameters showing a wide variation in peak, breakdown final and setback viscosity values. Peak viscosities of 217, 295 and 201 RVU have been reported for bitter yam starches (Okunlola and Odeku, 2011; Sahore *et al.*, 2007; Farhat *et al.*, 1999), which were closer to values obtained for the yellow bitter yam starch (183.63 RVU) in this study rather than the white bitter yam starch (366.70RVU). Collado and Corke (1999) reported that peak viscosity was significantly and negatively correlated with amylose contents of starch, an assertion in agreement with the result obtained in this study. Final viscosity shows the ability of a starch-containing material to form a viscous paste or gel after heating and cooling cycles (RVA-S4 manual, 2010). Marked differences were observed in the final viscosities of the starches investigated in this study. Starches of the NXs002 (Table 4.4), NCe005 (Table 4.6) and yellow bitter yam (Table 4.7) had their final viscosities plateau above peak viscosities indicating an increased tendency to retrogradation (Eliasson, 2004). High setback viscosity, which is also associated with retrogradation/syneresis or 'weeping' during freezing and thawing cycles, is highest in NXs002 starch (107.96 RVU) and least in NCe003 starch (50.09 RVU). Generally, the *Colocasia spp* starches showed narrower and lower range of setback viscosity values (50.9-88.13 RVU) implying a reduced tendency towards retrogradation than the *Xanthosoma spp* starches (68.04-107.96 RVU). The viscosity profile of the native starches (Table 4.4) showed that the starch from NCe003 showed the lowest pasting temperature and the starch from NCe005 showed the highest.

Generally, the pasting temperature of the starch from the cocoyam and bitter yam cultivars were of the order: NCe003 (72.25^{o}C)<NCe010 (82.48^{o}C)<NXs003 (82.83^{o}C)<NXs001 (83.43^{o}C)<NXs002 (84.00^{o}C)<NCe001 (85.15^{o}C)<NCe002 (86.03^{o}C)<White bitter yam (86.70^{o}C)<NCe004 (87.35^{o}C)<Yellow bitter yam (88.45^{o}C)<NCe005 (88.88^{o}C). Pasting temperature is an indication of the amount of heat required to cause relaxation to the intra-granular binding forces within the granules and is important for energy requirement calculations in commercial processes (RVA-S4 manual, 2010).

Botanical source, modification, test conditions, agronomic practices and interactions with other materials like lipids, phosphate esters, sugars, and pH modifiers have been reported to affect the pasting properties of starches (Yamada *et al*, 1987; Zhu, 2015; Lin & Czuchajowska, 1998). Pasting properties of the modified starches reduced except for pasting temperatures and peak time. Puncha-Arnon and Uttapap (2013) reported a reduction in all pasting parameters while reduced peak viscosity was observed by Yadav *et al.* (2013) for rice and water chestnut starches respectively.

Table 4.6. Pasting properties of native and modified cocoyam starches

Cultivar	Modification	Peak viscosity (RVU)	Trough viscosity (RVU)	Breakdown viscosity (RVU)	Final viscosity (RVU)	Setback viscosity (RVU)	Peak time (min)	Pasting temperature (^{O}C)
NCe 001	Native	284.92±4.12^{cd}	161.71±1.00^{bc}	123.21±3.13^{c}	234.5±0.47^{bcd}	72.80±0.53^{bc}	4.80±0.09^{c}	85.15±0.78^{ab}
	Ann	348.21±3.71^{a}	183.58±0.24^{c}	164.63±3.48^{a}	277.46±2.30^{c}	93.88±2.06^{d}	5.07±0.00^{e}	87.38±0.04^{e}
	Acid	1.50±0.11^{c}	0.83±0.12^{cd}	0.67±0.00^{b}	1.33±0.00^{cd}	0.50±0.12^{e}	4.47±0.00^{a}	71.85±2.05^{ab}
	HMT18	202.83±4.95^{d}	159.79±2.65^{d}	43.04±2.30^{b}	265.54±5.60^{d}	105.75±2.95^{c}	5.60±0.00^{e}	94.20±0.99^{a}
	HMT24	67.71±1.47^{d}	61.83±1.30^{c}	5.88±0.18^{b}	100.96±3.36^{d}	39.13±2.06^{d}	6.17±0.05^{c}	81.75±1.77^{a}
	HMT27	227.79±0.41	214.67±4.83	13.13±4.42	369.17±4.48	154.50±0.35	6.73±0.00	75.95±0.92
NCe 002	Native	332.80±5.48^{ab}	152.21±1.4^{bcd}	180.59±4.12^{a}	207.50±2.48^{de}	55.29±1.12^{c}	4.65±0.02^{de}	86.03±0.39^{ab}
	Ann	154.29±1.71^{i}	89.29±4.53^{h}	65.00±6.25^{h}	160.13±2.18^{j}	70.83±2.36^{f}	5.40±0.09^{b}	94.90±0.57^{b}
	Acid	1.17±0.12^{de}	0.92±0.12^{c}	0.25±0.00^{fg}	1.83±0.00^{b}	0.92±0.12^{c}	4.90±1.27^{a}	61.3±20.1^{abc}
	HMT18	3.58±0.12^{i}	3.04±0.06^{i}	0.54±0.06^{f}	4.63±0.06^{i}	1.58±0.00^{h}	5.67±0.19^{e}	75.10±0.28^{cd}
	HMT24	2.08±0.00^{g}	1.83±0.00^{e}	0.25±0.24^{c}	3.29±0.06^{g}	1.46±0.06^{h}	6.27±0.57^{bc}	77.15±6.86^{a}
	HMT27	2.38±0.65	21.7±0.47	0.21±0.18	3.54±0.65	1.38±0.18	6.50±0.33	63.50±13.58
NCe 003	Native	207.58±29.7^{e}	115.88±21.0^{e}	91.71±8.67^{d}	165.96±29.3^{e}	50.09±8.96^{c}	4.67±0.04^{de}	72.25±20.93^{b}
	Ann	213.71±1.00^{h}	127.67±1.65^{g}	86.04±2.65^{g}	184.04±0.77^{h}	56.38±2.42^{h}	5.23±0.05^{c}	91.70±0.57^{c}
	Acid	1.21±0.06^{d}	0.75±0.00^{cde}	0.46±0.06^{cd}	1.50±0.00^{c}	0.75±0.00^{d}	4.07±0.09^{a}	75.00±0.00^{a}
	HMT18	14.71±0.41^{gh}	12.79±0.53^{h}	1.92±0.12^{f}	30.96±1.47^{g}	18.17±0.94^{e}	7.00±0.00^{a}	68.70±0.42^{d}
	HMT24	7.88±0.06^{ef}	6.96±0.18^{d}	0.92±0.12^{c}	13.67±0.12^{f}	6.71±0.06^{f}	7.00±0.00^{a}	72.00±12.73^{a}
	HMT27	10.71±0.18	9.96±0.06	0.75±0.12	17.13±0.18	7.17±0.12	6.97±0.05	83.15±4.03
NCe 004	Native	249.50±0.82^{d}	165.29±5.48^{bc}	84.21±4.66^{d}	233.92±2.5^{bcd}	68.63±3.00^{bc}	4.73±0.00^{cd}	87.35±0.00^{ab}
	Ann	237.88±0.65^{f}	135.33±0.24^{f}	102.54±0.41^{f}	172.42±0.71^{i}	37.08±0.94^{k}	5.00±0.00^{e}	89.73±0.11^{d}
	Acid	1.13±0.06^{de}	0.54±0.06^{ef}	0.58±0.12^{bc}	0.92±0.00^{fg}	0.38±0.06^{e}	3.80±0.09^{a}	57.9±16.8^{abc}
	HMT18	14.96±0.29^{gh}	12.67±0.24^{h}	2.29±0.06^{ef}	19.92±0.35^{h}	7.25±0.12^{g}	5.47±0.00^{e}	79.85±14.2^{bc}
	HMT24	9.38±0.18^{ef}	7.71±0.06^{d}	1.67±0.12^{c}	12.04±0.06^{f}	4.33±0.00^{g}	5.23±0.^{1d}	75.90±14.28^{a}
	HMT27	7.38±0.18	6.63±0.18	0.75±0.00	9.63±0.06	3.00±0.12	5.33±0.09	79.00±18.38

NCe 005	Native	202.50±0.94^{e}	145.88±0.8^{bcd}	56.63±0.18^{e}	233.3±0.94^{bcd}	87.46±1.71^{ab}	5.00±0.00^{b}	88.88±0.04^{a}
	An n	310.46±3.36^{c}	194.13±2.53^{b}	116.33±0.82^{d}	292.17±3.18^{b}	98.04±0.65^{c}	5.17±0.05^{cd}	87.33±0.35^{e}
	Acid	1.17±0.00^{de}	0.75±0.00^{cde}	0.42±0.00^{de}	1.13±0.06^{def}	0.38±0.06^{e}	4.40±0.19^{a}	48.50±0.71^{bc}
	HMT18	106.35±7.19^{e}	100.00±6.48^{e}	6.33±0.71	136.79±2.18^{e}	36.79±4.30^{d}	6.13±0.09^{cd}	87.50±0.71^{ab}
	HMT24	9.00±0.00^{ef}	8.08±0.00^{d}	0.92±0.00c	16.50±0.00^{ef}	8.42±0.00^{e}	6.93±0.00^{a}	77.50±4.95^{a}
	HMT27	6.04±0.06	5.25±0.00	0.79±0.06	10.38±0.06	5.13±0.06	6.97±0.05	72.50±2.05
NCe 010	Native	312.33±0.00^{bc}	168.08±0.35^{bc}	144.25±0.35^{b}	256.21±1.71^{bc}	88.13±1.36^{ab}	4.27±0.00^{f}	82.48±0.11^{ab}
	Ann	315.29±1.47^{b}	160.25±0.35^{d}	155.04±1.83^{b}	273.13±0.65^{d}	112.88±1.00^{b}	4.17±0.05^{h}	82.93±0.53^{g}
	Acid	0.88±0.29^{ef}	0.67±0.12^{def}	0.21±0.18^{fg}	1.04±0.18^{efg}	0.38±0.06^{e}	4.50±0.33^{a}	58.70±8.9^{abc}
	HMT18	242.00±3.53^{c}	201.42±4.60^{c}	40.58±1.06^{b}	342.92±0.94^{c}	141.50±3.65^{a}	5.47±0.00^{e}	94.73±0.32^{a}
	HMT24	70.79±1.60^{c}	64.38±3.00^{c}	6.42±1.41^{b}	121.13±3.24^{c}	56.75±0.24^{b}	7.00±0.00^{a}	76.00±1.41^{a}
	HMT27	-	-	-	-	-	-	-
NXs001	Native	262.50±4.95^{d}	170.92±4.00^{b}	91.59±0.94^{d}	262.71±4.89^{b}	91.79±8.90^{ab}	4.56±0.0^{e}	83.43±0.46^{ab}
	Ann	302.42±0.71^{d}	136.42±0.94^{f}	166.00±1.65^{a}	215.79±1.36^{e}	79.38±0.41^{e}	4.47±0.0^{g}	84.95±0.07^{f}
	Acid	0.89±0.09^{ef}	0.56±0.10^{ef}	0.33±0.00^{def}	0.92±0.14^{fg}	0.36±0.05^{e}	3.47±2.0^{a}	58.30±10.37^{abc}
	HMT18	390.17±1.41^{a}	278.88±3.36^{a}	111.29±4.77^{a}	421.50±1.53^{a}	142.63±1.83^{a}	5.40±0.1^{e}	93.30±0.57^{a}
	HMT24	236.71±2.24^{a}	221.63±3.83^{a}	15.08±1.41^{a}	380.83±4.36^{a}	159.21±0.53^{a}	6.63±0.1^{ab}	83.00±7.07^{a}
	HMT27	-	-	-	-	-	-	-
NXs 002	Native	187.92±13.3^{e}	133.21±9.8^{de}	54.71±3.48^{e}	241.2±15.^{bcd}	107.96±5.48^{a}	4.67±0de	84.00±0.21^{ab}
	Ann	298.75±2.12^{d}	245.71±3.59^{a}	53.04±1.47^{i}	310.29±0.41^{a}	64.58±3.18^{g}	6.47±0.0^{a}	97.75±0.35^{a}
	Acid	0.79±0.06^{f}	0.50±0.12^{f}	0.29±0.06^{efg}	0.83±0.12^{g}	0.33±0.00^{e}	4.90±0.9^{a}	46.00±0.00^{c}
	HMT18	92.17±2.24^{f}	72.42±2.00^{f}	19.75±0.24^{d}	111.79±2.30^{f}	39.38±0.29^{d}	7.00±0.0^{a}	87.50±2.12^{ab}
	HMT24	6.79±0.06^{f}	5.75±0.00^{d}	1.04±0.06^{c}	12.08±0.12^{f}	6.33±0.12^{f}	7.00±0.0^{a}	85.30±1.84^{a}
	HMT27	-	-	-	-	-	-	-
NXs 003	Native	327.46±3.48^{b}	154.8±3.4^{bcd}	172.63±0.06^{a}	222.9±3.7^{bcd}	68.04±0.30^{bc}	4.3±0.04^{f}	82.83±0.32^{ab}
	Ann	319.47±1.27^{b}	192.14±0.60^{b}	127.33±1.86^{c}	313.11±0.88^{a}	120.97±1.11^{a}	4.7±0.04^{f}	85.13±0.41^{f}
	Acid	0.96±0.18^{def}	0.79±0.18^{cd}	0.17±0.00^{g}	0.17±0.12^{de}	0.38±0.06^{e}	1.13±0.0^{b}	63.75±8.27^{abc}
	HMT18	279.91±2.12^{b}	252.96±0.65^{b}	26.96±2.77^{c}	378.63±1.12^{b}	125.67±1.77^{b}	5.73±0.0^{de}	94.85±0.35^{a}
	HMT24	98.13±2.18^{b}	92.08±1.77^{b}	6.04±0.4`1^{b}	143.75±2.47^{b}	51.67±0.71^{c}	6.80±0.1^{a}	80.70±0.99^{a}
	HMT27	-	-	-	-	-	-	-

Means in columns not followed by same alphabet(s) (by modification) are significantly different at 5% level (P<0.05).

Table 4.7. Pasting properties of native and modified bitter yam starches

Cultivar	Sample	Peak vis (RVU)	Trough viscosit (RVU)	Break down (RVU)	Final viscosity (RVU)	Setback (RVU)	Peak time (min)	Pasting temperature
White	Native	366.70±1.82^{a}	214.5±4.2^{a}	152.29±6.07^{b}	314.33±2.8^{a}	99.83±7.07^{a}	5.14±0.02^{a}	86.7±1.38^{ab}
	Ann	232.17±2.7^{g}	145.8±1.4^{e}	86.33±1.29^{g}	187.29±1.4^{g}	41.46±0.06^{j}	5.10±0.03^{de}	87.75±0.57^{e}
	Acid	3.83±0.12^{a}	1.88±0.06^{a}	1.96±0.06^{a}	4.38±0.06^{a}	2.50±0.00^{b}	4.73±0.09^{a}	70±14.14^{abc}
	HMT18	21.04±0.6^{g}	20.46±0.1^{g}	0.58±0.00^{f}	34.54±0.18^{g}	14.1±0.12^{ef}	6.57±0.42^{b}	78.±.41^{bcd}
	HMT24	7.54±0.18^{ef}	7.33±0.12^{d}	0.21±0.06^{c}	12.54±0.06^{f}	5.21±0.06^{fg}	6.63±0.24^{ab}	80.5±7.07^{a}
	HMT27	-	-	-	-	-	-	-
Yellow	Native	183.63±44.3^{e}	145.5±23.5^{cd}	38.17±20.74^{f}	213.2±55.7^{cd}	67.75±32.2^{bc}	4.83±0.09^{c}	88.45±1.06^{a}
	Ann	255.92±0.71^{e}	147.2±0.4^{e}	108.75±0.35^{e}	192.29±0.7^{f}	45.13±0.29^{i}	5.03±0.05^{e}	92.33±0.39^{c}
	Acid	3.50±0.00^{b}	1.67±0.00^{b}	1.83±0.00^{a}	4.58±0.12^{a}	2.92±0.12^{a}	4.33±0.00^{a}	57.5±0.71^{abc}
	HMT18	8.46±0.06^{hi}	8.29±0.06^{hi}	0.17±0.00^{f}	17.79±0.18^{h}	9.50±0.12^{fg}	6.53±0.38^{bc}	79.1±4.4^{bcd}
	HMT24	9.88±0.18^{e}	9.63±0.18^{d}	0.25±0.00^{c}	18.96±0.29^{e}	9.33±0.12^{e}	6.90±0.05^{a}	80.00±2.83^{a}
	HMT27	5.21±0.06	5.00±0.00	0.21±0.06	8.46±0.06	3.46±0.06	6.63±0.42	76.55±19.2

Means in columns not followed by same alphabet(s) (by modification) are significantly different at 5% level ($P<0.05$).

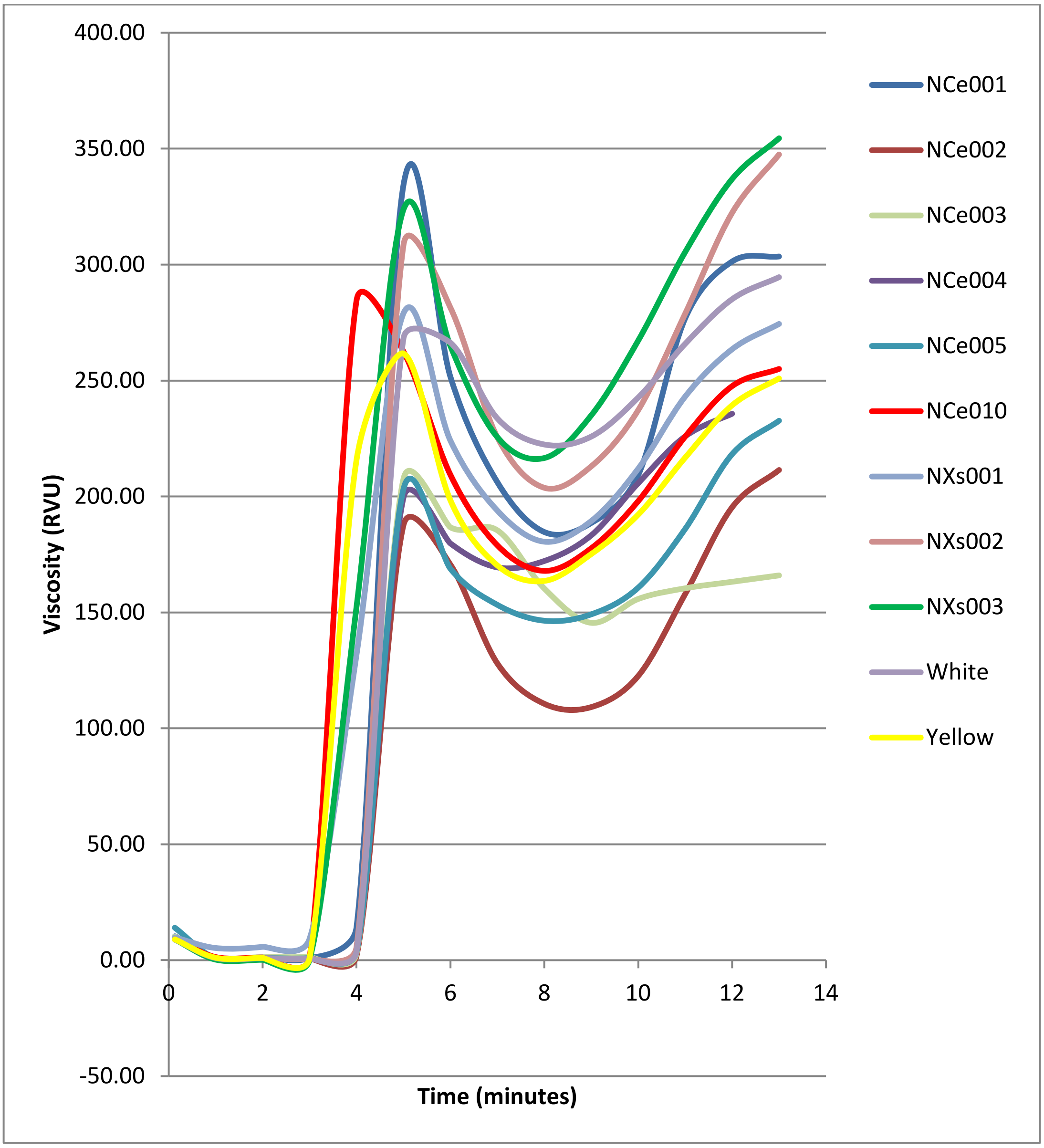


Figure 4.16. Pasting profile of native cocoyam and bitter yam starches

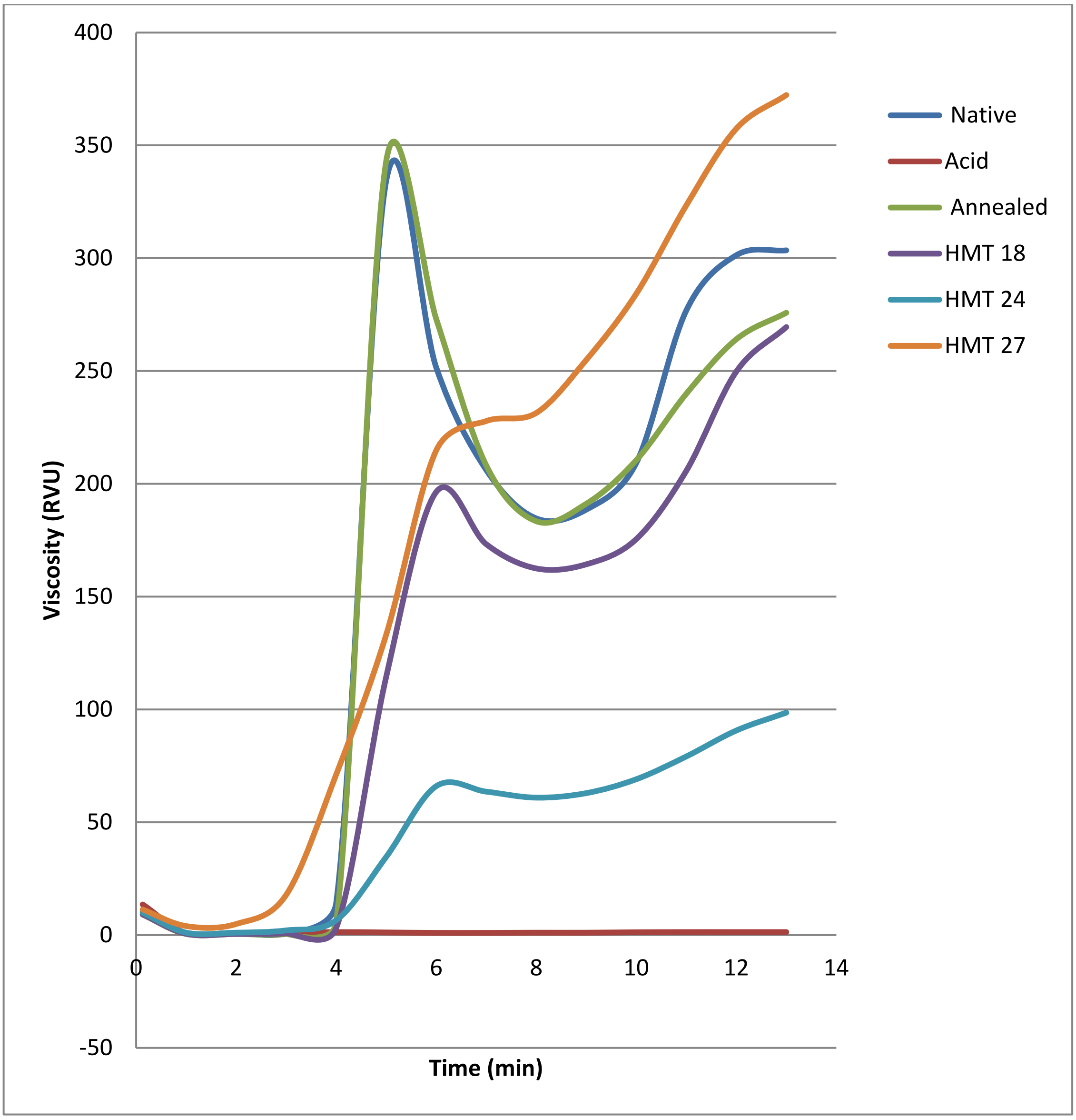


Figure 4.17. Effect of modification methods on pasting patterns of starch from NCe001

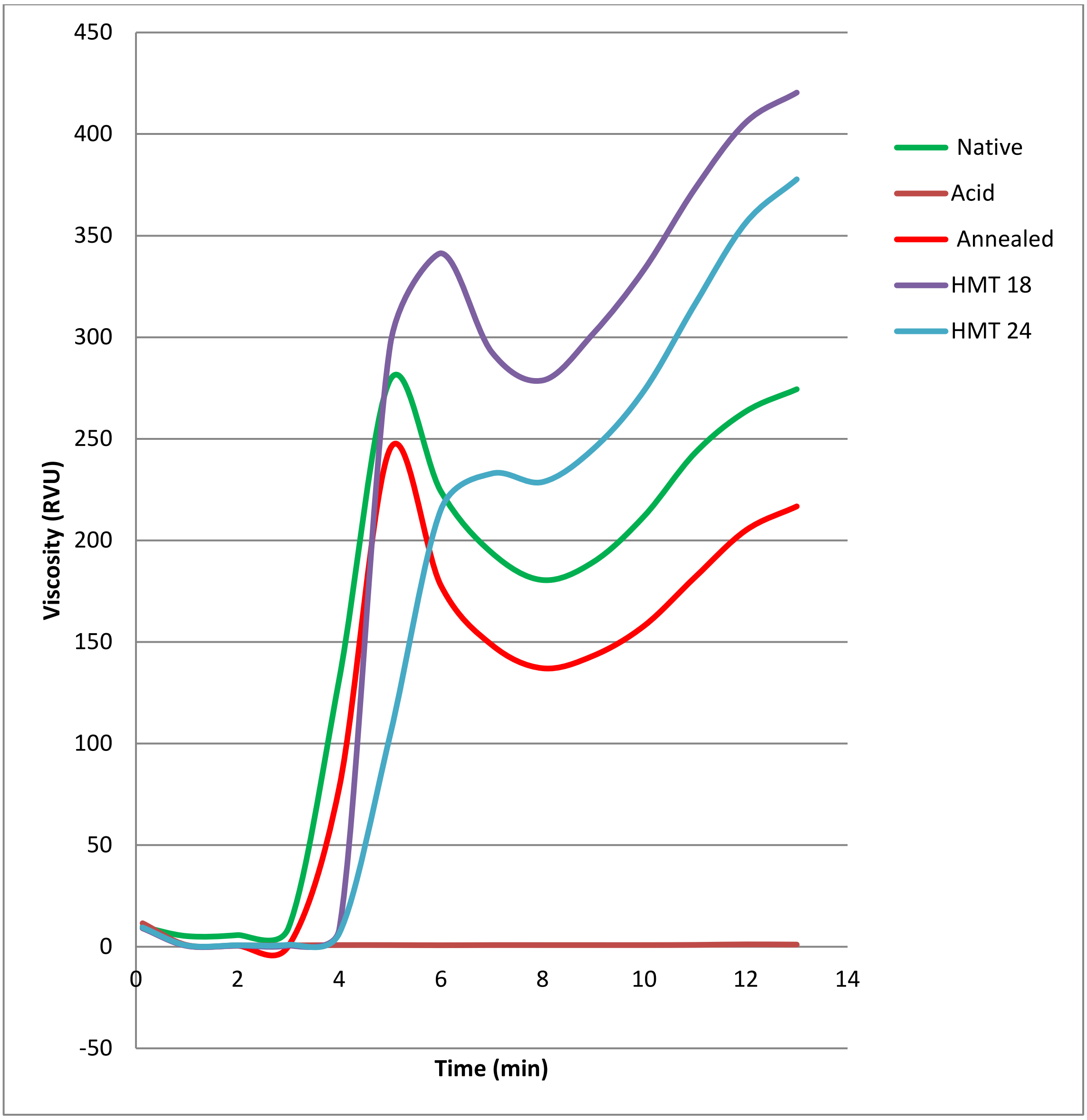


Figure 4.18. Influence of modification on pasting properties of NXs001 starch

Generally, pasting temperature of the starches increased following annealing treatments. The observed increase in temperature required for granule relaxation and subsequent paste formation in the starches may be attributed to increased intra-granule bonding and crosslinking forces as a result of improved chains interactions in the annealed starch granules. Earlier, similar trend has been reported for annealed African yam beans (Adebowale *et al.*, 2009), new cocoyam (Lawal, 2005), white sorghum (Olayinka *et al.*, 2008), wheat, oat, potato and lentils starches (Hoover and Vasanthan, 1994). The pasting temperature which is an indication of the minimum amount of heat required to cook a given sample, have implications on the stability of other components in a formula and also indicate energy costs or requirements (RVA-S4 manual, 2010).

Tables 4.6 revealed peak time of native starch from the NCe001 cocoyam was 0.27, 0.80, 1.37 and 1.93 minutes shorter than that of the annealed and heat-moisture modified samples at 18, 24 and 27% moisture levels, respectively, with similar trend observed for all the modified starches. This confirmed that annealing and heat-moisture modifications caused increase in pasting time of native cocoyam and bitter yam starches, with length of time increasing as severity of modification increased. Setback viscosity values were found to reduce for annealed starches from of NCe004, NXs001, NXs002 cocoyam cultivars and for both the white and yellow bitter yam cultivars. This implied a reduced tendency towards retrogradation for the modified starches compared with their native counterparts. Although other phenomena like increased gel firmness, increased crystallinity, turbidity changes, change of polymorph type and syneresis are indicators of retrogradation based on comparative roles of amylose and amylopectin during starch paste storage (Zhu, 2015; Alcazar-Alay and Meireles, 2015), the magnitude of setback viscosity values in pasting analysis is considered to reflect the retrogradation tendency of amylose in a starch paste. These starches may therefore find application in products requiring high anti-staling ability, stability and in frozen products for this desirable attribute. Among the *Colocasia spp.* starches, NCe003 starch showed consistently lowest values for pasting temperature, final and setback viscosities while NCe002 gave the highest values for peak and breakdown viscosities. Breakdown viscosity which is associated with paste fragility was lowered significantly by heat-moisture modification for most of the starches showing that they had stable viscosities and could withstand shear-induced disintegration. The NCe001 starch experienced a drop in breakdown viscosity from 123.21RVU in the native sample to 43.04, 5.88 and 13.13RVU in heat-moisture treated samples at 18, 24 and 27% moisture levels. Annealing had varied effect on breakdown viscosity values; increasing for NCe001

(123.21 to 164.63RVU), NCe004 (84.21 to 102.54RVU), NCe005 (56.63 to 116.33RVU) and NCe010 (144.25 to 155.04RVU) in the *Colocasia spp*, NXs001 (91.59 to 166.0RVU) in the *Xanthosoma spp* and yellow cultivar of *Dioscorea dumetorum* starches (38.17 to 108.75RVU), reduced in value for other annealed starches.

Acid thinning was noted to significantly cause a marked loss of viscosity for all the native cocoyam and bitter yam starches. Similar loss or reduction of paste viscosity has been obtained by different workers (Ulbrich *et al.,* 2014; Santana and Meireles, 2014; Koteswara *et al.,* 2015; Zavareze *et al.,* 2012; Atichokudomchai *et al.,* 2004). Okunlola and Odeku (2011) also reported a sharp reduction in peak viscosity of acid-hydrolysed starch from four *Dioscorea* species. This behavior of acid-thinned starches may be attributed to disintegration or partial disruption of granular structure caused by hydrolysis of long chains of the starch granules to form shorter chains. As shown by scanning electron microscopy, different crystalline types of starches after acid hydrolysis have been observed to show gradual corrosion and erosion until completely formed into many small lumps (Xia *et al.,* 2010). This agrees with the result of polarized light microscopy in this study in which some level of clumping and aggregation of starch granules were observed after acid-thinning.

4.7 Swelling power of starches

Swelling power depicts the gelatinization behaviour of starch granules in a heated starch-water mixture and shows the structural characteristic. It illustrates the interactions of the polymeric amorphous and crystalline chains in starch granule fractions (Zhang *et al.,* 2005). Variation of swelling power of native and modified cocoyam and bitter yam starches with temperature (50-90^{o}C) are as presented in Tables 4.8 and 4.9. A progressive increase in swelling of all starches was observed with increase in temperature showing that temperature has a profound influence on swelling power with unmodified starches exhibiting higher swelling power than the modified derivatives. Swelling power of native starches at 50^{o}, 60^{o}, 70^{o}, 80^{o} and 90^{o}C ranged from 2.42 to 6.30, 4.67 to 11.20, 10.10 to 15.90, 13.75 to 24.61 and 18.75 to 34. 15 g/g for *Colocasia spp.* starches, 3.45 to 4.22, 5.27 to 7.37, 9.31 to 14.10, 12.93 to 21. 28 and 18.92 to 29. 41 g/g for *Xanthosoma spp* starches and 5.05 to 7.30, 3.60 to 7.90, 4.20 to 8.30, 10.25 to 14.10 and 17.30 to 26.10 g/g for bitter yam starches respectively. The starches differed significantly between the crops and the cultivars in their swelling capacities. Yellow cultivar of bitter yam starch had higher swelling power at lower temperatures (50^{o}, 60^{o} and 70^{o}C) than the white cultivar but recorded significantly lower swelling at 80° and 90°C. In this study, at 50°C, highest swelling (7.3g/g) was recorded for the yellow bitter yam. *Dioscorea* starches have been reported to have lower swelling power compared with potato starch (Gunaratne and Hoover, 2002). Amani *et al.* (2004) reported swelling power of 11.8-16.8 g/g for eleven genotypes of *Dioscorea cayenensis-rotundata* and 14.9 g/g at 60°C for *Dioscorea dumetorum*, a value higher than that the 7.90 g/g at same temperature reported in this study. Amylose has been shown to inhibit swelling by acting as a diluent (Singh *et al.*, 2003; Tang *et al.,* 2002; Otegbayo *et al.,* 2014) while amylo-lipid complexes formed in starches can cause restrictions to swelling (Morrison *et al.,* 1993). Amylose reinforce granules internal network to also limit swelling (Tester and Morrison, 1990). This effect was only evident in native starches at 50°, 80° and 90°C for cocoyam starches and only at 80 and 90°C for bitter yam starches as swelling power varied inversely with amylose content at those temperatures. The starch from NCe005 with amylose content of 18.01% had swelling power of 13.75g/g at 80°C while NCe001 with amylose content of 10.11% had swelling power of 24.61g/g, the highest at the same temperature.

As gelatinization commenced when starch-water mixture was heated, the capacity of the starch molecules to hold water through hydrogen bonding determined its swelling power. More granular stability may have occurred at the early stage of gelatinization as long chain amylopectin molecules associate to perfect crystalline structure of granules. The effect of starch granule sizes may be related to swelling capacities as large granules are postulated to have less molecular bonding (Otegbayo *et al.,* 2014), therefore resulting in faster swelling at initial stages of gelatinization. However, this holds only with *Colocasia spp.* of cocoyam at temperatures ≤70°C as starches with larger granule sizes including those from NCe010, NCe003 and NCe002 had higher swelling power of 11.20, 6.30 and 15.90g/g) at 60°, 50° and 70°C compared to the corresponding smaller granules of NCe005, NCe004 and NCe003 which showed lowest swelling power of 4.67, 2.42 and 10.10g/g, respectively at same temperature (Table 4.8). The variation of swelling powers with granule size however did not follow similar pattern with the *Xanthosoma spp.* Thus, factors other than amylose content like amylopectin chain length, molecular and morphological structure of granules influence swelling powers of cocoyam and bitter yam starches.

Heat-moisture treatments, annealing and acid hydrolysis generally resulted in reduction of swelling power of most native cocoyam and bitter yam starches at all temperatures. Similar observations have been reported following heat-moisture modifications of starches from different sources (Tattiyakul *et al.,* 2006; Gunaratne and Hoover, 2002; Lawal, 2005) while annealing resulted in decreased granular swelling of *D. alata* and *D. esculenta* starches (Jayakody *et al.,* 2009) and in 35% w/v suspension of water chestnut starch at 65^{o}C (Yadav *et al.,* 2013). Falade and Ayetigbo (2015) reported a reduction in swelling capacity of yam at 33% w/v starch suspension. This may be attributed to the effect of physical modification of the starch which caused a re-organization in the structural network of granules, resulting in increased crystallinity. Bonding forces within the granules are thus rearranged to favour the formation of clustered side chains of amylopectin with ordered double helices which restrict swelling. Similar views were expressed by Tester and Morrison (1990) and Lawal (2005). For this study, annealing increased the swelling power of white bitter yam (Figure 4.20) and NXs003 starches (Figure 4.21) at 60^{o}, 70^{o} and 80^{o}C. Both physical modification methods resulted in increased swelling at low temperature (60^{o}C) for starch from NCe004 but there was significantly higher swelling at 90^{o}C for starches from NCe001, NCe002 and NCe003 cocoyams (Table 4.8). Acid thinning caused a significant ($P<0.05$) reduction in swelling power of all starches (Table 4.8 and 4.9), the result of loss or partial disruption of granular structure caused by hydrolysis of the starch granules.

4.8 Solubility index of starches

Solubility, which reflects the ability of starch solids to disperse in aqueous solutions (Falade and Christopher, 2015), increased as temperature increased between 50^{o}C and 90^{o}C (Table 4.9), and varied between the crops and within their cultivars. Solubility was found to sharply increase after 70^{o}C for most of the native starches to peak at 90^{o}C. This infer that greater dissociation and disintegration of granules occur at temperatures around gelatinization temperatures (which occurs after 70^{o}C and as confirmed by the pasting temperatures recorded from RVA studies) leading to better dispersion in water. Native starches from *Dioscorea dumetorum* had significantly lower solubilities (11.50-12.0%) compared with the cocoyam cultivars (20.0-27.50%) at 50^{o}C (Tables 4.10 and 4.11). Modification of starches from cocoyam and bitter yam cultivars caused increment or reduction in solubility at different degrees. Starch solubility was found to decrease for heat-moisture modified white and yellow cultivars of bitter yam at all temperatures studied except for HMT 18 and HMT 24 at 50^{o}C and HMT 18 at 70^{o}C in the white cultivar only. The starch from NXs001 showed a reduction in solubility at 70^{o}, 80^{o} and 90^{o}C for the heat-moisture modified starch at all moisture levels.

Table 4.8. Swelling power of native and modified cocoyam starches.

Cultivar	Modification	50°C	60°C	70°C	80°C	90°C
NCe001	Native	5.72±0.73^{abc}	7.12±1.02^{abc}	12.70±0.00^{cd}	24.61±3.69^{a}	34.15±2.34^{a}
	Ann	5.85±0.63^{a}	6.76±0.62^{ab}	9.86±0.76^{abc}	10.52±0.29^{ef}	19.23±0.25^{de}
	Acid	2.95±1.34^{a}	2.47±0.47^{c}	2.00±0.00^{c}	7.22±0.02^{b}	11.08±0.04^{abc}
	HMT18	5.19±0.69^{a}	3.73±0.86^{c}	7.67±2.87^{ab}	9.52±0.25^{bcde}	14.21±0.98^{bcd}
	HMT24	4.27±0.94^{a}	3.36±0.48^{b}	7.19±3.70^{abcd}	10.29±1.34^{ab}	11.93±0.60^{cd}
	HMT27	3.22±0.02^{ab}	3.10±0.71^{abcd}	6.38±3.85^{abcd}	6.46±0.20^{c}	10.72±0.02^{cd}
NCe002						
	Native	5.10±0.71^{bcd}	10.09±4.96^{ab}	15.90±0.00^{a}	21.21±1.26^{ab}	33.65±0.49^{ab}
	Ann	4.16±0.08^{bcd}	10.35±5.87^{a}	11.28±2.58^{ab}	11.93±1.31^{de}	26.65±2.33^{a}
	Acid	2.92±0.26^{a}	2.61±0.55^{c}	6.47±1.60^{ab}	8.39`±0.75^{abc}	11.25±0.35^{abc}
	HMT18	3.63±0.25^{b}	5.47±0.33^{a}	9.97±2.17^{a}	10.71±0.57^{abcde}	17.39±1.39^{ab}
	HMT24	3.28±0.32^{ab}	3.75±1.20^{b}	4.75±0.78^{bcd}	9.68±0.48^{ab}	15.51±0.30^{ab}
	HMT27	2.99±0.30^{b}	3.92±0.59^{a}	8.05±0.64^{ab}	9.56±0.62^{b}	16.15±1.34^{a}
NCe003	Native	6.30±0.13^{ab}	8.26±0.08^{abc}	10.10±0.00^{ef}	17.99±2.04^{bc}	33.18±6.12^{ab}
	Ann	5.65±0.77^{a}	5.27±1.47^{b}	9.12±3.93^{abc}	13.81±0.50^{cd}	25.85±1.20^{ab}
	Acid	2.85±0.21^{a}	3.71±1.43^{bc}	5.20±2.83^{ab}	6.36±0.06^{c}	11.79±2.20^{abc}
	HMT18	3.60±0.00^{b}	5.83±0.74^{a}	8.47±0.47^{ab}	9.35`±0.42^{cde}	13.34±0.02^{cd}
	HMT24	3.23±0.47^{ab}	3.68±0.60^{b}	4.91±0.07^{bcd}	7.22±1.16^{bc}	12.78±1.10^{bc}
	HMT27	2.54±0.19^{c}	2.44±0.23^{cd}	3.57±0.38^{d}	6.10±1.84^{cd}	9.95±1.31^{de}
NCe004	Native	2.42±0.17^{e}	5.70±0.00^{abc}	15.30±0.00^{ab}	18.88±2.51^{bc}	27.13±1.52^{bcd}
	Ann	3.68±0.17^{bcd}	5.40±0.14^{b}	13.25±1.06^{a}	15.60±0.85^{bc}	25.50±0.85^{ab}
	Acid	2.30±0.00^{a}	6.50±2.55^{abc}	6.00±0.00^{ab}	9.00±2.83^{abc}	9.83±2.09^{c}
	HMT18	2.24±0.06^{e}	5.36±0.06^{a}	9.35±0.00^{a}	13.40±1.27^{a}	20.55±0.78^{a}
	HMT24	3.08±1.16^{ab}	7.50±2.83^{a}	10.40±1.84^{a}	12.85±0.21^{a}	16.33±2.93^{a}
	HMT27	2.41±0.28^{c}	2.27±0.06^{d}	6.14±0.66^{abcd}	8.83±0.57^{b}	15.50±0.28^{a}
NCe005	Native	4.67±0.18^{bcd}	4.67±0.90^{bc}	11.30±0.71^{de}	13.75±0.35^{def}	22.25±3.04^{def}
	Ann	3.61±0.01^{bcd}	5.31±0.59^{b}	9.73±0.95^{abc}	13.01±1.42^{cde}	22.79±0.94^{bc}
	Acid	2.79±0.01^{a}	4.35±0.77^{bc}	6.55±1.48^{ab}	6.67±2.36^{c}	10.65±1.63^{bc}
	HMT18	2.90±0.28^{cde}	3.86±0.91^{c}	9.22±3.93^{a}	9.01±1.92^{de}	15.90±2.18^{bcd}
	HMT24	2.84±0.34^{b}	3.84±0.93^{b}	8.40±3.53^{abc}	9.12±1.10^{ab}	13.65±0.62^{abc}
	HMT27	3.05±0.07^{b}	3.60±0.10^{ab}	7.33±3.21^{abcd}	8.54±0.21^{b}	12.32±0.45^{bc}
NCe010	Native	3.55±0.49^{de}	11.20±4.95^{a}	11.29±0.00^{de}	17.78±0.74^{bc}	18.75±0.35^{f}
	Ann	3.54±0.19^{cd}	6.67±0.32^{ab}	11.90±0.00^{ab}	17.15±1.20^{ab}	17.83±0.11^{e}
	Acid	2.50±0.57^{a}	9.20±5.66^{a}	8.30±0.00^{a}	10.26±0.02^{ab}	13.03±0.39^{abc}
	HMT18	2.52±0.12^{de}	5.10±0.28^{ab}	8.40±0.57^{ab}	12.27±0.10^{abc}	14.73±0.11^{bcd}
	HMT24	2.54±0.23^{b}	3.90±0.00^{b}	8.90±0.00^{ab}	12.00±0.14^{a}	13.58±1.17^{abc}
	HMT27	2.45±0.16^{c}	3.78±0.11^{a}	9.13±0.67^{a}	11.48±0.67^{a}	13.15±0.64^{b}

NXs001	Native	3.45±0.35^{de}	6.60±1.41^{abc}	9.31±0.71^{fg}	12.93±0.39^{ef}	18.92±3.51^{f}
	Ann	3.81±0.56^{bcd}	4.70±0.57^{b}	10.82±3.37^{ab}	12.22±1.44^{de}	19.35±2.90^{cde}
	Acid	2.99±0.44^{a}	3.50±0.00^{bc}	7.17±2.59^{ab}	10.51±0.21^{a}	14.10±0.99^{ab}
	HMT18	3.15±0.22^{bcd}	4.07±0.23^{bc}	8.10±2.83^{ab}	11.94±1.04^{abcd}	16.15±0.21^{bcd}
	HMT24	2.64±0.20^{b}	3.85±0.21^{b}	8.31±1.40^{abc}	11.73±0.75^{a}	15.73±0.11^{cd}
	HMT27	2.42±0.17^{c}	3.59±0.11^{ab}	7.90±0.71^{abc}	11.23±0.50^{a}	13.18± 1.24^{b}
NXs002	Native	4.00±1.13^{cde}	7.37±0.09^{abc}	14.10±0.00^{bc}	16.99±0.34^{cd}	20.15±0.49^{ef}
	Ann	3.90±0.00^{bcd}	5.83±0.74^{b}	9.70±0.00^{abc}	17.35±2.47^{ab}	20.55±0.35^{cde}
	Acid	2.52±0.11^{a}	7.80±0.57^{ab}	8.10±0.00^{a}	11.38±0.74^{a}	12.30±0.00^{abc}
	HMT18	2.59±0.27^{de}	3.38±0.25^{c}	5.65±0.21^{ab}	11.79±0.16^{abcd}	12.60±2.55^{cd}
	HMT24	2.47±0.18^{b}	3.65±0.35^{b}	5.75±0.35^{bcd}	6.90±0.42^{bc}	9.73±0.39^{d}
	HMT27	2.33±0.01^{c}	3.30±0.30^{abc}	4.55±0.47^{d}	6.15±0.78^{cd}	8.66±0.47^{e}
NXs003	Native	4.22±0.17^{cde}	5.27±1.46^{bc}	10.75±1.91^{ef}	21.28±0.40^{ab}	29.41±1.54^{abc}
	Ann	4.41±0.01^{b}	6.83±0.69^{ab}	11.10±0.00^{ab}	19.76±0.62^{a}	20.79±1.99^{cde}
	Acid	3.29±0.98^{a}	4.92±0.45^{abc}	7.15±0.35^{ab}	11.13±1.80^{a}	9.46±3.46^{c}
	HMT18	2.82±0.31^{cde}	3.65±0.16^{c}	10.06±1.20^{a}	12.33±3.01^{ab}	16.35±3.32^{bcd}
	HMT24	2.80±0.28^{b}	3.71±0.70^{b}	10.30±0.71^{a}	11.70±4.74^{a}	14.65±1.77^{abc}
	HMT27	2.48±0.25^{c}	2.64±0.23^{bcd}	3.96±0.71^{d}	6.33±0.15^{cd}	10.45±0.29^{d}

Means in columns not followed by same alphabet(s) (by modification) are significantly different at 5% level ($P<0.05$).

Table 4.9. Swelling power of native and modified bitter yam starches.

Cultivar	Modification	50°C	60°C	70°C	80°C	90°C
White Bitteryam	Native	5.05±2.05^{bcd}	3.60±0.00^{c}	4.20±0.00^{h}	14.10±0.28^{de}	26.10±4.10^{cde}
	Ann	4.30±0.00^{bc}	5.20±0.14^{b}	8.30±0.14^{bc}	14.60±0.99^{bcd}	21.35±0.07^{cd}
	Acid	3.60±0.14^{a}	3.15±0.07^{bc}	4.00±0.14^{bc}	8.40±0.00^{abc}	14.70±0.85^{a}
	HMT18	3.45±0.07^{bc}	3.60±0.14^{c}	4.10±0.00^{b}	4.05±0.07^{f}	7.35±0.07^{e}
	HMT24	3.45±0.07^{ab}	3.65±0.07^{b}	4.05±0.07^{d}	4.30±0.00^{c}	6.55±0.21^{e}
	HMT27	3.50±0.00^{a}	3.55±0.07^{ab}	3.75±0.07^{d}	3.95±0.07^{e}	6.15±0.07^{f}
Yellow Bitteryam	Native	7.30±0.57^{a}	7.90±0.14^{abc}	8.30±0.14^{g}	10.25±0.07^{f}	17.30±1.13^{f}
	Ann	3.35±0.07^{d}	5.00±0.14^{b}	6.00±0.57^{c}	8.85±0.64^{f}	11.35±1.34^{f}
	Acid	3.60±0.00^{a}	3.90±0.00^{bc}	4.35±0.07^{bc}	6.65±0.07^{c}	9.85±0.07^{c}
	HMT18	3.70±0.00^{b}	4.25±0.07^{bc}	6.60±0.14^{ab}	8.25±0.21^{e}	12.55±0.07^{d}
	HMT24	3.50±0.00^{ab}	3.75±0.07^{b}	4.45±0.07^{cd}	4.85±0.07^{c}	6.80±0.85^{e}
	HMT27	3.50±0.00^{a}	3.70±0.00^{ab}	4.15±0.07^{cd}	4.75±0.07^{de}	5.25±0.07^{f}

Means in columns not followed by same alphabet(s) (by modification) are significantly different at 5% level ($P<0.05$).

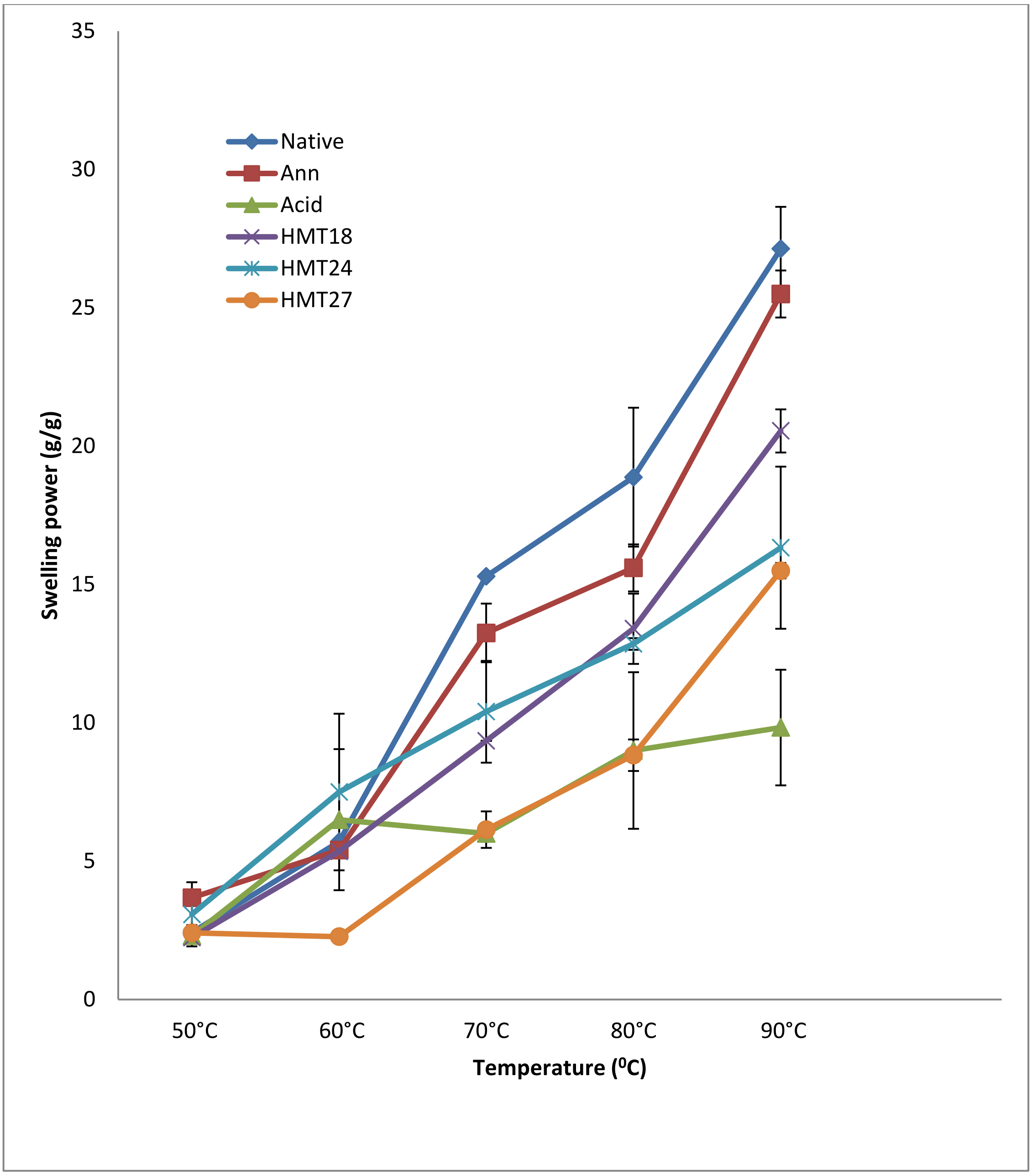


Figure 4.19. Effect of modification on swelling power of starch from NCe004 cocoyam culivar

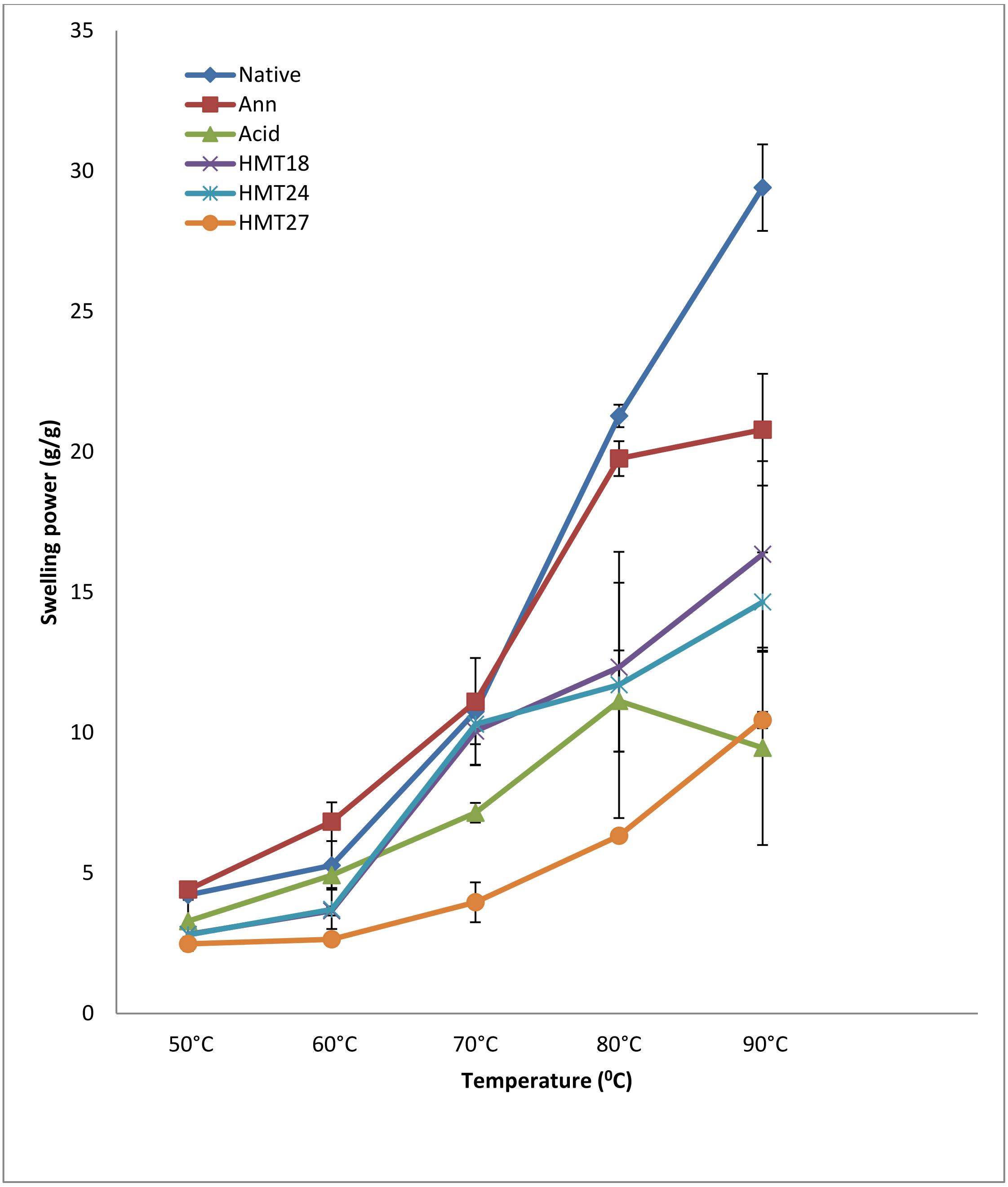


Figure 4.20. Effect of modification on swelling power of starch from NCe003 cocoyam culivar

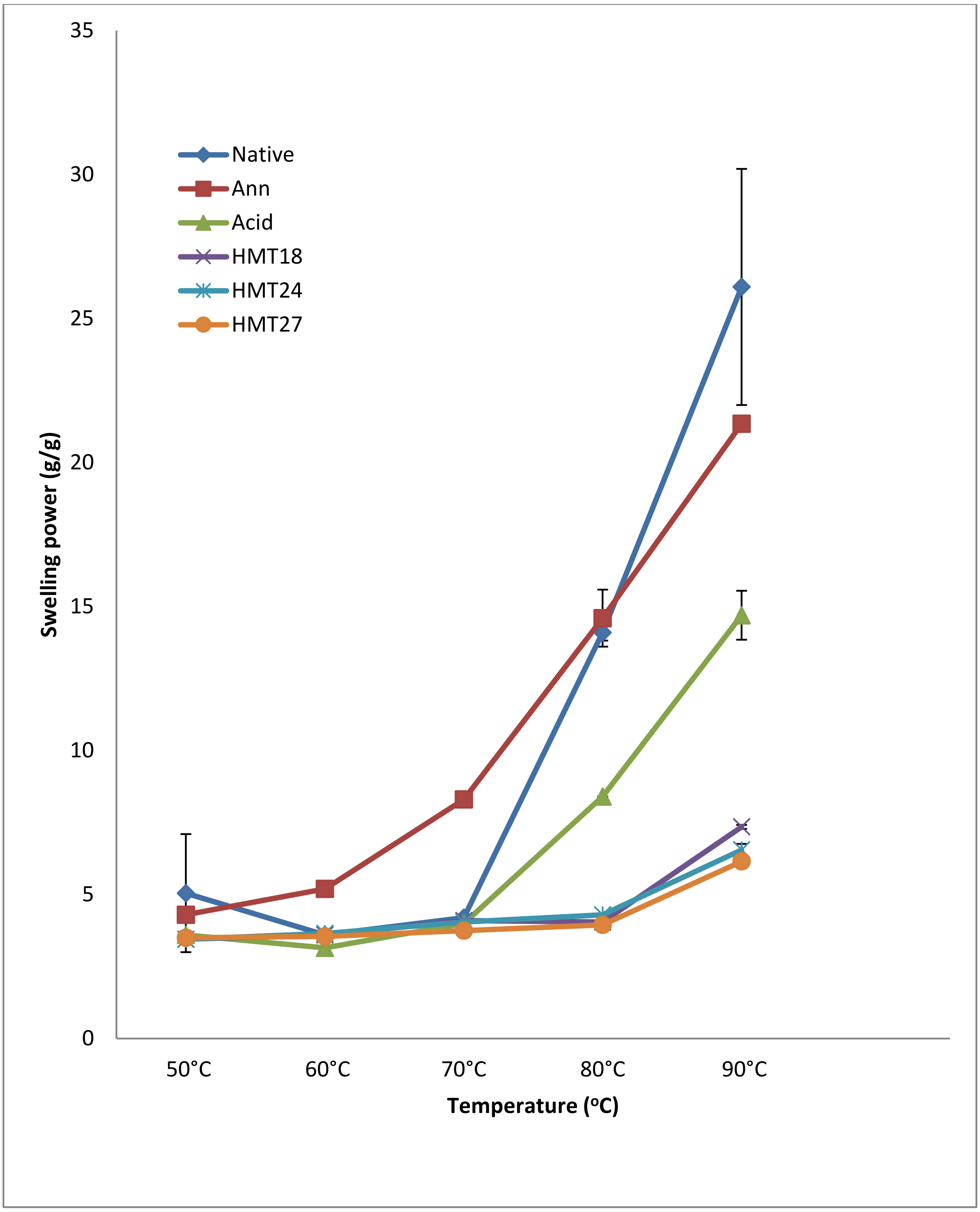


Figure 4.21. Effect of modification on swelling power of starch from white bitter yam

Solubility of the native starch increased from 23.50% to 25.0% in the HMT 27 at 50^{o}C, while same modification caused an insignificant increase for HMT 27 in NXs002 from 23.50% to 24.0%. Improved perfection of small crystalline region and greater stability caused by the reorganization of the granule structural network during modification could justify the general decrease in solubility of heat-moisture treated starches. This is because heat moisture treatment and annealing as physical methods of starch modification alters the crystallinity of starch granules (Chiu and Solarek, 2009). On the contrary, heat-moisture treated starches of African locust bean, maize, finger millet, red sorghum, cassava, arrow root and sweet potato were found to have higher solubilities compared with the native untreated starches by earlier authors (Sankhon *et al.,* 2014; Adebowale *et al.,* 2005a; 2005b; Jyothi, *et al.,* 2010). Lorenz and Kulp (1982) have posited that cereal starches have increased solubilities while tuber starches have their solubilities reduced by heat-moisture treatments especially at high temperatures (90^{o}C), though a reduction had been reported in the solubility of heat-moisture treated sorghum starch (Sun *et al.,* 2014). Yadav *et al.* (2013) have also reported reduction in solubility of heat-moisture treated and annealed water chestnut starches. This suggests differences in the type of reorganization taking place in starch polymers from different origin as a result of heat moisture treatments.

Acid hydrolysed starch samples recorded the highest levels of solubility at all temperatures for all *X. sagittifolium, D. dumetorum,* NCe002 and NCe010 starches. Acid catalyzed hydrolysis of the starches may have resulted in the preferential hydrolysis of the amorphous region that joined crystallites in the granules making it microporous, fragile and easily dispersed in aqueous medium (Rafiq *et al.,* 2016). The preferential hydrolysis of the amorphous region contributed to increasing the amount of leached, dissociated or solubilized amylose, hence the increased solubility. Kong *et al.* (2012) reported similar increase in solubility of acid-thinned starch from amaranth. The solubility increased with the modification methods and the order was: acid>annealed>HMT18>HMT24>native=HMT27 in white bitter yam starch at 50^{o}C (Figure 4.24) while the order differ at 60^{o}C; Acid>native>annealed>HMT18>HMT24>HMT27 at 31, 29, 28.5, 20.5, 19.5 and 15.5% respectively.

Table 4.10. Solubility indices of native and modified cocoyam

Cultivar	Sample	50°C	60°C	70°C	80°C	90°C
NCe001	Native	25.50±0.71^{ab}	45.50±3.54^{bcde}	74.50±3.54^{bc}	149.00±1.41^{a}	154.50±2.12^{b}
	Annealin	23.50±0.71^{cd}	52.00±1.41^{ab}	75.00±0.00^{bcd}	152.50±0.71^{a}	163.00±15.56^{a}
	Acid	26.00±0.00^{ab}	50.00±2.83^{b}	82.50±4.95^{ab}	150.50±0.71^{c}	178.50±6.36^{a}
	HMT18	24.00±1.41^{ab}	55.00±1.41^{a}	74.50±2.12^{cd}	148.50±0.71^{a}	154.50±3.54^{b}
	HMT24	26.00±0.00^{ab}	54.50±0.71^{b}	78.00±1.41^{b}	154.50±2.12^{a}	164.50±0.71^{cd}
	HMT27	28.00±1.41^{a}	53.50±0.71^{b}	76.00±4.24^{b}	148.50±0.71^{ab}	166.50±0.71^{a}
NCe002	Native	27.50±2.12^{a}	57.50±6.36^{a}	63.00±1.41^{d}	139.00±1.41^{b}	155.00±1.41^{b}
	Ann	27.00±1.41^{ab}	53.50±3.54^{a}	66.00±2.83^{e}	138.50±9.19^{cd}	157.00±1.41^{a}
	Acid	29.50±6.36^{a}	54.50±0.71^{a}	76.50±2.12^{b}	141.50±2.12^{d}	168.00±7.07^{b}
	HMT18	26.00±2.83^{a}	52.00±2.83^{b}	66.50±0.71^{e}	139.50±6.36^{b}	157.50±0.71^{ab}
	HMT24	28.00±0.00^{a}	53.50±0.71^{b}	66.50±2.12^{d}	138.00±8.49^{ab}	154.50±0.71^{bc}
	HMT27	28.00±1.41^{a}	55.50±0.71^{a}	68.00±0.00^{cd}	137.50±10.61^{c}	158.00±0.00^{bc}
NCe003	Native	21.50±2.12^{cde}	53.00±5.66^{ab}	80.00±2.83^{a}	149.00±5.66^{a}	155.50±0.71^{b}
	Ann	29.50±0.71^{a}	49.00±1.41^{abc}	80.50±0.71^{a}	137.00±4.24^{d}	153.00±4.24^{a}
	Acid	24.50±0.71^{ab}	52.50±0.71^{ab}	86.50±2.12^{a}	156.00±0.00^{a}	167.50±0.71^{b}
	HMT18	22.00±1.41^{bc}	51.50±0.71^{b}	78.50±0.71^{bc}	143.50`±2.12^{ab}	159.00±1.41^{a}
	HMT24	24.00±1.41^{bc}	61.00±1.41^{a}	69.50±0.71^{d}	140.50±2.12^{c}	157.00±5.66^{b}
	HMT27	23.50±0.71^{bc}	50.50±0.71^{c}	73.50±2.12^{b}	151.00±4.24^{a}	159.50±2.12^{b}
NCe004	Native	20.50±0.71^{de}	40.50±2.12^{ef}	78.00±2.83^{ab}	133.00±4.24^{b}	159.00±1.41^{ab}
	Ann	25.00±1.41^{bc}	47.00±5.66^{bc}	79.00±1.41^{ab}	142.50±3.54^{bcd}	154.00±0.00^{a}
	Acid	21.50±3.54^{b}	42.50±3.54^{c}	76.50±6.36^{b}	136.50±3.54^{e}	162.50±0.71^{b}
	HMT18	20.50±0.71^{bc}	37.00±1.41^{d}	67.50±0.71^{de}	129.00±1.41^{c}	144.00±1.41^{c}
	HMT24	23.50±0.71^{bc}	48.50±3.54^{c}	80.50±2.12^{b}	142.00±0.00^{c}	150.50±2.12^{c}
	HMT27	21.50±2.12^{cd}	48.50±0.71^{d}	71.00±2.83^{bcd}	138.00±2.83^{c}	148.00±1.41^{d}
NCe005	Native	22.00±1.41^{cde}	38.50±0.71^{ef}	77.50±2.12^{abc}	134.50±3.54^{b}	155.00±1.41^{b}
	Ann	24.00±0.00^{cd}	44.50±2.12^{c}	74.50±0.71^{cd}	148.00±1.41^{ab}	159.00±1.41^{a}
	Acid	22.00±1.41^{b}	42.00±1.41^{c}	80.50±0.71^{ab}	143.00±2.83^{d}	163.00±0.00^{b}
	HMT18	22.00±1.41^{bc}	51.00±1.41^{b}	82.50±0.71^{b}	145.00±1.41^{ab}	156.50±0.71^{ab}
	HMT24	20.00±1.41^{de}	54.00±1.41^{b}	68.50±0.71^{d}	144.50±2.12^{bc}	157.50±0.71^{b}
	HMT27	18.50±0.71^{d}	43.50±0.71^{e}	66.00±1.41^{d}	141.50±2.12^{bc}	155.00±1.41^{bcd}
NCe010	Native	20.00±0.00^{e}	45.00±1.41^{cde}	73.00±1.41^{c}	151.00±1.41^{a}	163.50±0.71^{a}
	Ann	21.50±0.71^{def}	50.50±0.71^{ab}	76.00±1.41^{bc}	139.50±0.71^{cd}	156.00±2.83^{a}
	Acid	23.50±0.71^{ab}	51.50±0.71^{ab}	79.00±1.41^{b}	155.00±1.41^{ab}	165.00±0.00^{b}
	HMT18	21.50±2.12^{bc}	49.00±0.00^{b}	71.00±1.41^{cde}	144.50±2.12^{ab}	157.50±0.71^{ab}
	HMT24	18.50±0.71^{e}	44.00±1.41^{d}	68.00±1.41^{d}	151.00±1.41^{ab}	155.00±1.41^{bc}
	HMT27	19.50±0.71^{d}	43.50±0.71^{e}	68.00±1.41^{cd}	150.50±0.71^{a}	155.00±1.41^{bcd}

NXs001	Native	23.50±0.71^{bc}	43.50±2.12^{de}	77.00±1.41^{abc}	146.00±1.41^{a}	158.50±0.71^{f}
	Ann	23.00±0.00^{cd}	44.50±0.71^{c}	74.50±0.71^{cd}	142.50±0.71^{bcd}	155.00±1.41^{a}
	Acid	25.00±1.41^{ab}	53.50±0.71^{ab}	81.50±0.71^{ab}	152.00±1.41^{abc}	161.50±2.12^{b}
	HMT18	21.00±1.41^{bc}	44.00±1.41^{c}	70.50±0.71^{de}	142.50±2.12^{ab}	156.00±2.83^{ab}
	HMT24	21.50±0.71^{cd}	41.00±1.41^{d}	67.50±0.71^{d}	140.00±0.00^{c}	155.00±1.41^{bc}
	HMT27	25.00±1.41^{ab}	44.00±1.41^{e}	72.50±0.71^{bc}	140.00±1.41^{bc}	156.50±0.71^{bc}
NXs002	Native	23.50±0.71^{bc}	51.00±1.41^{abcd}	81.50±0.71a	151.00±1.41^{a}	162.50±0.71^{a}
	Ann	22.00±1.41^{de}	47.00±1.41^{bc}	77.00±1.41^{abc}	145.50±0.71^{abc}	154.50±0.71^{a}
	Acid	24.50±0.71^{ab}	54.50±0.71^{a}	82.50±0.71^{ab}	154.50±0.71^{abc}	165.00±0.00^{b}
	HMT18	20.50±0.71^{bc}	43.50±0.71^{c}	138.00±2.83^{a}	144.00±1.41^{ab}	159.00±1.41^{a}
	HMT24	22.00±2.83^{cd}	41.50±2.12^{d}	133.50±2.12^{a}	142.50±0.71^{c}	155.50±2.12^{bc}
	HMT27	24.00±1.41^{bc}	45.50±0.71^{e}	141.00±1.41^{a}	145.50±0.71^{abc}	151.50±3.54^{cd}
NXs003	Native	23.00±0.00^{bcd}	52.00±2.83^{abc}	74.50±0.71^{bc}	135.50±0.71^{b}	155.50±2.12^{b}
	Ann	23.50±2.12^{cd}	51.50±0.71^{ab}	71.00±1.41^{d}	137.00±1.41^{d}	159.50±0.71^{a}
	Acid	25.00±1.41^{ab}	52.00±1.41^{ab}	82.50±0.71^{ab}	151.00±1.41^{bc}	164.00±0.00^{b}
	HMT18	20.00±1.41^{c}	42.50±0.71^{c}	72.00±9.90^{cde}	133.00±1.41^{c}	155.00±1.41^{ab}
	HMT24	23.50±0.71^{bc}	51.00±1.41^{bc}	74.50±0.71^{c}	144.50±2.12^{bc}	160.00±4.24^{ab}
	HMT27	21.50±2.12^{cd}	51.00±1.41^{c}	75.00±2.83^{b}	137.00±2.83^{c}	157.50±0.71^{bc}

Means in columns not followed by same alphabet(s) (by modification method) are significantly different at 5% level ($P<0.05$)

Table 4.11. Solubility indices of native and modified bitter yam starches

Cultivar	Sample	50°C	60°C	70°C	80°C	90°C
White Bitteryam	Native	11.50±0.71^{e}	29.00±1.41^{g}	40.50±0.71^{e}	96.50±3.54^{c}	132.50±4.95^{c}
	Ann	20.00±1.41^{ef}	28.50±0.71^{d}	45.50±3.54^{f}	83.50±0.71^{e}	119.00±1.41^{b}
	Acid	21.50±3.54^{b}	31.00±1.41^{d}	55.00±2.83^{d}	102.50±0.71^{f}	139.50±4.95^{c}
	HMT18	19.00±1.41^{c}	20.50±0.71^{e}	44.00±1.41^{f}	76.50±3.54^{d}	115.50±2.12^{d}
	HMT24	15.50±2.12^{f}	19.50±0.71^{e}	40.50±0.71^{e}	73.50±0.71^{d}	103.50±0.71^{e}
	HMT27	11.50±0.71^{e}	15.50±0.71^{f}	37.50±2.12^{e}	71.50±0.71^{d}	102.50±9.19^{f}
Yellow Bitteryam	Native	12.00±1.41^{e}	33.50±3.54^{fg}	53.50±2.12^{e}	95.00±4.24^{c}	122.00±2.83^{f}
	Ann	19.00±1.41^{f}	27.00±1.41^{d}	48.50±2.12^{f}	84.00±1.41^{e}	116.00±0.00^{b}
	Acid	24.50±2.12^{ab}	40.50±2.12^{c}	64.00±1.41^{c}	103.50±2.12^{f}	135.00±1.41^{c}
	HMT18	11.00±0.00^{d}	22.00±0.00^{e}	44.00±1.41^{f}	77.00±2.83^{d}	117.00±0.00^{d}
	HMT24	10.00±0.00^{g}	16.50±2.12^{e}	41.50±2.12^{e}	71.50±0.71^{d}	117.50±2.12^{d}
	HMT27	10.50±0.71^{e}	12.50±0.71^{g}	37.50±2.12^{e}	69.00±1.41^{d}	113.00±1.41^{e}

Means in columns not followed by same alphabet(s) (by modification method) are significantly different at 5% level ($P<0.05$)

The same trend was observed in the yellow cultivar but with higher solubility values at the same temperatures. At 60^{o}C, solubility of acid treated, native, annealed, HMT 18, 24 and 27 was 40%, 33.5% 27.0%, 22, 16.5 and 12.5, respectively (Figure 4.23). Annealing had greater effect on solubility of NCe005, NCe004, NCe003 and NCe001 starches at 50^{o} and 60^{o}C. The starch from NCe010 showed solubility of the order: acid>annealed>native>HMT18>HMT24>HMT27 at 51.5, 50.5, 45, 49, 44 and 43.5% respectively (Figure 4.25). In all, acid modified NCe0001 starch recorded the highest solubility at 90^{o}C (178.5%) while HMT 27 of white *D. dumetorum* had the lowest value at same temperature (102.5%). The least value of solubility was recorded for HMT 24 of yellow *D. dumetorum* starch at 50^{o}C (10.0%) while acid treated NCe002 had the highest value at same temperature (29.5%).

4.9 Loose and Packed Bulk Density (BD) and starch porosity

There were significant differences in the bulk density determined for *Colocaisa spp.* and *Xanthosoma spp.* of cocoyam and bitter yam starches. The packed bulk density of native starches from cocoyam (*Colocasia* and *Xanthosoma spp.)* and bitter yam ranged from 0.50-0.79g/mL, 0.61-0.66g/mL and 0.53-0.63g/mL, respectively (Tables 4.12, 4.13 and 4.14). The NCe003 had the highest values at 0.79 g/mL while NCe005 had the least values at 0.50 g/mL. All modification methods caused significant increase in loose and packed bulk densities of the starches but had inverse effect on porosity. This is not in agreement with the findings of Awolu and Olofinlae (2016) where packed bulk density of *D. alata* starch was reduced with acetylation, oxidation and acid-thinning modifications.

Bulk density, a function of particle size (Iheagwara, 2013), is an indicator of porosity and free-flowing ability in powdered materials like starches. It finds relevance in the design for packaging requirements and material handling of particulate materials influencing commercial acceptability of products in the food industry.

Loose and packed bulk density of a powder describes its packing behavior during the various unit operations encountered in the food processing (Ortega-Rivas *et al.,* 2006). This behavior when in a package is determined by the particulate material's initial microstructure and the ensuing mechanical processes including compression, shear, vibration and impact, which occur mostly during transportation (Thakur *et al.,* 2014).

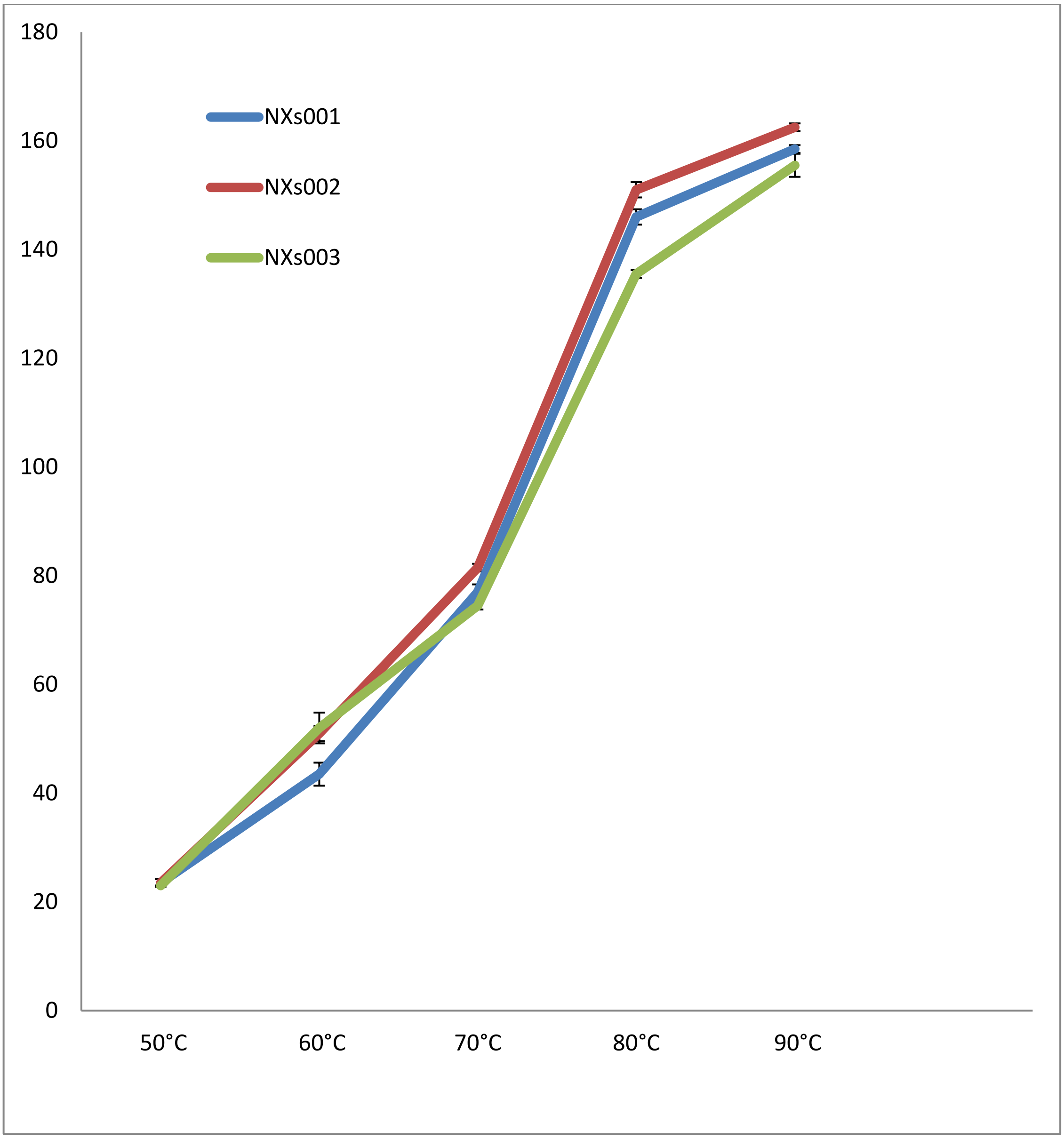


Figure 4.22. Solubility pattern of native *X. sagittifolium* starches with temperature

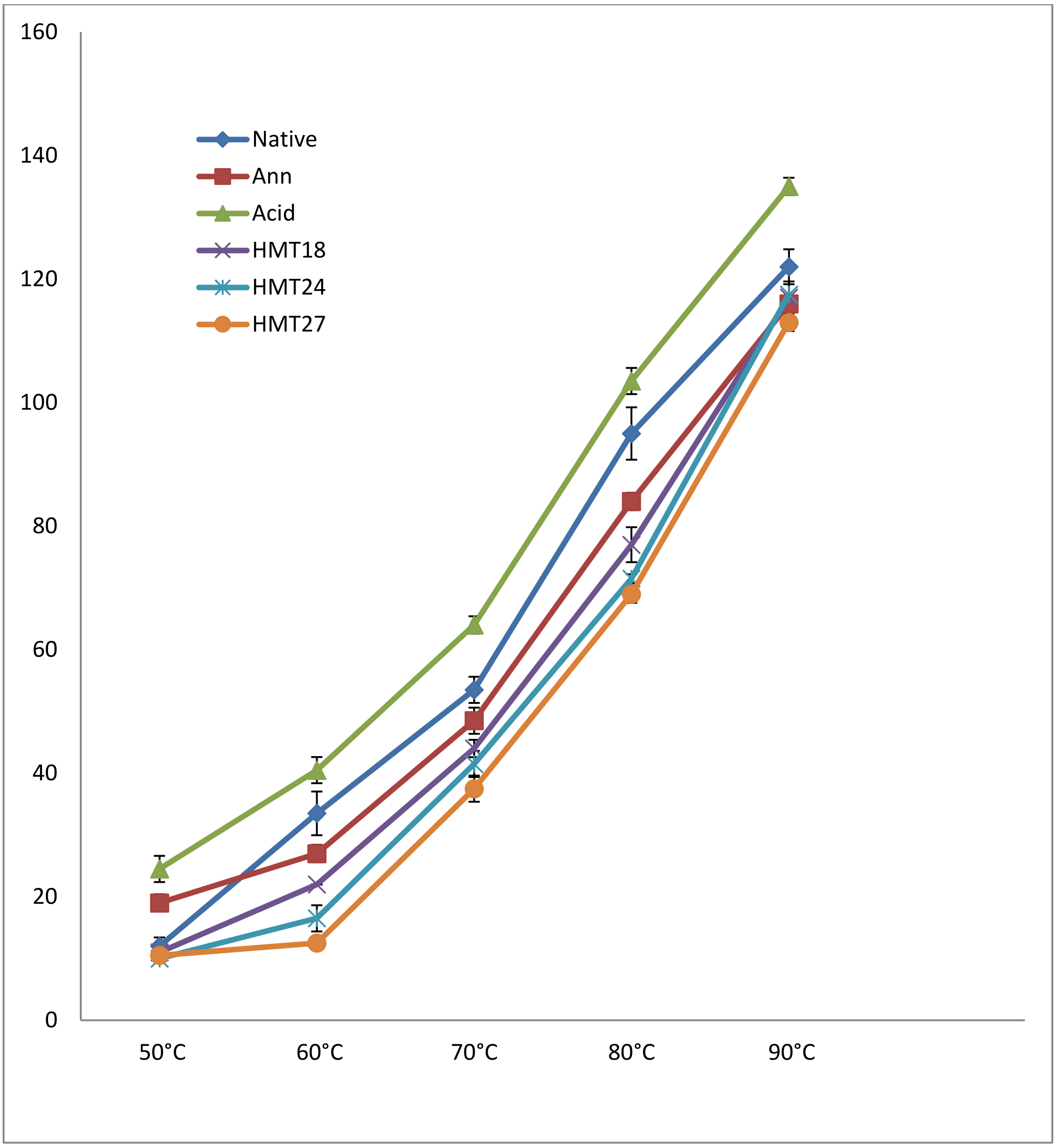


Figure 4.23. Solubility of native and modified yellow *D. dumetorum* starch at different temperatures (50-90^{o}C)

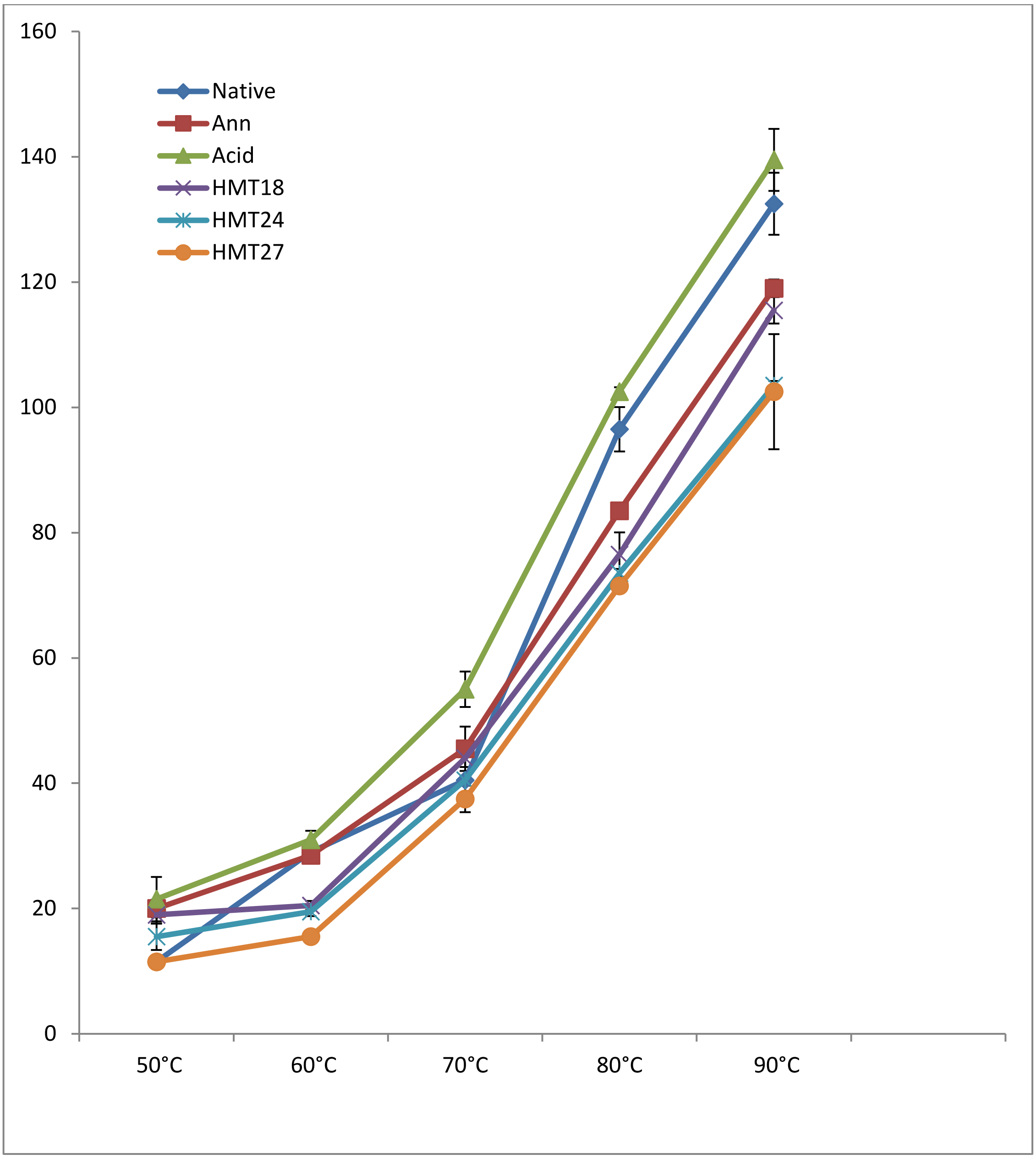


Figure 4.24. Solubility of native and modified white *D.dumetorum* starch at different temperatures (50-90^{o}C)

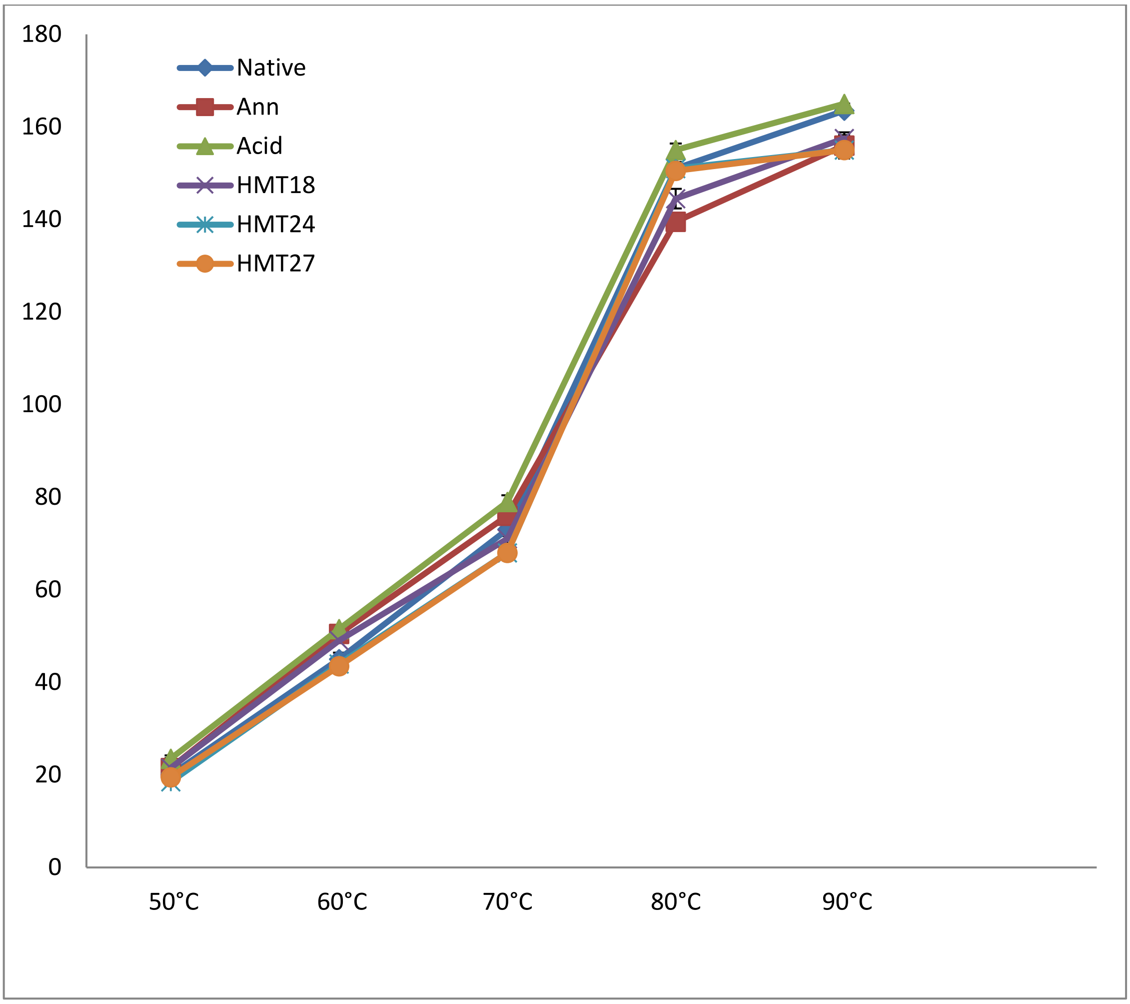


Figure 4.25. Solubility of native and modified NCe010 starches at different temperatures (50-90^{o}C).

High values may be desirable in food processing because more quantity of powdered products can be compacted in less volume. Closely packed materials will have less inter-particle voids or pores and a low density, the void fraction indicating its porosity. Starch from yellow bitter yam exhibited the highest porosity (0.46) due to packing while NXs003 showed the lowest (0.32). Porosity varied significantly with the modifications showing a general decreasing ranking order Native>Annealed>Acid>HMT18>HMT24>HMT27 for both cultivars of bitter yam. However, HMT18 and annealed starches had lower compacted fill volume than the native starches from cocoyam starches indicating lower inter-particulate voids. In previous similar studies, native corn starch had packed bulk density of 0.766 g/mL while its acid-thinned derivative was not significantly affected at 0.770g/mL bulk density (Yousif *et al.*, 2012). *D. dumetorum* flour was found to have a bulk density of 1.02g/mL (Medoua *et al.*, 2005b) while native potato starch recorded 0.866g/mL (Gadallah *et al.*, 2014). Falade and Ayetigbo (2015) while associating bulk densities of starches to granule size, shape and distribution, reported values for bitter yam starch loose and packed bulk density at 0.364 and 0.56g/mL comparable to the 0.340 and 0.53g/mL of the white cultivar and 0.34 and 0.63g/mL of the yellow cultivars in this study. Higher loose and packed bulk densities of 0.454g/mL and 0.682g/mL have been reported for native bitter yam starch (Odeku and Picker-Freyer, 2007). These differences could be attributed to differences in starch moisture contents. Moisture content has been reported to strongly influence the bulk density of starch (Stasiak *et al.*, 2014).

4.10 Water (WAC) and Oil (OAC) absorption capacities of starches

Water and oil absorption capacities of native and modified starches under study are presented in Figures 4.26, 27, 28 and 29. These parameters vary significantly between bitter yam and cocoyam starches and among their cultivars. For the native *C. esculenta* starches, the WAC range between 1.090 to 1.445g/g with the highest value recorded for NCe004 starch while the least was recorded for NCe002.

The WAC of the native starches from *C. esculenta* was of the order: NCe004 > NCe010> NCe005> NCe003> NCe001> NCe002 with the values 1.445, 1.425, 1.385, 1.375, 1.230 and 1.090g/g respectively. Comparatively, significantly higher WAC was observed among the *X. sagittifolium* (NXs001- 1.50, NXs002- 1.675 and NXs003- 1.305g/g), and the white *D. dumetorum* starches (1.635g/g). In starches from *X. sagittifolium*, the observed WAC trend was NXs002>NXs001>NXs003.

Table 4.12. Bulk densities of native and modified starches from *Colocasia esculenta*

Cultivar	Modification	Loose Volume (mL)	Packed Volume (mL)	Loose bulk Density (g/mL)	Packed bulk Density (g/m	Porosity
NCe 001	Native	15.45±0.21^{ab}	8.80±0.28^{c}	0.32±0.00^{e}	0.57±0.02^{e}	0.43±0.10^{abc}
	Ann	14.35±0.07^{bc}	8.15±0.07^{de}	0.35±0.00^{f}	0.61±0.01^{de}	0.43±0.00^{bc}
	Acid	10.25±0.07^{f}	6.60±0.14^{e}	0.49±0.00^{a}	0.76±0.02^{b}	0.36±0.01^{bc}
	HMT18	13.10±0.14^{b}	7.40±0.14^{cd}	0.38±0.00^{e}	0.68±0.01^{cd}	0.44±0.00^{b}
	HMT24	8.60±0.14^{d}	5.75±0.07^{f}	0.58±0.01^{c}	0.87±0.01^{a}	0.33±0.00^{bc}
	HMT27	7.55±0.07^{f}	5.50±0.14^{fg}	0.66±0.01^{c}	0.91±0.01^{ab}	0.27±0.01^{f}
NCe 002	Native	14.65±0.21^{c}	7.95±0.07^{de}	0.34±0.00^{d}	0.63±0.01^{c}	0.46±0.00^{ab}
	Ann	13.25±0.35^{d}	7.35±0.07^{fg}	0.38±0.01^{e}	0.68±0.01^{b}	0.45±0.01^{b}
	Acid	10.70±0.00^{ef}	7.00±0.14^{d}	0.47±0.00^{ab}	0.71`±0.01^{c}	0.35±0.01^{bcd}
	HMT18	12.20±0.14^{c}	6.80±0.00^{f}	0.41±0.00^{d}	0.74±0.00^{a}	0.44±0.01^{b}
	HMT24	9.35±0.07^{c}	5.85±0.07^{ef}	0.53±0.00^{d}	0.85±0.01^{ab}	0.37±0.01^{ab}
	HMT27	8.55±0.07^{e}	5.45±0.07^{g}	0.58±0.00^{d}	0.92±0.01^{a}	0.36±0.01^{c}
NCe 003	Native	11.15±0.21^{f}	6.35±0.07^{g}	0.45±0.01^{a}	0.79±0.01^{a}	0.43±0.02^{abc}
	Ann	14.25±0.07^{bc}	9.25±0.21^{a}	0.35±0.00^{f}	0.54.±0.01^{g}	0.35±0.02^{e}
	Acid	11.00±0.14^{de}	6.05±0.07^{f}	0.45±0.01^{bc}	0.83±0.01^{a}	0.45±0.00^{a}
	HMT18	11.45±0.21^{d}	7.00±0.00^{e}	0.44±0.01^{c}	0.71`±0.00^{b}	0.39±0.01^{d}
	HMT24	8.60±0.14^{d}	5.80±0.28^{ef}	0.58±0.01^{c}	0.86±0.04^{a}	0.33±0.02^{bc}
	HMT27	7.50±0.00^{f}	5.65±0.07^{ef}	0.67±0.00^{c}	0.89±0.01^{c}	0.25±0.01^{g}
NCe 004	Native	13.75±0.21^{d}	8.60±0.07^{c}	0.36±0.01^{c}	0.58±0.01^{e}	0.37±0.00^{ef}
	Ann	14.15±0.21^{c}	8.90±0.14^{b}	0.35±0.01^{f}	0.56±0.01^{g}	0.37±0.00^{de}
	Acid	11.55±0.64^{cd}	7.10±0.14^{d}	0.43±0.02^{d}	0.70±0.01^{c}	0.38±0.05^{b}
	HMT18	13.05±0.07^{b}	7.95±0.07^{b}	0.38±0.00^{e}	0.63±0.01^{e}	0.39±0.00^{d}
	HMT24	8.60±0.14^{d}	6.15±0.21^{de}	0.58±0.01^{c}	0.81±0.03^{bc}	0.28±0.04^{cde}
	HMT27	6.65±0.07^{h}	5.60±0.00^{fg}	0.75±0.01^{a}	0.89±0.00^{bc}	0.16±0.01^{h}
NCe 005	Native	16.10±0.14^{a}	10.00±0.00^{a}	0.31±0.00^{c}	0.50±0.00^{g}	0.38±0.01^{def}
	Ann	10.85±0.07^{g}	6.60±0.00^{h}	0.46±0.00^{b}	0.76±0.00^{a}	0.39±0.00^{d}
	Acid	11.45±0.07^{cd}	7.55±0.07^{c}	0.44±0.00^{cd}	0.66±0.01^{d}	0.34±0.01^{bcd}
	HMT18	11.35±0.07^{d}	6.75±0.07^{f}	0.44±0.00^{c}	0.74±0.01^{a}	0.41±0.00^{cd}
	HMT24	8.50±0.28^{d}	6.25±0.07^{cd}	0.59±0.02^{c}	0.80±0.01^{cd}	0.26±0.03^{e}
	HMT27	6.90±0.00^{g}	5.80±0.00^{e}	0.72±0.0^{b}	0.86±0.00^{d}	0.16±0.00^{h}
NCe 010	Native	12.50±0.14^{e}	8.20±0.00^{d}	0.40±0.00^{b}	0.61±0.00^{d}	0.34±0.01^{fg}
	Ann	11.85±0.07^{e}	7.95±0.07^{e}	0.42±0.00^{d}	0.63±0.01^{d}	0.33±0.00^{f}
	Acid	10.35±0.21^{f}	7.15±0.07^{d}	0.48±0.00^{a}	0.70±0.01^{c}	0.31±0.02^{d}
	HMT18	11.20±0.28^{de}	7.50±0.00^{c}	0.45±0.01^{bc}	0.67±0.00^{d}	0.33±0.02^{f}
	HMT24	8.55±0.35^{d}	5.70±0.00^{f}	0.59±0.02^{c}	0.88±0.00^{a}	0.33±0.03^{bc}
	HMT27	11.35±0.07^{c}	7.55±0.07^{b}	0.44±0.00^{f}	0.66±0.01^{f}	0.33±0.01^{d}

Means in columns not followed by same alphabet(s) are significantly different at 5% level (P<0.05).

Table 4.13. Bulk densities of native and modified starches from *Xanthosoma sagittifolium*.

Cultivar	Modificatio	Loose Volume (mL)	Packed Volume (mL)	Loose bulk Density (g/ mL)	Packed bulk Density (g/ mL)	Porosity
NXs 001	Native	13.75 ± 0.21^{d}	8.15 ± 0.00^{d}	0.36 ± 0.01^{c}	0.61 ± 0.01^{cd}	0.41 ± 0.00^{cde}
	Ann	13.10 ± 0.14^{d}	8.50 ± 0.00^{c}	0.38 ± 0.00^{e}	0.59 ± 0.00^{f}	0.35 ± 0.01^{e}
	Acid	11.65 ± 0.21^{c}	7.95 ± 0.07^{b}	0.43 ± 0.00^{d}	0.63 ± 0.01^{e}	0.32 ± 0.02^{cd}
	HMT18	13.15 ± 0.07^{b}	8.50 ± 0.00^{a}	0.38 ± 0.00^{e}	0.59 ± 0.00^{f}	0.35 ± 0.00^{e}
	HMT24	9.65 ± 0.07^{c}	6.55 ± 0.07^{c}	0.52 ± 0.00^{d}	0.76 ± 0.01^{d}	0.32 ± 0.01^{cd}
	HMT27	12.50 ± 0.14^{a}	7.40 ± 0.00^{b}	0.40 ± 0.00^{h}	0.68 ± 0.00^{f}	0.41 ± 0.01^{a}
NXs 002	Native	13.15 ± 0.21^{de}	7.60 ± 0.00^{f}	0.38 ± 0.01^{c}	0.66 ± 0.00^{b}	0.42 ± 0.01^{bc}
	Ann	10.05 ± 0.07^{h}	8.30 ± 0.00^{cd}	0.50 ± 0.00^{a}	0.60 ± 0.00^{ef}	0.17 ± 0.01^{g}
	Acid	11.65 ± 0.07^{c}	7.75 ± 0.07^{bc}	0.43 ± 0.00^{d}	0.65 ± 0.01^{de}	0.33 ± 0.01^{cd}
	HMT18	10.95 ± 0.07^{e}	6.95 ± 0.07^{e}	0.46 ± 0.00^{b}	0.72 ± 0.01^{b}	0.37 ± 0.01^{e}
	HMT24	8.00 ± 0.00^{e}	5.80 ± 0.14^{ef}	0.63 ± 0.00^{b}	0.86 ± 0.02^{a}	0.28 ± 0.02^{de}
	HMT27	8.55 ± 0.07^{e}	5.45 ± 0.07^{g}	0.58 ± 0.00^{d}	0.92 ± 0.01^{a}	0.36 ± 0.01^{c}
NXs 003	Native	11.25 ± 0.35^{f}	7.70 ± 0.00^{ef}	0.31 ± 0.01^{e}	0.65 ± 0.00^{b}	0.32 ± 0.02^{g}
	Ann	11.45 ± 0.21^{f}	7.20 ± 0.00^{g}	0.44 ± 0.00^{c}	0.69 ± 0.00^{b}	0.37 ± 0.01^{de}
	Acid	10.50 ± 0.14^{ef}	6.95 ± 0.07^{d}	0.48 ± 0.01^{a}	0.72 ± 0.01^{c}	0.34 ± 0.02^{cd}
	HMT18	10.60 ± 0.14^{f}	7.30 ± 0.00^{d}	0.47 ± 0.01^{a}	0.68 ± 0.00^{c}	0.31 ± 0.01^{g}
	HMT24	7.45 ± 0.07^{f}	6.50 ± 0.00^{c}	0.67 ± 0.01^{a}	0.77 ± 0.00^{d}	0.13 ± 0.01^{f}
	HMT27	11.45 ± 0.07^{c}	7.95 ± 0.07^{a}	0.44 ± 0.00^{fg}	0.63 ± 0.01^{g}	0.31 ± 0.01^{e}

Means in columns not followed by same alphabet(s) are significantly different at 5% level (P<0.05).

Table 4.14. Bulk densities of native and modified starches from *Dioscorea dumetorum* cultivars.

	Sample	Loose Volume (mL)	Packed Volume (mL)	Loose bulk Density (g/mL)	Packed bulk Density (g/mL)	Porosity
White	Native	16.00±0.71^{a}	9.38±0.18^{b}	0.34±0.01^{d}	0.53±0.10^{f}	0.41±0.04^{cd}
	Ann	15.25±0.21^{a}	8.90±0.00^{b}	0.33±0.00^{g}	0.56±0.00^{g}	0.42±0.01^{c}
	Acid	14.95±0.35^{a}	8.45±0.07^{a}	0.33±0.01^{f}	0.59±0.00^{f}	0.43±0.02^{a}
	HMT18	13.70±0.00^{a}	7.25±0.07^{d}	0.36±0.00^{f}	0.69±0.01^{c}	0.47±0.01^{a}
	HMT24	12.45±0.07^{a}	7.60±0.28^{a}	0.40±0.00^{e}	0.66±0.02^{e}	0.39±0.03^{a}
	HMT27	11.65±0.07^{b}	7.15±0.07^{c}	0.43±0.00^{g}	0.70±0.01^{e}	0.39±0.00^{b}
Yellow	Native	14.80±0.28^{bc}	8.00±0.00^{d}	0.34±0.01^{d}	0.63±0.00^{cd}	0.46±0.01^{a}
	Ann	14.60±0.14^{b}	7.60±0.28^{f}	0.34±0.00^{f}	0.66±0.02^{c}	0.48±0.01^{a}
	Acid	13.40±0.00^{b}	7.55±0.07^{c}	0.37±0.00^{e}	0.66±0.01^{d}	0.44±0.01^{a}
	HMT18	12.30±0.14^{c}	7.25±0.07^{d}	0.41±0.00^{d}	0.69±0.01^{c}	0.41±0.00^{c}
	HMT24	11.90±0.00^{b}	7.20±0.00^{b}	0.42±0.00^{e}	0.69±0.00^{e}	0.39±0.00^{a}
	HMT27	10.65±0.07^{d}	6.95±0.07^{d}	0.47±0.00^{e}	0.72±0.01^{e}	0.35±0.01^{cd}

Means in columns not followed by same alphabet(s) are significantly different at 5% level ($P<0.05$).

Native white bitter yam recorded the highest WAC among all native starches studied at 1.635g/g with the yellow cultivar recording the overall lowest values at 1.085g/g. Adebowale and Lawal (2003) have earlier reported WAC and OAC of native Mucuna bean starch to be 1.215 and 2.211g/g while other workers reported varying values of WAC and OAC for rice cultivars (0.9373-1.4335 and 0.5997-1.5198g/g), bitter yam (0.903 and 1.003g/g), cocoyam (1.3g/g), sweet potato (1.2g/g) and cassava (1.2g/g) at ambient temperatures (Falade and Christopher, 2015; Falade and Ayetigbo, 2015; Mweta, 2009). Higher values of OAC was generally observed for all the native starches with the starch from NCe005 (1.75g/g) recording the highest, and NCe002 and NCe004 (1.285g/g) showed the lowest value. However, all the native starches (except NCe004, NXs003 and white bitter yam) showed higher OAC than WAC under similar conditions suggesting a higher number of lipophilic than hydrophilic binding sites on the starch granule surfaces. Previously, Lawal (2005) have reported WAC of 57.8g/100g and OAC of 92.3g/100g for new cocoyam (*X. sagittifolium*); values much lower than those recorded for the *X. sagittifolium* starches in this study. This may be attributed to differences in lipid, protein and carbohydrate constituents of the different starches since presence and amount of these polymers influence the hydrophilic/lipophilic polar side chains the starch molecules bear (Eltayeb *et al.*, 2011) which in turn enhance or hinder affinity for oil or water. The modification methods had varied effects on the WAC and OAC of the different starches from cocoyam and bitter yam cultivars. Generally, annealing and acid treatments increased hydrophobicity in some of the starches while HMT reduced it. In starch from NCe002 (Figure 4.29), annealing caused increase in WAC from 1.090 to 1.23g/g while acid hydrolysis lowered the value to 0.92g/g. The HMT improved the WAC as level of moisture in treated starch increased to 1.245, 1.220 and 1.450g/g respectively. The OAC was significantly increased by acid treatment to 1.465g/g, and increased in the 18 and 24% starches treated by HMT to 1.175 and 1.360g/g, respectively.

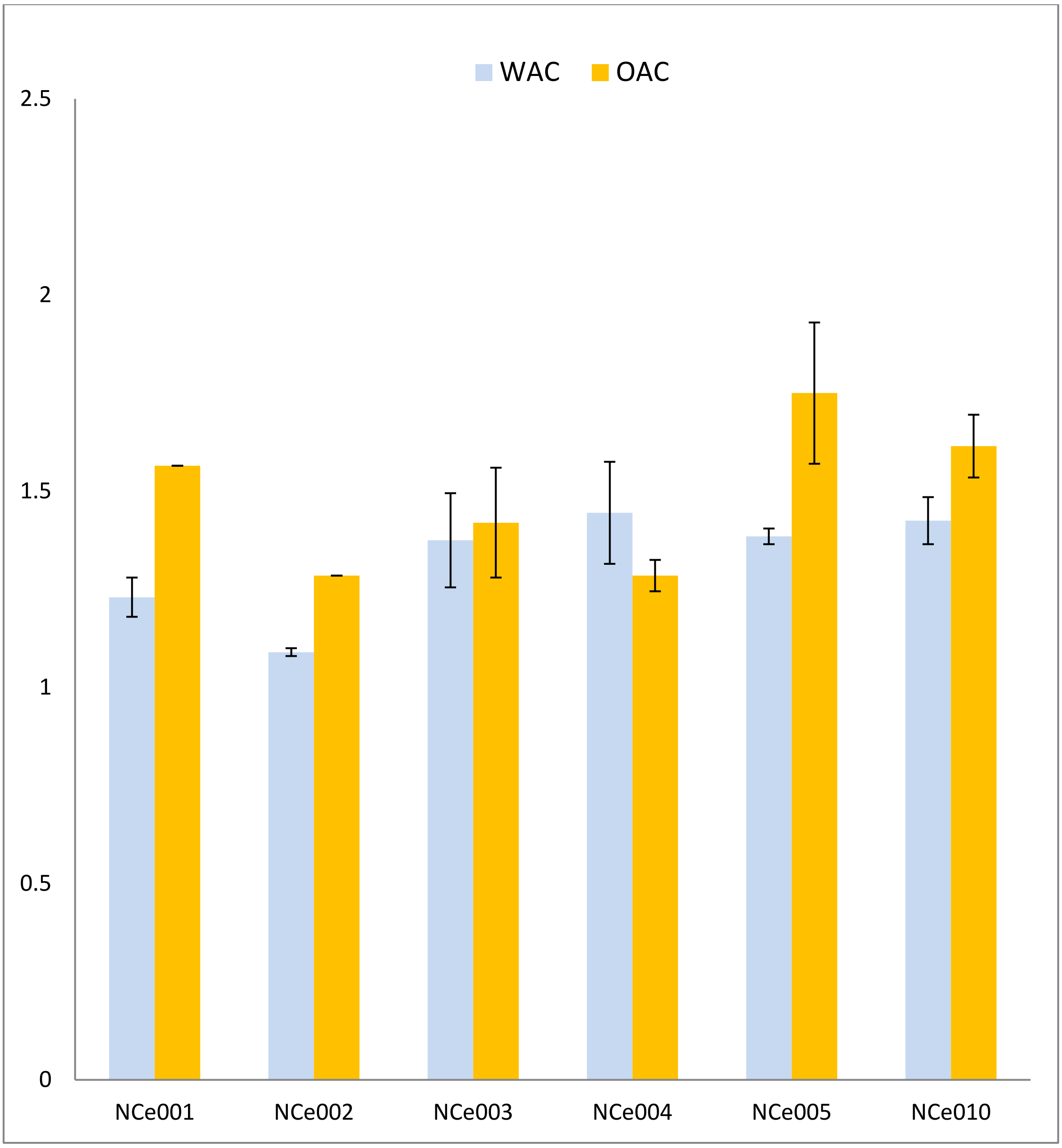


Figure 4.26. Water and oil absorption capacities of native *C. esculenta* starches

In starch from NXs003, WAC was reduced by 49% from 1.510 to 0.765 by acid thinning. Similarly, acid thinning reduced WAC of native starch from NCe010 by 43% from 1.425g/g to 0.805g/g and that of NXs001 (Figure 4.28) by 40% from 1.465g/g to 0.88g/g. Acid thinning and HMT increased OAC of native starch from NXs001 to 1.595, 1.605 and 1.545g/g from 1.50g/g. In the starch from white bitter yam, the OAC was of the order: Native>acid>HMT24>HMT27>HMT18>annealed (Figure 4.27). Lawal (2005) reported a progressive increase in WAC with HMT and reduction with annealing and acid thinning of starch from new cocoyam. The reduced WAC observed with acid treatment in the starches could be attributed to increase in crystallinity and subsequent shrinking of the amorphous regions implying a reduction in the available binding sites for water in the starch granules (Olu-Owolabi *et al.*, 2014). The strength of aligning hydrogen bonds within starch chains rather than with water or oil molecules are affected by modification and therefore would influence the degree of oil or water affinity they possess. Witono *et al.* (2014) opined that the rate of water penetration into a starch gel was determined by polymer chain relaxations rather than by osmotic driven diffusion when cassava starch was grafted with polyacrylic acid to produce a hydro-absorbent. The degree of water absorption was drastically elevated up to 63g/g water under severe suction in the study. This showed the influence of surfactants on WAC/OAC of starches. Other factors that have been shown to influence WAC and OAC include particle size, amylose/amylopectin ratio, conformational characteristics of granules, and thermodynamic properties of system, pH, temperature, size and shape of granules (Chou and Morr, 1979; Lawal, 2005; Mweta, 2009; Eltayeb *et al.*, 2011; Abraham, 1993).

4.11 Least Gelation Concentration (LGC) of starches

Least gelation capacities of starches from cocoyam and bitter yam varied with cultivars and modification methods (Table 4.15 and 4.16). The LGC of native starches from *C. esculenta* starches ranged between 6 and 14% (w/v). The LGC of starch from NXs001, NXs002 and NXs003 was 6%, 6% and 8% (w/v), respectively. The starches from white and yellow cultivars of bitter yam differ in their gelation capacities at 6 and 10%, respectively. These values were different from values reported for starch from white cultivar of bitter (16%, w/v) yam by Otegbayo *et al.* (2014). Based on the values of the LGC, the starches may thus be grouped into high (2-6%), medium (8-12%) and low (>12%) gelling starches. The starches from NCe001, NXs001, NXs002 and white bitter yam could be categorised within the high gelling range.

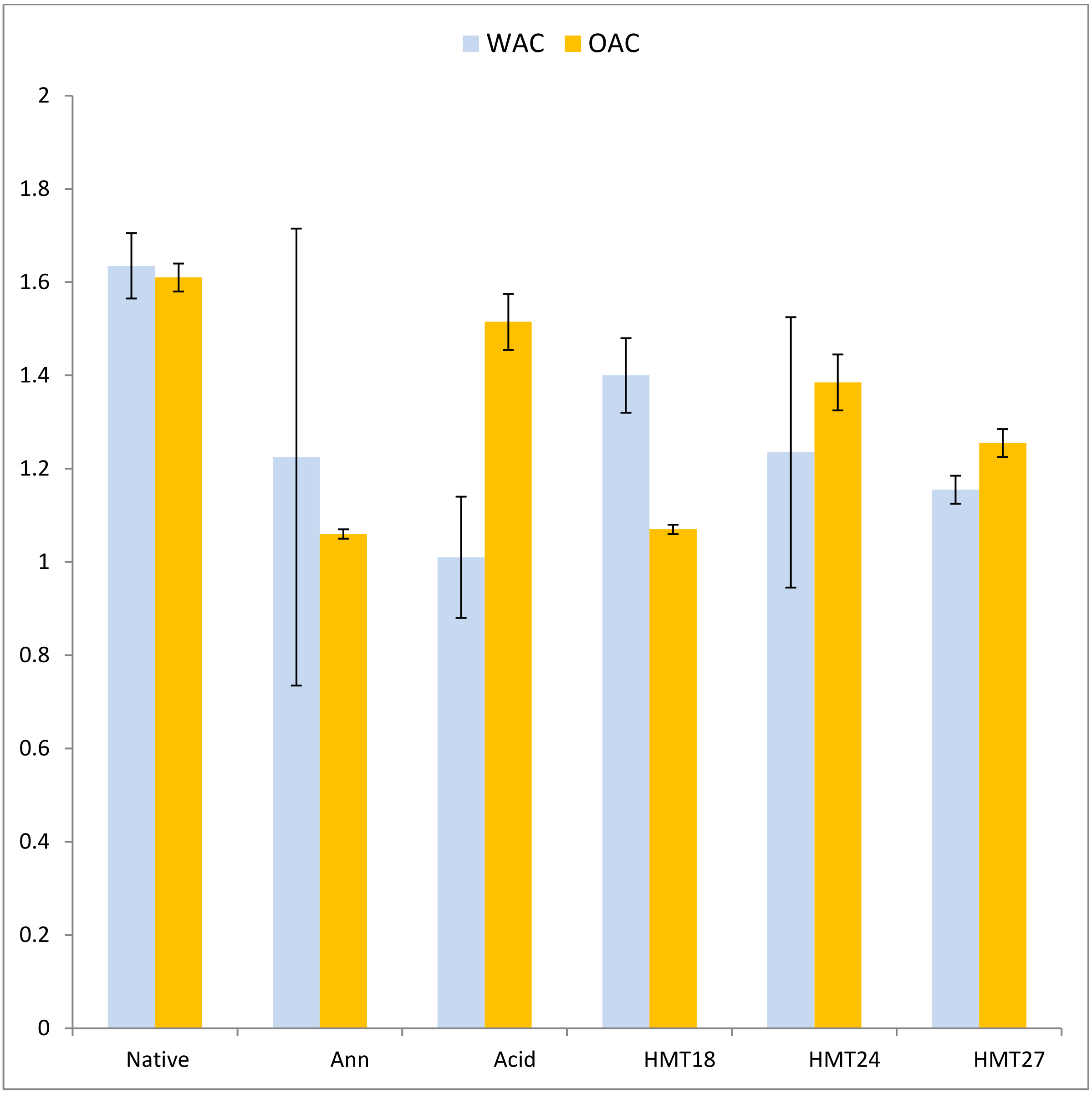


Figure 4.27. Effect of modification methods on WAC and OAC of starch of white bitter yam

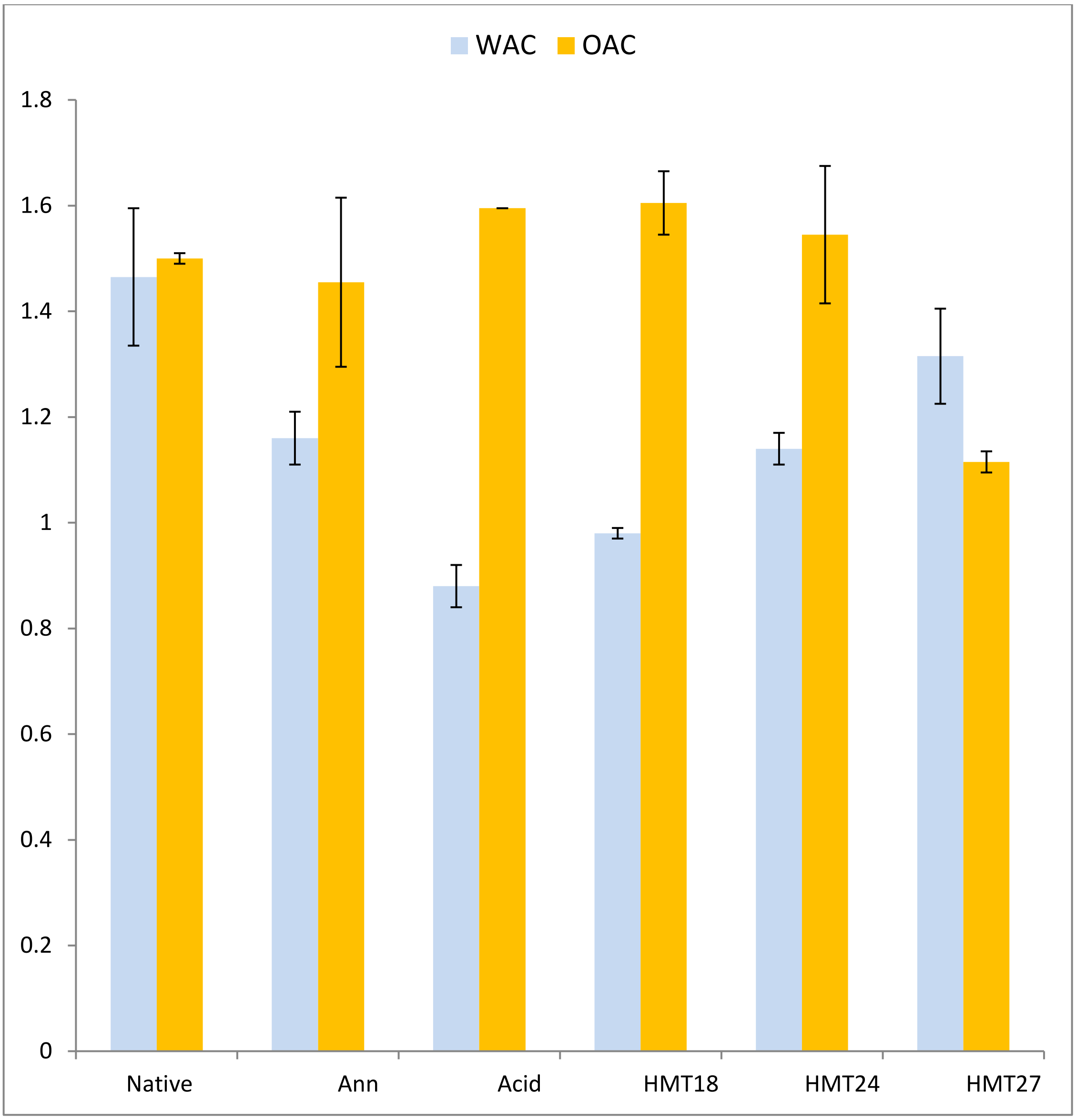


Figure 4.28. Effect of modification methods on WAC and OAC of NXs001 starch

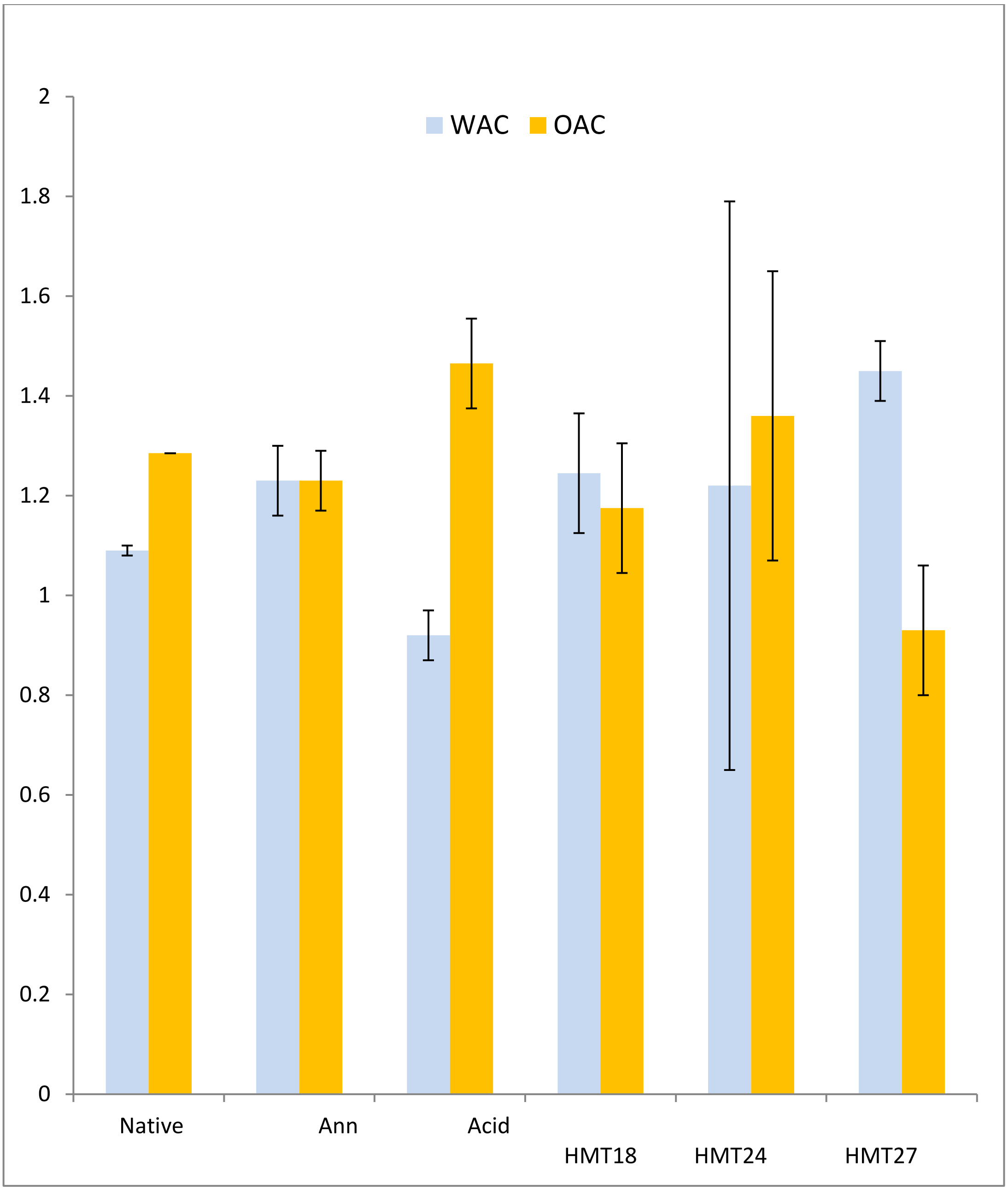


Figure 4.29. Effect of modification methods on WAC and OAC of NCe002 starch

The starches from NCe002, NCe003, NCe004, NCe010, NXs003 and yellow bitter yam could be categorised within the medium range while only starch from NCe005 was categorized as low gelling.

Native starch from NCe004 didn't form firm gel even at 18% (w/v) concentration while starches from NCe001 and NCe002 cocoyam cultivars formed firm gels at 10 and 12%. Starches from all the *X. sagittifolium* including NXs001, NXs002 and NXs003 cultivars formed firm gels at 10% concentration and formed very firm gels at 14, 14 and 16% concentrations, respectively. This may be linked to easy association of polymeric chains causing a stiffer or rigid gel on cooling of acid hydrolysed starches. A high value of LGC indicate minimal interaction or association between leached amylose and swollen or collapsed starch granules when cooled in a network of imbibed water, hence low gelation. After gelatinization, solubilized amylose links intact and fragmented starch granules at junction zones, binds entrapped and unabsorbed water to form linear and branched 3-dimensional gel network structure. This implies that solubilized amylose will have greater efficiency than granular amylose in providing a stronger gel structure. Amylose may then be taken to be responsible for the short term gelation of starches while amylopectin causes the long term crystallization by reinforcement of the amylose matrix (Miles *et al.*, 1985; Wang and Wang, 2001).

Heat-moisture treated starches (HMT) generally presented higher LGC than the native starches, increasing as level of moisture conditioning increased except for 18% HMT starch of NXs002 which gelled at 4% (w/v) starch rather than at 6% of the native starch. The HMT also did not alter gelation of starches from NXs001 of the HMT 18 and NXs002 of the HMT 27. This observation did not agree with the findings of earlier authors who reported increased gelling capacity (low LGC) with heat-moisture conditioning in mucuna beans, finger millet, African yam beans, new cocoyam and bambara (Adebowale and Lawal, 2003; Adebowale *et al.*, 2005; Adebowale *et al.*, 2009; Lawal, 2005; Adebowale *et al.*, 2002). They attributed the increase to structural reordering and realignment of amylose and amylopectin to form crystalline micelles bound by molecular filaments which enhanced intra-granular binding forces, thus improving gel strength. It is opined in this study that since partial gelatinization and starch granule weakening (reduced granular stability) occur following HMT, the crystalline packing was already disrupted by leached amylose in the amorphous region by the modification. The gelatinization process leading to gelation then caused a faster hydration of the hydrogen bonding sites and increased water retention, reduced amylose leaching and consequently less 'junction zones' (for Van der

Waals and hydrogen associations) resulting in weak or watery gel. Reduced availability of amylose for intermolecular hydrogen-bonding disrupts long-range interactions within the gel resulting in decreased cohesiveness of the structure (Wang *et al.*, 2015). Tang and Copeland (2007) reported formation of soft gel from waxy (low amylose) starch and showed that aggregate and not network arrangement of the structure was formed, a reflection of the effect and interactions of amylose. This clearly demonstrates that the increase or decrease in gelation capacity following modification may be as a result of interplay of more than one factor.

Annealing treatment generally did not alter or resulted in increased gelation capacity for all cocoyam cultivars, whereas the gelation capacities of the bitter yam cultivars were markedly and considerably reduced. Starches from NCe001, NCe004, NXs001, NXs002 and NXs003 retained their LGC at 6, 8, 6, 6 and 8 % (w/v) while those from NCe002, NCe003, NCe005 and NCe010 had their LGC reduced by annealing from 8 to 6%, 12 to 10%, 14 to 10% and from 12 to 8% (w/v) respectively. Annealing produced opposite effects in bitter yam starches in that their LGCs were increased from 6 to 12% (white cultivar) and 10 to 14% (yellow cultivar) demonstrating the effect of differences in botanical origin. Extra reinforcing of –D- (16) linkages in the annealed starches (Jacobs *et al.*, 1998) and increased granular stability as a result of the annealing treatment (Hoover and Vasanthan, 1994) may be adduced as the reasons for increase in gelation capacity of the cocoyam starches while the effect of reduced amylose leaching in the annealed bitter yam starches which probably negates the plasticizing effect of water in the amorphous lamella regions of the semi-crystalline growth ring (Perry and Donald, 2000) may be the reason for their reduced gelation.

Acid thinning significantly increased gelation capacity of all *X. sagittifolium* and *D. dumetorum* cultivars while the ones of *C. esculenta* were reduced, unaltered or increased. All three *X. sagittifolium* starches gelled at 4% while the white and yellow bitter yam gelled at 4 and 6% respectively. The NCe001 and NCe004 starches had increased LGC, NCe002 and NCe005 were unaltered, while NCe003 and NCe010 had reduced LGC from 12 to 8% and from 12 to 10% respectively (Table 4.14). Acid thinning causes de-polymerization of starch granule chains and primarily attack the amorphous regions within the starch granule, hydrolyzing both amylose and amylopectin simultaneously (Wang and Wang, 2001). The eroded amorphous region presents minimal restriction to formation of double helical chain network resulting in better formation of hydrogen and Van der Waals bonding and thus stronger gels are formed. Amylose which predominantly occupies the amorphous region has been reported to be responsible for the disruption of ordered crystalline packing in starch granules (Lawal, 2004). However, more amorphous granule structure had been reported to favour greater crosslinking of linear and branched fractions of starch as well as a higher proportion of long than short chains in starch granules (Ulbrich *et al.,* 2015). The varied responses of acid hydrolysed starches could be as a result of differences in varietal source as Lawal (2004) also reported a reduction in LGC of acid thinned new cocoyam starch from 8 to 6% (w/v) while Wang and Wang (2001) reported increased gelation of acid treated corn, potato and rice starches. Similarly, acid thinning of corn starch resulted in higher gel strenght (Ulbrich *et al.*, 2015).

Starches with high LGC may therefore be utilized in applications that require low bulk volume and low viscosity on cooling like complementary/weaning or geriatric diets. Textural properties of some food products like pastries, jellies and gums may also be modified by addition of these starches. Starches with low LGC (high gelatin power) like the acid modified starches will be applicable in processes as thickeners, stabilizers and gelling agents. This is more so as modified starches have been found to be better gelling agents than gum or others from synthetic sources.

4.12 Fourier Transformed Infra-red Spectroscopy (FT-IR)

The effect of cultivar and method of modification on absorption and type of vibrations in cocoyam and bitter yam starches are shown in Tables 4.17 and 4.18. Eight major characteristic broadband areas were observed in the starches with minimum and maximum absorptions ranging between 532 and 577cm^{-1}, 1021 and 1036cm^{-1}, 1362 and 1434cm^{-1}, 1642 and 1656cm^{-1}, 2067 and 2140cm^{-1}, 2347 and 2375cm^{-1}, 2922 and 2929cm^{-1} and at 3350 and 3464cm^{-1}. The native bands are similar in form and intensities to the ones reported by Aboubakar *et* al. (2008). Generally, the bands at <1600 are the most important in polymer identification. All native and modified starches from cocoyam and bitter yam showed the broad peaks with strong intensities at 3350-3469cm^{-1}, which are assigned to the hydroxyl group stretching of the O-H bonds and bound water common to starches (Synytsya *et al*, 2003). The Sp^3 hybridized alkane bands at around 2925cm^{-1} associated with CH_2 or CH_3 symmetrical stretching vibrations are also prominent in all spectra (Table 4.16). Asymmetric stretching of the carboxylates (C=O bonds), evidence of the presence of anhydro-glucose rings are observed in absorption peaks around 1642-1656cm^{-1} in all starches under study. Similar conjugated effects may be present as in C=C (alkenes) or C=N (amides) vibrations with all dienes having Sp^2 hybridization.

Table 4.15. Least gelation concentration of cocoyam starches

Cultivar	Modification	Starch concentration								
		2%	4%	6%	8%	10%	12%	14%	16%	18%
NCe001										
	Native	—L	—V	†G	†G	†FG	†FG	†FG	†VFG	†VFG
	Annealed	—L	—V	†G	†G	†G	†G	†FG	†FG	†VFG
	Acid Thinned	—L	—L	—V	†G	†G	†G	†FG	†FG	†VFG
	HMT18	—L	—L	—L	—V	—V	—V	†G	†G	†G
	HMT24	—L	—L	—L	—V	—V	†G	†G	†FG	†FG
	HMT27	—L	—L	—L	—V	—V	—V	—V	†G	†G
NCe002										
	Native	—L	—V	—V	†G	†G	†FG	†FG	†FG	†VFG
	Annealed	—L	—V	†G	†G	†G	†FG	†FG	†FG	†VFG
	Acid thinned	—L	—L	—V	†G	†G	†FG	†FG	†FG	†FG
	HMT18	—L	—L	—L	—L	—V	†G	†FG	†FG	†FG
	HMT24	—L	—L	—L	—L	—V	—V	†G	†G	†FG
	HMT27	—L	—L	—L	—L	—V	—V	†G	†G	†G
NCe003										
	Native	—L	—L	—V	—V	—V	†G	†G	†G	†FG
	Annealed	—L	—L	—V	—V	†G	†G	†FG	†FG	†VFG
	Acid thinned	—L	—L	—V	†G	†G	†G	†FG	†FG	†VFG
	HMT18	—L	—L	—L	—L	—V	—V	†G	†G	†FG
	HMT24	—L	—L	—L	—L	—L	—V	†G	†G	†FG
	HMT27	—L	—L	—L	—V	—V	†G	†G	†G	†FG
NCe004										
	Native	—L	—L	—V	†G	†G	†G	†G	†G	†G
	Ann	—L	—L	—V	†G	†G	†G	†G	†FG	†FG
	Acid	—L	—L	—V	—V	†G	†G	†G	†FG	†FG
	HMT18	—L	—L	—L	—L	—V	†G	†G	†FG	†FG
	HMT24	—L	—L	—L	—L	—L	—L	—V	†G	†FG
	HMT27	—L	—L	—L	—L	—L	—L	—V	†G	†FG
NCe005										
	Native	—L	—L	—L	—V	—V	—V	†G	†G	†FG
	Ann	—L	—L	—L	—V	†G	†G	†G	†FG	†FG
	Acid	—L	—L	—L	—V	—V	—V	†G	†FG	†VFG
	HMT18	—L	—L	—L	—L	—L	—V	—V	†G	†FG
	HMT24	—L	—L	—L	—L	—L	—V	—V	†G	†FG
	HMT27	—L	—L	—L	—L	—L	—V	—V	†G	†FG
NCe010										
	Native	—L	—L	—L	—V	—V	†G	†G	†FG	†FG
	Ann	—L	—L	—V	†G	†G	†G	†FG	†FG	†VFG
	Acid	—L	—L	—V	—V	†G	†FG	†FG	†FG	†VFG
	HMT18	—L	—L	—L	—L	—L	—V	†G	†FG	†VFG
	HMT24	—L	—L	—L	—L	—V	—V	†G	†FG	†FG
	HMT27	—L	—L	—L	—L	—V	†G	†G	†FG	†FG
NXs001										
	Native	—L	—V	†G	†G	†FG	†FG	†VFG	†VFG	†VFG
	Ann	—V	—V	†G	†G	†FG	†FG	†FG	†FG	†VFG
	Acid	—V	†G	†G	†G	†G	†FG	†FG	†FG	†VFG
	HMT18	—V	—V	†G	†G	†FG	†FG	†FG	†FG	†VFG
	HMT24	—L	—L	—L	—V	†G	†FG	†FG	†VFG	†VFG
	HMT27	—L	—L	—V	—V	†G	†FG	†FG	†VFG	†VFG

NXs002										
	Native	—L	—L	†G	†G	†FG	†FG	†VFG	†VFG	†VFG
	Ann	—V	—V	†G	†FG	†FG	†FG	†FG	†VFG	†VFG
	Acid	—V	†G	†G	†FG	†FG	†FG	†FG	†FG	†VFG
	HMT18	—V	†G	†G	†FG	†FG	†FG	†FG	†FG	†VFG
	HMT24	—L	—L	—V	†G	†FG	†FG	†FG	†FG	†VFG
	HMT27	—L	—V	†G	†G	†FG	†FG	†FG	†VFG	†VFG
NXs003										
	Native	—L	—V	—V	†G	†FG	†FG	†FG	†VFG	†VFG
	Ann	—L	—L	—V	†G	†G	†FG	†FG	†FG	†VFG
	Acid	—V	†G	†G	†G	†FG	†FG	†FG	†VFG	†VFG
	HMT18	—L	—L	—L	—V	†G	†FG	†FG	†VFG	†VFG
	HMT24	—L	—L	—L	—V	†G	†FG	†FG	†FG	†VFG
	HMT27	—L	—L	—L	—V	†G	†FG	†FG	†FG	†FG

—L-Liquid, —V-Viscous, †G-Gel, †FG-Firm gel, †VFG-Very firm gel

Table 4.16: Least gelation concentration of bitter yam starches

Cultivar	Modification	Starch concentration								
		2%	4%	6%	8%	10%	12%	14%	16%	18%
White										
Bitter yam	Native	—L	—V	†G	†G	†G	†FG	†FG	†FG	†VFG
	Ann	—L	—L	—L	—L	—V	†G	†G	†G	†G
	Acid	—L	†G	†G	†FG	†FG	†VFG	†VFG	†VFG	†VFG
	HMT18	—L	—L	—L	—L	—L	—V	—V	—V	†G
	HMT24	—L	—L	—L	—L	—L	—L	—L	—V	†G
	HMT27	—L	—L	—L	—L	—L	—L	—L	—V	†G
Yellow										
Bitter yam	Native	—L	—L	—V	—V	†G	†FG	†FG	†VFG	†VFG
	Ann	—L	—L	—L	—L	—V	—V	†G	†G	†G
	Acid	—L	—V	†G	†FG	†FG	†VFG	†VFG	†VFG	†VFG
	HMT18	—L	—L	—L	—L	—L	—L	—L	—V	†G
	HMT24	—L	—L	—L	—L	—L	—L	—L	—V	†G
	HMT27	—L	—L	—L	—L	—L	—L	—V	—V	†G

—L-Liquid, —V-Viscous, †G-Gel, †FG-Firm gel, †VFG-Very firm gel

These bands may be linked to ester linkages involving carboxylic and hydroxyl group of the starch polymer chains (Alves *et al,* 2011). All starches exhibited weak and broad stretching vibrations at 532-577cm^{-1} associated with the possible presence of the halo-alkanes groups (C-X). Bromide had earlier been identified as the functional group present at absorption bands around 576cm^{-1} (Sacithraa *et al.*, 2013).

Absorptions at 3369 cm^{-1} and 2090 cm^{-1} in native NCe001 starch were observed to increase in intensity with increasing moisture levels in heat-moisture treated samples to 3390 cm^{-1} and 2100 cm^{-1} in HMT18, to 3417 cm^{-1} and 2112 cm^{-1} in HMT24 and to 3440 cm^{-1} and 2140 cm^{-1} in HMT27 respectively. This may be attributed to reduction in crystalline order and structural rearrangements as a result of hydration of the O-H and C-H stretch vibrations following heat-moisture treatment. Vibrations at bands between 1434 and 1362cm^{-1} which confirm deformation in aliphatic structure gradually became weak and shallow shoulders in the HMT samples while there was no significant difference in same bands with the annealed and acid-modified samples of NCe001. Additional bands at 455.94 cm^{-1} also appeared for the HMT27. Bands at around 1541cm^{-1} representing adsorbed water in amorphous regions of starch (Kizil *et al.*, 2002) appeared in native NCe003 and in annealed NCe002 starches. Acid hydrolysis caused a broadening of the intensity of bands at around 3382cm^{-1} in starches from NCe001, NCe003, NCe005, NCe010, NXs001 and yellow bitter yam, suggesting a disruption of the crystalline order. Annealing modification resulted in the appearance of a weak band 2369.74 cm-1 in NCe004 starch that was absent in the native starch. This particular band was found to be present in all native and modified starches from NCe002, NCe005, and yellow bitter yam, while absent in all NCe003 starches. It appeared only in starch from HMT18, NCe010, all HMT modified starches from NXs001, native starch from NXs002, all HMT modified starches from NXs003 and all modified starches from white bitter yam, showing no particular trend. It has been established that this characteristic band at approximately 2300-2400cm^{-1} corresponds to CO_2 absorption (Alves *et* al, 2011) which may be as a result of measuring conditions, and is therefore not relevant in starch identification and fingerprinting study. Major influence of modification is evident in the HMT starches at bands above 3300cm^{-1} where the broad hydroxyl bands intensities in the native starches were progressively increased while bands at 1036cm^{-1} were contrarily reduced but sharpened with increasing moisture levels. This shows a stretching and weakening of the hydroxyl group in the polymeric units and a stretching of the C-O and C-N bonds in the modified starches.

Table 4.17. Effect of Cultivar and modification on absorption and type of vibrations in cocoyam starches

	Cultivar	Modificat	Wavelenghts (cm-1)	Assignment	Suspected compounds
Colocasia esculenta	NCe001	Native	1644.39, 1035.80	Assymetric stretching of the carboxylate R(CO$_2$)H, C=C alken bonds, C=N amide bonds, aliphatic amine, C-O-H bending and deformation	α-D-Glucose, β-1, 4 Glucopyranose, A-Cyclodextrin
		Annealed	2097.00, 1035.58	C≡C stretch, C-O-H bending and deformation	β-1, 4 Glucopyranose, α-D-Glucose
		Acid	1646.89, 570.07	Secondary amines, conjugated alkanones, alkyl halide	A-Cyclodextrin, B-Cyclodextrin, L-Glyceraldehyde
		HMT18	1646.82, 1031.40	carboxylate R(CO2)H, C=C alkenyl bonds, C=N amide bonds, O-H bending	A-Cyclodextrin, Diacetone-D-Glucose
		HMT24	1650.55, 559.44	Amide, conjugated alkanone, alkyl halide C-X	L-Glyceraldehyde, D-Galactose
		HMT27	1648.61, 1030.23	carboxylate R(CO2)H, C=C alkenyl bonds, C-O-H bending an deformation	β-1, 4 Glucopyranose, L-Glyceraldehyde, trichloroacetonitrile
	NCe002	Native	2928.46, 1036.25	C-H stretch of Sp^3 alkane bonds, C-O-H bending, aliphatic ami P-OR esters	β-1, 4 Glucopyranose, α-D-Glucose, Diaceto D-Glucose
		Annealed	1036.00, 573.00	O-C stretch cyclic ring, conjugated alkanone, alkyl halide C-X	β-1, 4 Glucopyranose, α-D-Glucose, Diaceto D-Glucose
		Acid	2095.23, 1369.00	C≡C stretch of alkyne, Thiol ester CH3-C-S stretch	
		HMT18	1650.11, 1034.13	δ(O-H) bending , Carboxylates R(CO2)H, Amide, P-OR esters	β-1, 4 Glucopyranose, A-Cyclodextrin
		HMT24	1647.20, 1399.00	δ(O-H) bending , carbonyl group, C=C alkene, amide, thiol gro (S-H stretch)	A-Cyclodextrin, B-Cyclodextrin, L-Glyceraldehyde
		HMT27	1650.83, 1026.31	carboxylate R(CO2)H, C=C alkenyl bonds, C=N amide bonds, aliphatic amine, aliphatic amine	β-1, 4 Glucopyranose, Ethyl-B-cyclodextrin

NCe003	Native	1541.25, 1030.81	Amide 11 N-H bending vibration, C-O-H stretch	Diacetone-D-Glucose, β-1, 4 Glucopyranose, Amino-acetophenone
	Annealed	1644.82, 577.52	Conjugated alkanones, alkyl halide C-X	Acetobromo α-D-Galactose, α-D-Glucose
	Acid	1366.43, 1036.54	Nitro RNO2 group, aliphatic amines, P-OR esters	Acetobromo α-D-Glucose, β-1, 4 Glucopyranose, B-Cyclodextrin
	HMT18	2926.06, 1035.69	C-H stretch of Sp3 alkane bonds, C-O-H bending, aliphatic amine, P-OR esters	α-D-Glucose, Hexyl α-D-Glucopyranose
	HMT24	2927.00, 1382.00	C-H stretch of Sp3 alkane bonds, Thiol S-H stretch	A-Cyclodextrin, Phenyl acetonitrile
	HMT27	1409.79, 1025.48	Thiol ester CH3-C-S stretch, polysulphide	Neryl-α-D-Glucose, β-1, 4 Glucopyranose, Tolylacetonitrile
NCe004	Native	1644.07, 1036.40	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds	α-D-Glucose, A-Cyclodextrin, β-1, 4 Glucopyranose
	Annealed	2087.00, 574.42	Alkynyl C≡C stretch , alkyl halide C-X bonds	Acetobromo α-D-Galactose, α-D-Glucose
	Acid	1365.40, 1035.15	asymmetric vibration of C-O	Acetobromo-α-D-Glucose, Hexyl Phthalate, Diacetone-D-Glucose
	HMT18	1647.36, 1035.00	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds	Trimethyl Hexyl Phthalate, α-D-Glucose, A-Cyclodextrin
	HMT24	2924.36, 565.03	CH asymmetric stretching, alkyl halide C-X	Acetonitrile, A-Cyclodextrin, B-Cyclodetrin
	HMT27	1651.65, 1028.32	carboxylate R(CO2)H, C=O, C=C and conjugated amides C=N, aliphatic amines	Acetonitrile, A-Cyclodextrin, Acetone oxime
NCe005	Native	1366.00, 1034.87	Thiol ester CH3-C-S, S=O stretch, polysulphide, aliphatic amine	α-D-Glucose, A-Cyclodextrin, β-1, 4 Glucopyranose
	Annealed	2086.00, 570.00	Alkynyl C≡C stretch , alkyl halide C-X bonds	Thenoyl triflouro Galactosamine, L-Glyceraldehyde, α-D-Glucose
	Acid	1649.35, 1033.44	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, aliphatic amines	A-Cyclodextrin, β-1, 4 Glucopyranose

		HMT18	2089.00, 569.38	Alkynyl C≡C stretch , alkyl halide C-X bonds	Diacetone-D-Glucose, Neryl-β-D-Glucopyran
		HMT24	1652.48, 1396.00	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, thiol S=O group	β-Acetoxy-5-Glyceraldehyde, A-Cyclodextrin
		HMT27	1651.25, 1404.19	Deformation of OCH, COH and CCH, conjugated amines	Neryl-Acetyl-D-Galactoseamine, Fructose
	NCe010	Native	1650.80, 1028.20	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds	Neryl-β-Glucopyranose, A-Cyclodextrin,D-Galactosamine
		Annealed	1368.27, 1037.56	Aromatic phosphate esters P-OR, thiol S=O group	Neryl-β-Glucopyranose, A-Cyclodextrin,D-Galactosamine
		Acid	1648.67, 1367.56	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, thiol S=O group	Acetobromo- α-D-Glucose, A-Cyclodextrin,D Galactosamine
		HMT18	2089.63, 1028.36	Alkynyl C≡C stretch, P-OR esters	Acetobromo- α-D-Glucose, A-Cyclodextrin,D Galactosamine
		HMT24	1654.10, 548.25	Disulphide S-S, C=O stretching, amides	Acetobromo- α-D-Glucose, A-Cyclodextrin,D Galactosamine
		HMT27	2926.22, 1647.89	C-H stretch, deformation of OCH, COH and CCH, conjugated amines	D-Galactosamine, α-D-Glucose
Xanthosoma sagittifolium	NXs001	Native	1366.42, 1036.00	Secondary amines, conjugated alkanones, thiol S=O group	Hexyl-β-Glucopyranose, Acetobromo-α-D-Glucose, Diacetone-D-Glucose
		Annealed	2086.00, 1366.14	Alkynyl C≡C stretch , thiol S-H stretch	Hexyl-β-Glucopyranose, α-D-Glucose, Diacetone-D-Glucose
		Acid	1648.18, 1035.44	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, aliphatic amines	Acetobromo-α-D-Glucose, Diacetone-D-Gluc
		HMT18	1648.88, 573.00	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, alkyl halides C-X	Neryl-β-glucopyranose, A-Cyclodextrin,D-Galactosamine
		HMT24	1373.42, 1027.56	Secondary amines, conjugated alkanones, thiol S=O group	Neryl-β-glucopyranose, A-Cyclodextrin,D-Galactosamine

	HMT27	2925.46, 1036.24	Alkynyl C≡C stretch , NH bend	A-Cyclodextrin, L-Glyceraldehyde
NXs002	Native	2106.44, 1032.00	Alkynyl C≡C stretch , NH bend	L-Glyceraldehyde, α-D-Glucose
	Annealed	1647.58, 1031.61	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, NH bend	Diacetone-D-Glucose, B-Cyclodextrin, L-Glyceraldehyde
	Acid	1646.74, 1030.53	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, NH bend	A-Cyclodextrin, B-Cyclodextrin, L-Glyceraldehyde
	HMT18	1030.39, 568.66	Conjugated alkanones, alkyl halide C-X	Hexyl-β-Glucopyranose, A-Cyclodextrin, α-D-Glucose
	HMT24	1401.39, 1024.00	aliphatic amines, C-C stretching	Hexyl--β-Glucopyranose, A-Cyclodextrin
	HMT27	2924.31, 567.00	Alkynyl C≡C stretch , alkyl halide C-X bonds	Neryl-β-glucopyranose, A-Cyclodextrin
NXs003	Native	2922.52, 1366.26	C-H stretching, alkynyl C≡C stretch-CH3 stretching	Neryl-β-glucopyranose, A-Cyclodextrin, B-Cyclodextrin
	Annealed	2089.63, 1031.00	Alkynyl C≡C stretch , NH bend	A-Cyclodextrin, B-Cyclodextrin
	Acid	1649.13, 1367.55	O-H bending of water, C-CH3 stretching	N-Acetyl-D-Galactosamine, α-D-Glucose
	HMT18	1650.94, 1028.50	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, aliphatic amines NH bend	Hexyl Phthalate, L-Glyceraldehyde
	HMT24	1434.96, 1021.00	aliphatic amines, C-C stretching	A-Cyclodextrin, L-Glyceraldehyde
	HMT27	1395.41, 1029.65	aliphatic amines, C-C stretching	Hexyl Phthalate, L-Glyceraldehyde, A-Cyclodextrin

Table 4.18. Effect of Cultivar and modification on absorption and type of vibrations in bitter yam starches

	Cultivar	Modification	Wavelenghts (cm-1)	Assignment	Suspected compounds
Dioscorea dumetorum	White	Native	1647.58, 1036.33	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, aliphatic amines	Acetobromo-α-D-Glucose, Diacetone-D-Glucose, L-Glyceraldehyde
		Annealed	2092.00, 1365.33	Alkynyl C≡C stretch , C-CH3 stertching	Acetobromo-α-D-Glucose, Diacetone-D-Glucose, D-Galactosamine
		Acid	2084.03, 1033.80	Alkynyl C≡C stretch , aliphatic amines, P-OR esters	α-D-Glucose, Diacetone-D-Glucose, D-Galactosamine
		HMT18	1647.18, 1035.54	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, aliphatic amines	Hexyl-β-glucopyranose, α-D-Glucose
		HMT24	1648.56, 573.00	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, alkyl halides C-X	Hexyl-β-glucopyranose, α-D-Glucose
		HMT27	1368.12, 573.00	aliphatic amines, C-C stretching, alkyl halides C-X	Hexyl-β-glucopyranose, α-D-Glucose, L-Glyceraldehyde
	Yellow	Native	2087.00, 1035.90	Alkynyl C≡C stretch , aliphatic amines, P-OR esters	Acetobromo-α-D-Glucose, Hexyl Phthalate, Diacetone-D-Glucose
		Annealed	1645.78, 573.68	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, alkyl halides C-X	Acetobromo-α-D-Glucose, Hexyl Phthalate, Diacetone-D-Glucose
		Acid	1646.03, 1036.70	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, conjugated amines	Acetobromo-α-D-Glucose, Hexyl Phthalate, Diacetone-D-Glucose
		HMT18	2089.45, 1034.56	Alkynyl C≡C stretch , aliphatic amines, P-OR esters	A-Cyclodextrin, β-1, 4 glucopyranose
		HMT24	1648.45, 1035.98	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, aliphatic amines	Diacetone-D-Glucose, B-Cyclodextrin, L-Glyceraldehyde
		HMT27	1648.66, 1036.00	δ(O-H) bending , carbonyl group, C=C alkenyl, C=N amide or C=O bonds, aliphatic amines	β-1, 4 glucopyranose, A-Cyclodextrin

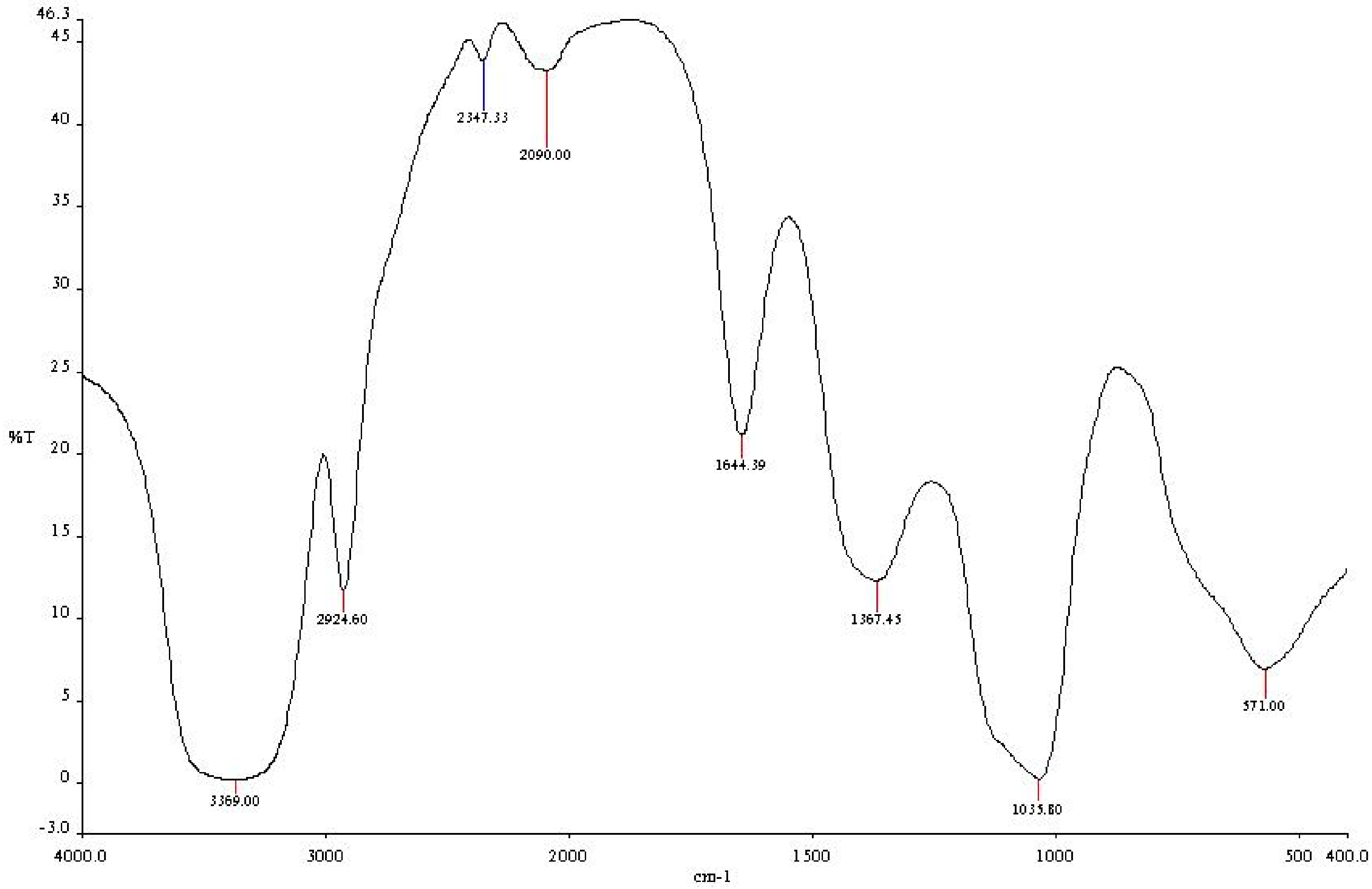


Figure 4.30. FTIR spectra of native NCe001 starch

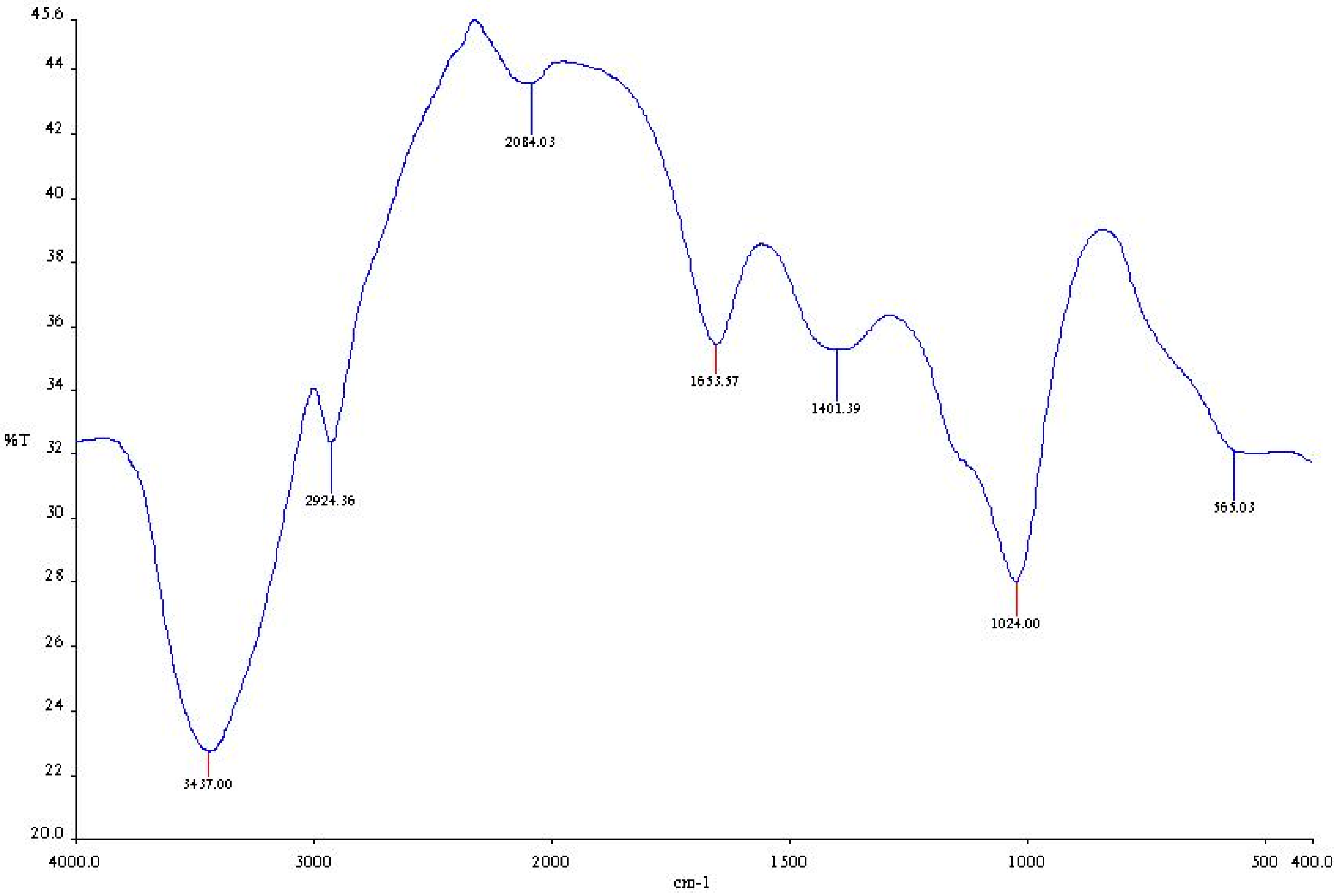


Figure 4.31. FTIR spectra of HMT24 NXs002 starch

Acid hydrolysis which resulted in a little increase in absorption intensities at peaks >3350cm^{-1} and >1036cm^{-1}, suggested de-polymerization, partial breakdown of starch chains and a disruption of the ordered structure of the native starches resulting in a less amorphous nature. The bands at around 1036cm^{-1} have been associated with the possible presence of cyclic oligosaccharides made up of α-D- glucopyranose monomers (Xia *et al*, 2010).

4.13 Starch paste clarity/light transmittance

The light transmittance of native starches from *C. esculenta* varied from 15.45 to 39.50% (Figure 4.32), *X. sagittifolium* 13.50-16.15%, *D. dumetorum* (white) 47.56% (Figure 4.33) and *D. dumetorum* (yellow) 16.46% showing significant differences between the crops and within their cultivars. The highest clarity was recorded for white bitter yam starch at 47.56% while NXs002 starch had the lowest at 13.50% on day 1 of measurement. These values varied from those reported for cassava (23.5-40.9%), cocoyam (10.9-20.4%) and sweetpotato (10.9-18.7%) grown in Malawi (Mweta, 2009). As storage days of all native and modified starches in refrigerated condition increased, the starch pastes gradually became more turbid, allowing less light transmission through it. Increase in opacity of starch gel with increase in storage days is attributed to the short term interaction of leached amylose after pasting with swollen and collapsed starch granules to form junction zones and long term recrystallization of amylopectin chains. The aggregation of these junction zones causes reflection or refraction of incident lights rather than transmitting it (Craig *et al.*, 1989; Lawal, 2005). In a similar comparative study of properties of cassava and cocoyam starches, higher values of transmittance were reported for cassava than cocoyam (Nwokocha *et al.,* 2009). Clarity of 1% (w/v) starch pastes of potato, tapioca, corn, high amylose corn and waxy corn had been reported to give transmittances of 96, 73, 41, 5 and 61% respectively showing the influence of amylose contents on paste clarity (Craig *et al.*, 1989; Amani *et al.*, 2005). Starch paste clarity is associated with brightness and aesthetic appeal in food products that contains it (Mweta, 2009; Otegbayo *et al.*, 2014).

The influence of amylose contents on starch paste clarity was obvious in this study as the starch from NXs002 with the highest amount of amylose had the least transmittance while the white bitter yam with the least amylose had the highest % transmittance with the other starches following similar pattern.

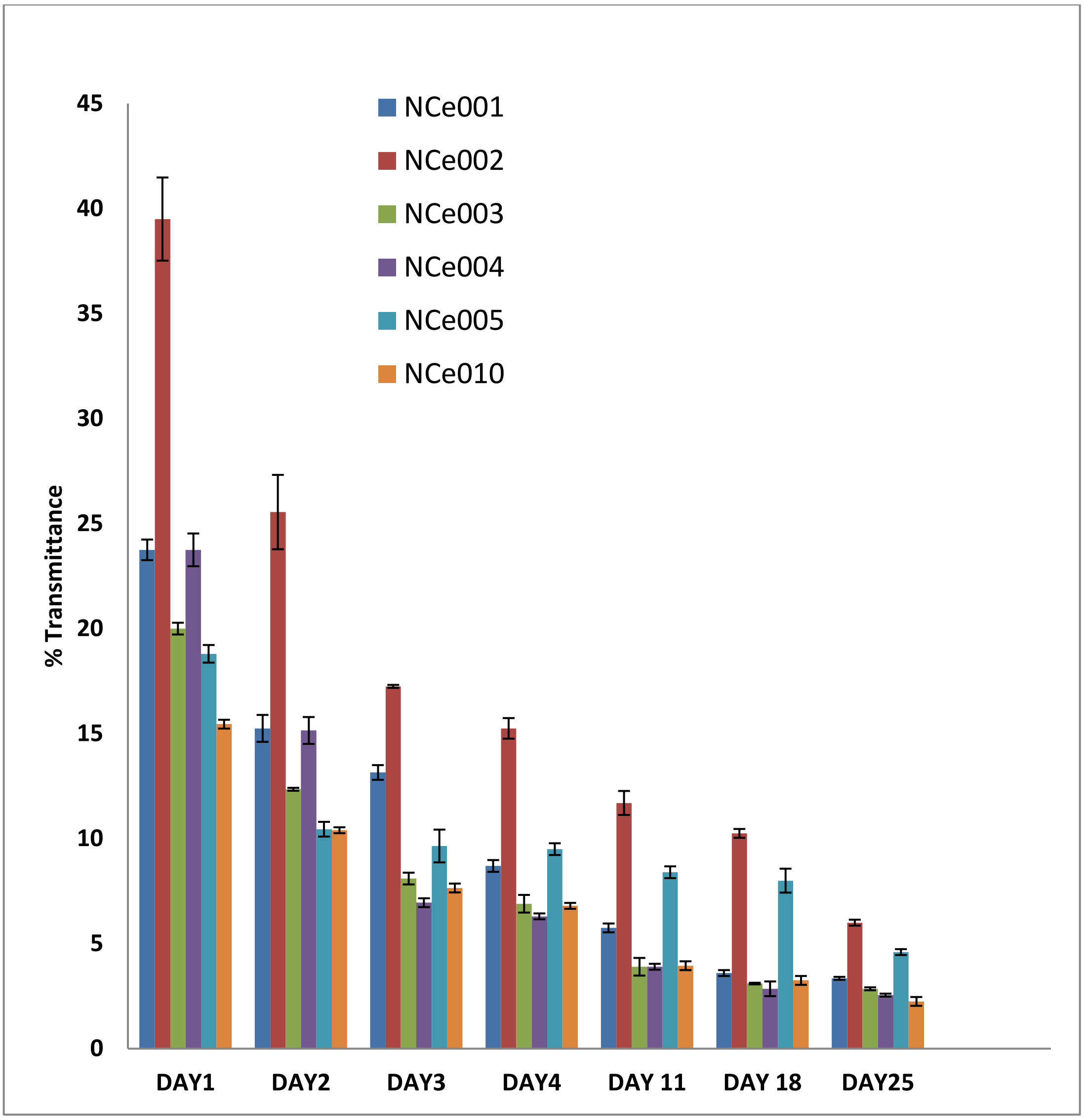


Figure 4.32. Effect of storage (days) on % light transmittance of native starches from *C. esculenta*

However, other factors that have been identified to affect clarity include phosphorus contents and presence of other solutes or impurities (Jane *et al.*, 1996), granule structure (Craig *et al.*, 1989), inter-chain association after pasting (Lawal, 2005; Craig *et al.*, 1989; Otegbayo *et al.*, 2014), susceptibility to retrogradation (Mélo *et al.*, 2003), botanical origin, modification method, crystallinity and swelling capacity.

Starch gels undergo structural changes during storage (Ferrero *et al.*, 1994). Thus, clarity of acid-modified starches was initially high, declining slowly for the first 3-4 days then rapidly and significantly until the 4th week of storage at 4°C. Long term retrogradation of starch gels which causes turbidity development has been associated with amylopectin retrogradation rather than the linear glucan retrogradation (Miles *et al.*, 1985). Acid hydrolysis reduces starch molar mass and density; hence the refractive index is reduced resulting in the initial high transmittance. However, the effect of amylopectin recrystallization as a result of increased mobility of its short fractions seems to be more prominent as storage days increased (Figure 4.32). Heat-moisture treatments were found to stabilize paste clarity with increase in storage days. Similar trend was observed by Lawal (2005) in his hydrothermal modification of new cocoyam and attributed it to increased crystallinity and reduction in the amount to leached amylose and amylopectin by the treatment. Annealing had similar effect as HMT in cocoyam starches but less influence on stability of bitter yam starches (Figure 4.33) with storage, the %transmittance declining as rapidly as the acid modified starches. Transparency is a desirable quality in products like fruit-pie fillings while opacity is desired in salad dressing and other products. The hydrothermal-modified starches could therefore find application in transparent products while native and acid-modified starches may be utilised as fitted.

4.14 Freeze-Thaw Stability of starch pastes of cocoyam and bitter yam

Starches from the cultivars of cocoyam and bitter yam exhibited wide variation in stability to freezing and thawing cycles with storage (Table 4.19 and 4.20). In this study, it was noticed that after the first week, exuded water in the thawed samples became difficult to separate because the samples became spongy. The different starches gave values of % syneresis which varied between cocoyam and bitter yam and according to modification method. Native white bitter yam starch had lower syneresis (21.85%) than the yellow cultivar (26.45%) indicating a higher tolerance to freezing and thawing. Generally, native and modified *D. dumetorum* starches present lower syneresis ranges (20.15-27.85%) after

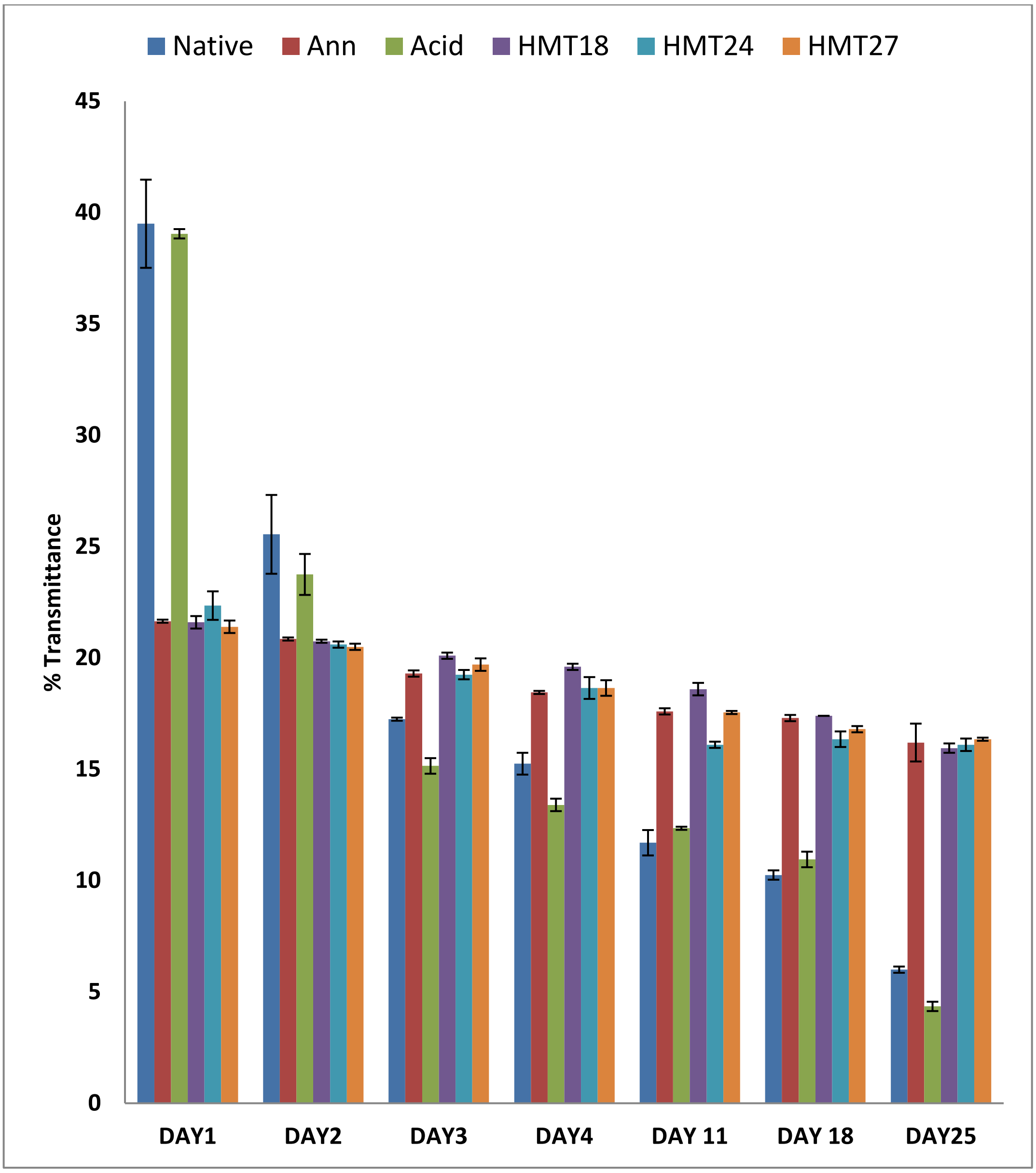


Figure 4.33. Effect of modification methods on light transmittance of starch from NCe002 cocoyam

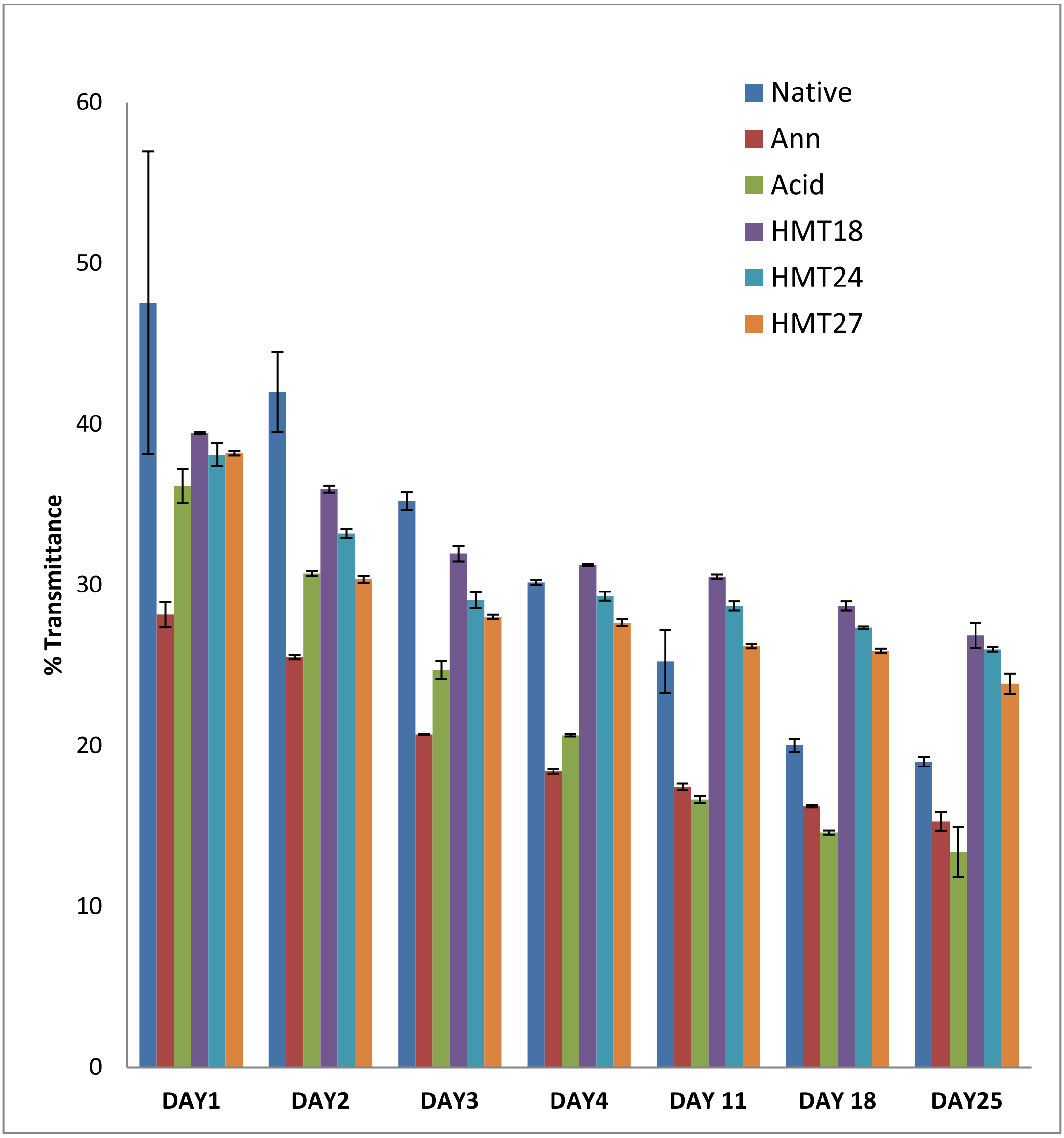


Figure 4.34. Effect of modification methods on light transmittance of starch from white *D. dumetorum* cultivar

the first freeze-thaw cycle than *C. esculenta* starches (26.9-47.45%) and *X. sagittifolium* starches (33.50-50.35%). The acid modified starch from white bitter yam cultivar exuded the overall least amount of water (20.15%). This may be due to stronger interaction of dispersed amylose/amylopectin and water molecules to form a spongy network and a reduced amorphous core of granules caused by the acid hydrolysis. This led to slow retrogradation of starch gels (Liu *et al.,* 2014). Kramer (2009) suggested that acid hydrolysis cause partial debranching of amylopectin, increasing the linear components and thereby conferring predominance of amylose-like behavior on the starch. On the contrary, Takizawa *et al.* (2004) and Thys *et al.* (2013) observed that acid-thinned starch from Pinhao and corn gave higher values of syneresis than the native starches and attributed this to intensive molecular re-association during acid hydrolysis. Starches from different botanical origin may therefore exude varying amount of water as a result of differences in thermal history, number of freeze-thaw cycles, centrifugation conditions and starch concentrations (Zhu, 2015). Native, acid-modified, annealed, HMT18, HMT24 and HMT27 NCe001 starches increased exudation by 1.5, 1.75, 6.95, 3.60, 3.0 and 5.30%, respectively, over the entire 5 cycles of freezing and thawing. These values were greater among starches from *X. sagittifolium* than among those from *C. esculenta* and *D. dumetorum*, showing a greater tendency to retrograde on frozen storage in the *X. sagittifolium* starches than others. The starch from NXs002 exuded the highest amount of water (47.25%) which increased with HMT treatments while starch from white bitter yam maintained the least %syneresis (26.65%) after the five (5) cycles. This implied that the high syneresis of these starches could predispose them to possible application in resistant starch production, slowly digesting starches and films formation by amylose rather than in frozen desserts, custards, puddings, and pie-filling and in products which require low temperature storage (Otegbayo *et al.*, 2014) in which ageing, staling and syneresis are not desirable. Previously, 28.9-49.2% syneresis has been reported for cocoyam starch cultivars (Mweta, 2009), values comparable to those of *C. esculenta* (26.90-54.35%) determined in this study. Crops from other origin have recorded varying degree of syneresis in the range of 32-38% for *T. africana* seed starch (Nwokocha and Williams, 2011), 24.7-40.7% for *Dioscorea spp.* (Amani *et al.,* 2004). Among the seven *Dioscorea spp.* starches studied for their functional properties, *D. dumetorum* presented the lowest % syneresis at 27% while *D. bulbifera* exuded as much as 57% after frozen storage (Sahore *et al.,* 2007). Freeze-thaw stability is a function of textural changes associated with storage of starch-based frozen products.

Table 4.19. Freeze-thaw stability of native and modified cocoyam starches.

	Sample	Week 1	Week 2	Week 3	Week 4	Week 5
NCe001						
	Native	34.40±0.28^{c}	34.60±0.14^{e}	34.80±0.14^{f}	34.65±0.07^{g}	35.90±0.14^{f}
	Annealed	33.45±0.07^{de}	34.50±0.14^{g}	35.30±0.14^{f}	36.15±0.21^{h}	40.30±0.42^{d}
	Acid thinned	26.90±0.14^{f}	27.15±0.35^{h}	27.65±0.64^{g}	28.10±0.42^{i}	28.65±0.64^{g}
	HMT18	37.15±0.07^{e}	37.60±0.28^{f}	38.05±0.07^{f}	39.65±0.21^{cd}	40.75±0.07^{de}
	HMT24	37.80±0.14^{de}	37.95±0.07^{f}	38.40±0.28^{ab}	39.30±0.14^{g}	41.80±0.57^{d}
	HMT27	37.10±0.14^{f}	38.30±0.28^{g}	39.30±0.14^{f}	40.20±0.99^{e}	42.40±0.42^{f}
NCe002						
	Native	32.40±0.14^{d}	33.60±0.14^{f}	33.95±0.07^{g}	35.30±0.28^{f}	37.60±0.42^{e}
	Annealed	36.25±0.21^{cd}	36.65±0.07^{e}	37.15±0.35^{e}	37.65±0.07^{g}	38.40±0.14^{f}
	Acid thinned	36.50±0.00^{c}	36.45±0.07^{d}	36.55±0.07^{e}	36.70±0.14^{g}	36.70±0.28^{e}
	HMT18	37.75±0.07^{e}	38.55±0.35^{e}	38.80±0.28^{e}	39.55±0.07^{cd}	40.15±0.21^{e}
	HMT24	38.40±0.14^{d}	38.75±0.07^{e}	40.05±0.35^{ab}	40.25±0.21^{f}	42.55±0.07^{d}
	HMT27	39.15±0.07^{de}	40.45±0.07^{ef}	41.25±0.07^{e}	42.20±0.28^{d}	42.85±0.07^{ef}
NCe003						
	Native	28.65±0.07^{e}	29.85±0.21^{g}	32.25±0.07^{h}	33.60±0.14^{h}	34.60±0.28^{g}
	Ann	30.55±0.07^{e}	31.95±0.21^{h}	33.50±0.14^{g}	34.80±0.14^{i}	35.60±0.00^{g}
	Acid	30.25±0.21^{e}	31.55±0.07^{f}	32.70±0.14^{f}	37.40±0.00^{f}	37.60±0.14^{e}
	HMT18	37.85±0.07^{e}	39.25±0.21^{d}	40.15±0.07^{d}	40.75`±0.21^{c}	41.65±0.49^{d}
	HMT24	38.55±0.07^{d}	39.85±0.21^{d}	25.90±0.07^{b}	42.05±0.21^{d}	42.50±0.14^{d}
	HMT27	39.40±0.28^{d}	42.40±0.14^{d}	42.90±0.00^{d}	43.65±0.07^{c}	44.05±0.07^{de}
NCe004						
	Native	42.65±0.07^{a}	43.40±0.14^{b}	44.20±0.14^{b}	44.70±0.14^{b}	45.70±0.14^{b}
	Ann	43.50±0.42^{ab}	45.45±0.21^{a}	46.75±0.07^{a}	47.40±0.14^{b}	48.45±0.07^{b}
	Acid	35.30±0.14^{c}	37.45±0.35^{d}	43.55±0.49^{c}	44.75±0.21^{c}	48.45±0.07^{a}
	HMT18	46.65±0.21^{b}	46.65±0.35^{b}	47.55±0.07^{b}	48.30±0.28^{b}	48.80±0.42^{b}
	HMT24	45.75±0.21^{b}	46.70±0.00^{b}	47.65±0.49^{a}	47.60±0.14^{c}	48.75±0.78^{c}
	HMT27	47.45±0.07^{b}	47.70±0.14^{b}	48.45±0.07^{b}	48.85±0.07^{b}	48.55±0.78^{c}
NCe005						
	Native	32.60±0.00^{d}	35.50±0.14^{d}	38.45±0.07^{d}	39.00±0.28^{d}	39.70±0.42^{d}
	Ann	32.80±0.28^{de}	37.75±0.07^{d}	38.60±0.28^{d}	40.25±0.35^{e}	40.40±0.28^{d}
	Acid	32.80±0.14^{d}	36.50±0.28^{d}	37.65±0.21^{d}	38.75±0.21^{e}	40.90±0.57^{d}
	HMT18	34.65±0.21^{f}	36.80±0.14^{g}	38.20±0.71^{f}	38.65±0.35^{d}	40.80±0.14^{de}
	HMT24	38.75±0.21^{d}	39.60±0.14^{d}	40.50±0.14^{ab}	41.10±0.14^{e}	41.70±0.71^{d}
	HMT27	38.85±0.07^{de}	40.75±0.07^{e}	42.45±0.21^{d}	43.65±0.07^{c}	44.55±0.35^{d}
NCe010						
	Native	40.40±0.14^{b}	45.50±0.14^{a}	46.05±0.21^{a}	46.25±0.21^{a}	45.90±0.42^{b}
	Ann	41.50±0.14^{ab}	43.15±0.07^{b}	45.60±0.14^{b}	46.40±0.57^{c}	45.75±0.21^{c}
	Acid	41.25±0.07^{b}	43.65±0.21^{b}	44.50±0.57^{b}	45.50±0.42^{b}	44.55±0.35^{c}
	HMT18	45.55±0.35^{c}	49.55±0.07^{a}	50.15±0.07^{a}	51.00±0.28^{a}	47.45±0.49^{c}
	HMT24	46.30±0.14^{b}	52.40±0.14^{a}	52.90±0.28^{a}	53.25±0.21^{a}	48.35±0.07^{c}
	HMT27	46.80±0.14^{b}	52.15±0.21^{a}	53.25±0.78^{a}	54.35±0.21^{a}	51.10±0.42^{b}
NXs001						
	Native	39.40±0.14^{b}	40.30±0.14^{c}	41.60±0.14^{c}	43.40±0.14^{c}	44.40±0.14^{c}
	Ann	40.30±0.42^{abc}	41.15±0.21^{c}	43.60±0.71^{c}	44.75±0.21^{d}	46.05±0.92^{c}
	Acid	40.15±0.07^{b}	42.30±0.00^{c}	43.40±0.14^{c}	44.15±0.07^{d}	46.10±0.57^{b}
	HMT18	42.35±0.07^{d}	44.60±0.14^{c}	46.60±0.14^{c}	48.35±0.21^{b}	50.15±0.35^{a}
	HMT24	43.35±0.35^{c}	45.15±0.07^{c}	46.70±0.42^{a}	48.85±0.07^{b}	50.60±0.28^{b}
	HMT27	43.75±0.07^{c}	45.85±0.07^{c}	46.85±0.21^{c}	48.65±0.49^{b}	51.05±0.21^{b}

NXs002						
	Native	43.45±0.07^{a}	45.50±0.14^{a}	45.90±0.00^{a}	46.25±0.21^{a}	47.25±0.78^{a}
	Ann	44.65±0.07^{a}	47.30±0.14^{a}	47.60±0.14^{a}	48.05±0.07^{a}	49.55±0.21^{a}
	Acid	43.50±0.57^{a}	46.30±0.14^{a}	46.75±0.07^{a}	47.25±0.07^{a}	48.50±0.57^{a}
	HMT18	48.25±0.21^{a}	49.45±0.21^{a}	50.40±0.28^{a}	50.85±0.49^{a}	51.30±0.57^{a}
	HMT24	49.15±0.21^{a}	52.65±0.49^{a}	52.75±0.07^{a}	53.00±0.14^{a}	53.30±0.14^{a}
	HMT27	50.35±0.07^{a}	52.40±0.57^{a}	53.50±0.42^{a}	54.65±0.64^{a}	55.45±0.21^{a}
NXs003						
	Native	33.65±0.07^{cd}	34.70±0.14^{e}	36.85±0.35^{e}	37.65±0.07^{e}	39.05±0.21^{d}
	Ann	38.95±6.29^{bc}	35.60±0.14^{f}	37.00±0.28^{e}	39.55±0.35^{f}	39.40±0.14^{e}
	Acid	33.50±0.00^{d}	35.40±0.42^{e}	36.55±0.35^{e}	38.45±0.07^{e}	39.75±0.07^{d}
	HMT18	33.65±0.35 ^{cd}	35.75±0.21^{h}	37.40±0.14^{g}	39.50±0.57^{cd}	40.05±0.21^{e}
	HMT24	37.35±0.21^{e}	38.70±0.28^{e}	40.15±0.07^{ab}	41.15±0.21^{e}	41.60±0.14^{d}
	HMT27	38.50±0.14^{de}	39.80±0.14^{f}	41.50±0.00^{e}	43.65±0.07^{c}	44.55±0.07^{d}

Means in columns not followed by same alphabet(s) (by modification) are significantly different at 5% level (P<0.05).

Table 4.20. Freeze-thaw stability of native and modified bitter yam starches

	Sample	Week 1	Week 2	Week 3	Week 4	Week 5
White Bitteryam	Native	21.85±2.33^{g}	24.35±0.07^{i}	25.60±0.57^{j}	25.55±0.07^{j}	26.65±0.07^{i}
	Ann	23.00±0.71^{f}	24.35±0.78^{i}	25.20±0.42^{i}	28.80±0.14^{k}	30.40±0.42^{i}
	Acid	20.15±0.07^{g}	26.35±1.20^{h}	27.95±0.21^{g}	27.95±0.07^{i}	29.95±1.77^{g}
	HMT18	20.60±0.28^{i}	22.40±0.28^{j}	23.80±0.00^{i}	27.05±2.33^{f}	29.55±0.49^{g}
	HMT24	24.10±0.99^{g}	25.45±0.21^{h}	26.20±0.14^{h}	28.25±0.07^{i}	29.20±0.42^{f}
	HMT27	25.00±0.99^{h}	25.65±0.92^{i}	27.60±0.07^{h}	30.55±0.07^{f}	32.50±0.28^{g}
Yellow Bitter yam	Native	26.45±0.07^{f}	26.80±0.14^{h}	28.25±0.21^{i}	29.35±0.21^{i}	30.70±0.42^{h}
	Ann	29.50±1.27^{e}	32.45±0.07^{h}	32.45±0.92^{h}	33.70±0.14^{j}	34.45±0.35^{h}
	Acid	27.50±1.70^{f}	27.60±0.28^{g}	28.20±0.14^{g}	30.80±0.28^{h}	32.65±0.07^{f}
	HMT18	24.00±0.85^{h}	27.95±0.21^{i}	28.95±0.07^{h}	30.30±0.14^{e}	33.00±1.27^{f}
	HMT24	27.85±0.78^{f}	29.15±0.21^{g}	30.40±0.00^{b}	32.55±0.07^{h}	34.00±0.28^{e}
	HMT27	27.45±0.21^{g}	28.80±0.14^{h}	28.85±0.35^{g}	29.65±0.21^{g}	31.65±1.48^{g}

Means in columns not followed by same alphabet(s) (by modification) are significantly different at 5% level ($P<0.05$).

Exudation of water or syneresis often accompanies retrogradation of amylose and amylopectin components of starch when they undergo freezing and thawing cycles.

4.15 Thermal properties of starches from cocoyam and bitter yam

The DSC generated information about heat changes and phase transitions that occurred in starch as a function as time and temperature without a change in sample mass. The onset, peak and conclusion temperatures, enthalpy of gelatinization and peak height index (PHI) of the native starches extrapolated from the DSC thermogram are presented in Table 4.21. Onset, peak and conclusion temperature of gelatinization for *C. esculenta* starches ranged from 72.3 (NCe002) to 92.7^{o}C (NCe004), 82.0 (NCe002) to 98.4 ^{o}C (NCe004) and 86.7 (NCe002) to 105.62 ^{o}C (NCe005). The starches from *X. sagittifolium* had slightly higher values than those from *C. esculenta* at 76.1(NXs002) to 85.3 ^{o}C (NXs003), 94.4 (NXs003) to 99.7 ^{o}C (NXs001 and NXs002) and 99.3 (NXs003) to 108.4 ^{o}C (NXs002) while starches from bitter yam showed relatively higher To, Tp and Tc than the cocoyam cultivars. A single endothermic melting event was observed for the starches under study. Entalpy of gelatinization (ΔH_{gel}) for the starches ranged from 9.26 to 18.45J/g which is within the range for starches (Bertolini, 2010).

Structural relations between the amorphous and crystalline regions within the starch granule are responsible for the sharpness of each of the transitions. Starch gelatinization have been reported to occur over a wide temperature range rather than a sudden order-disorder transition that takes place within a narrow temperature range (Ratnayake *et al.*, 2009) as is the case in this study. Interactions with other molecules within the starch matrix may influence thermal transitions in starches. These interactions may be with sugars, proteins, hydrocolloids or amylose complexations with lipids, aromas or flavours (Bertolini 2010). High-amylose starches are infact known to yield very broad endotherms with higher melting temperatures of 80-130^{o}C (Inouchi *et al.,* 1991). This is because when amylose diffuse out of its chain during gelatinization, a repeating disordering transition of amylose-lipid complexes are formed which produce additional reversible endothermic transition at around 95-105^{o}C (Bertolini, 2010). The presence of amylose therefore lowers the melting temperature of crystalline regions and the energy to start gelatinization. Mweta *et al.* (2008) reported lower gelatinization peaks of 69.4-81.4 ^{o}C, 68.5-79.2 ^{o}C and 60.1-76.8 ^{o}C for starches from cultivars of Malawian cocoyam, sweet potato and cassava respectively, although the values for enthalpy of gelatinization for cocoyam (13.4J/g) are within the range recorded in this study.

Table 4.21. DSC thermal properties of native *Colocasia esculenta, Xanthosoma sagittifolium and Dioscorea dumetorum* starch cultivars

	To (°C)	Tp (°C)	Tc (°C)	ΔHgel (J/g)	PHl	R
NCe001	83.60	91.80	93.20	18.45	2.25	8.20
NCe002	72.30	82.00	86.70	10.28	1.06	9.70
NCe003	74.30	90.10	93.80	15.74	0.99	15.80
NCe004	92.70	98.40	99.90	10.39	1.82	5.70
NCe005	80.39	97.72	105.62	17.76	1.03	17.33
NCe010	81.00	89.60	94.20	15.08	1.75	8.60
NXs001	82.70	99.70	108.10	13.58	0.80	17.00
NXS002	76.10	99.70	108.40	15.09	0.64	23.60
NXs003	85.30	94.40	99.30	10.45	1.15	9.10
Yellow	77.51	94.26	95.84	9.26	0.55	16.75
White	88.67	99.90	113.85	16.88	1.50	11.23

Onset temperature-To, peak temperature- Tp, conclusion temperature- Tc, temperature range (Tp-To)- R, peak height index- (ΔHgel/Tp-To)- PHI and gelatinization enthalpy- ΔHgel

Studies of starches from five *C. esculenta* varieties at starch-water ratio 1:3 gave gelatinization peaks of 43.0-63.3 ^{o}C and ΔH_{gel} of 6.8J/g (Jane *et al*., 1992) while Farhat *et al.* (1999) reported onset, peak and conclusion temperatures of 78.1, 81.3 and 86.4 ^{o}C and enthalpy of 18.6J/g for *D. dumetorum* starches, values similar to those determined in this study. Starch from native white bitter yam cultivar showed higher onset, peak and conclusion gelatinization temperatures (88.67, 99.9 and 113.85 ^{o}C) than the yellow cultivar (77.51, 94.26 and 95.84 ^{o}C) (Table 4.21). Enthalpy of gelatinization values for white are also higher (16.88J/g) than that of yellow (9.26J/g). High ΔH_{gel} values have been shown to indicate a more-closely packed granule structure (Nwokocha *et al.*, 2009). The high ΔH_{gel} values recorded in this study is consistent with the high pasting temperatures obtained by RVA analysis and also corroborates the report of Falade and Christopher (2015) on thermal transitions of rice starch. The ΔH_{gel} values may be a reflection of the number of double helices that unravel and melt during gelatinization (Jayakody and Hoover, 2008). Key functions of starches may thus be controlled by manipulations of the thermal transitions they undergo during processing as the DSC is an easy and fast technique for measuring concentrations of deformation induced effects during gelatinization (Setman, 2011).

For acid modified white bitter yam starch, considerable upward shift in gelatinization peaks and enthalpy was observed (Figure 4.37). The range also shifted from 11.23 in the native starch to 13.23 in acid treated starch. The starch from yellow cultivar showed a slightly different response to acid modification as range reduced from 16.75 to 8.37 indicating a narrowing of the thermogram. Earlier, acid thinning of normal corn starch resulted in an increase in T_o, T_p, T_c and a decrease in values of ΔH_{gel} and peak height index while acid thinning of waxy corn starch produced a contrary effect (Sandhu and Singh, 2007). Similar effect has also been previously reported in the study of thermal transitions of starch from native and acid hydrolysed new cocoyam and potato in which gelationization peaks and ΔH_{gel} values increased significantly by the acid treatment (Lawal, 2004; Wang and Wang, 2001). This may be attributed to increased granular crystallinity as an effect of increased amylose leaching occasioned by the acid hydrolysis. Annealing result in increased starch mobility within the amorphous regions leading to a molecular re-organization which involves the interaction of amylose-amylose and/or amylose-amylopectin chains (Atichokudomchai *et al*., 2002; Hoover and Vasanthan, 1994).

Annealing and heat-moisture treatments produced varying microcrystalline domains with different thermal stabilities in the native starches. Broadening of the range in starch of yellow cultivar of bitter yam from 16.75 was observed for HMT18 (19.54), HMT24

(21.14) and HMT27 (18.06) and for that of white cultivar from 11.23 in native to 11.79 in HMT24 and 12.78 in HMT27 showing increase with severity of modification. This is an indication of increased heterogeneity in the organization of amylose and amylopectin structure in the starch granules and is influenced by differences in amylose: amylopectin ratio and starch source (Hoover and Vasanthan, 1994). Tester and Morrison (1990) have postulated that changes to the gelatinization transition temperatures on annealing could be due to lengthening of the double helices that were not optimized during biosynthesis. Annealing was found to cause an increase in gelatinization temperatures of starch from white bitter yam from 94.26 ^{o}C to 108.46 ^{o}C and for yellow from 99.9 ^{o}C to 105.57 ^{o}C. Similar effect has been reported in annealed new cocoyam (Lawal, 2005), potato (Collado and Corke, 1999; Hoover and Vasanthan, 1994), old cocoyam (Jane *et al.,* 1992) and cassava (Atichokudomchai *et al.,* 2002). Annealing cause a melting of metastable crystallites by propagation without loss of granular intergrity (Bertolini, 2010) resulting in crystalline perfection. This suggests that the weakest crystallites are more susceptible to perfection and so have a more pronounced effect on onset temperature of gelatinization. The slight variation of ∆Hgel values with annealing show that the order of double helices is not affected by annealing rather the crystalline perfection is solely responsible for reorganization of molecules.

Gelatinization peaks for stored cocoyam starch generally increased on day 2 but subsequently decreased as storage days increased. On storage, gelatinized starch gel gradually attempt to recrystallize by ageing in an orderly manner leading to lower states of energy (Lawal, 2004). Retrogradation enthalpies (∆Hret) of native NCe001, NCe002, NCe003, NCe005, NXs001 and NXs002 progressively decreased until day four of storage when it increased slightly (Table 4.22) while those of NCe004, NCe010 and NXs003 decreased throughout the storage period. Enthalpy relaxation is a significant phenomenon that occurs during storage of food materials and is indicative of the ageing and retrogradation process. These alterations may be of significance for food products because they directly affect enthalpy, volume, mechanical, and diffusion properties (Bertolini, 2010).

Table 4.22: Effect of storage time on thermal properties of native cocoyam starches

Cultivar	Day	To (ºC)	Tp (ºC)	Tc (ºC)	ΔHgel/ ΔHret (J/g)	PHl	R
NCe001	1	83.60	91.80	93.20	18.45	2.25	8.20
	2	96.30	99.80	106.70	17.34	4.95	3.50
	3	84.60	87.80	91.70	14.91	4.66	3.20
	4	80.20	85.40	90.90	16.72	3.22	5.20
NCe002	1	72.30	82.00	86.70	10.28	1.06	9.70
	2	81.80	91.00	99.30	5.67	0.62	9.20
	3	67.20	72.80	79.00	6.28	1.12	5.60
	4	63.40	72.40	82.50	9.11	1.01	9.00
NCe003	1	74.30	90.10	93.80	15.74	1.00	15.80
	2	83.00	90.40	98.50	13.20	1.78	7.40
	3	62.40	69.90	76.60	8.89	1.19	7.50
	4	56.90	65.90	85.60	13.31	1.48	9.00
NCe004	1	92.70	98.40	99.90	10.39	1.82	5.70
	2	87.10	99.70	100.70	11.74	0.93	12.60
	3	80.30	86.60	93.40	8.38	1.33	6.30
	4	60.10	70.30	82.30	7.15	0.70	10.20
NCe005	1	80.39	97.72	105.62	17.76	1.03	17.33
	2	60.10	68.20	76.70	12.34	1.52	8.10
	3	58.90	62.90	73.40	7.81	1.95	4.00
	4	56.70	61.80	80.20	14.22	2.79	5.10
NCe010	1	81.00	89.60	94.20	15.08	1.75	8.60
	2	59.40	66.00	76.60	10.06	1.52	6.60
	3	57.30	63.00	73.80	8.67	1.52	5.70
	4	56.20	61.80	70.80	8.66	1.55	5.60
NXs001	1	82.70	99.70	108.10	13.58	0.80	17.00
	2	94.10	99.80	105.60	9.83	1.72	5.70
	3	62.20	67.00	75.10	5.60	1.17	4.80
	4	56.00	66.00	76.80	7.86	0.79	10.00
NXs002	1	76.10	99.70	108.40	15.09	0.64	23.60
	2	73.40	95.90	99.20	10.50	0.47	22.50
	3	75.70	94.20	96.10	8.32	0.45	18.50
	4	64.50	88.30	96.60	11.20	0.47	23.80
NXs003	1	85.30	94.40	99.30	10.45	1.15	9.10
	2	77.30	87.80	96.80	4.56	0.43	10.50
	3	70.20	78.70	88.00	4.82	0.57	8.50
	4	70.00	77.30	85.40	4.66	0.64	7.30

Table 4.23. Effect of modification on thermal properties of starches from Bitter yam

	To (ºC)	Tp (ºC)	Tc (ºC)	ΔHgel (J/g)	PHI	R
Yellow						
Native	77.51	94.26	95.84	9.26	0.55	16.75
Acid	90.30	98.67	105.45	16.31	1.95	8.37
Annealed	98.21	108.46	110.84	14.73	1.44	10.25
HMT18	76.49	96.03	108.22	21.87	1.12	19.54
HMT24	83.81	104.95	117.30	14.56	0.69	21.14
HMT27	75.01	93.07	105.75	15.02	0.83	18.06
White						
Native	88.67	99.90	113.85	16.88	1.50	11.23
Acid	80.13	93.36	118.35	26.31	1.99	13.23
Annealed	94.15	105.57	112.23	18.13	1.58	11.42
HMT18	98.69	106.81	116.52	17.72	2.18	8.12
HMT24	91.09	102.88	110.68	16.17	1.37	11.79
HMT27	87.77	99.95	111.72	25.93	2.13	12.18

Onset temperature-To, peak temperature- Tp, conclusion temperature- Tc, temperature range (Tp-To)- R, peak height index- (ΔHgel/Tp-To)- PHI and gelatinization enthalpy- ΔHgel

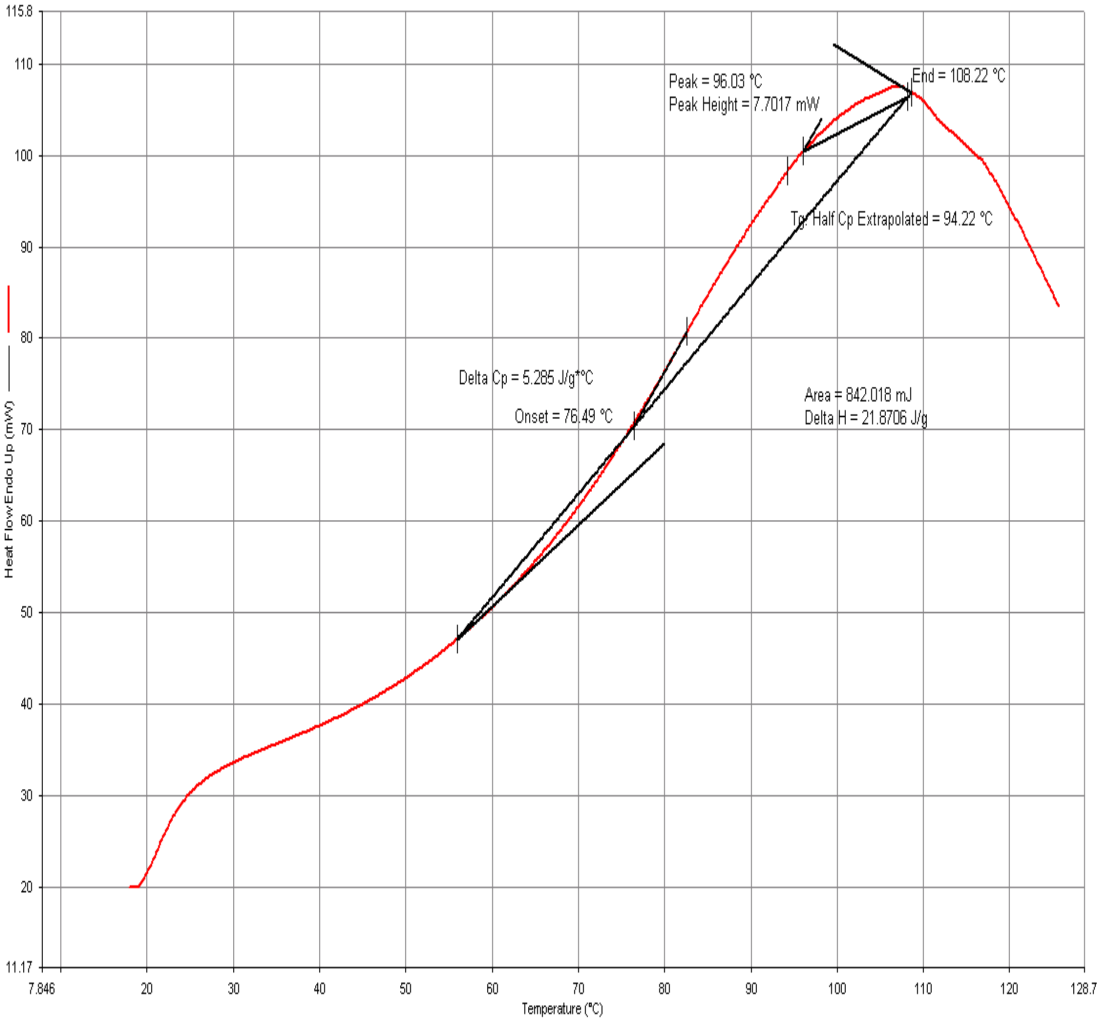


Figure 4.35. DSC thermogram of HMT18 *D.dumetorum* (Yellow cultivar) starch

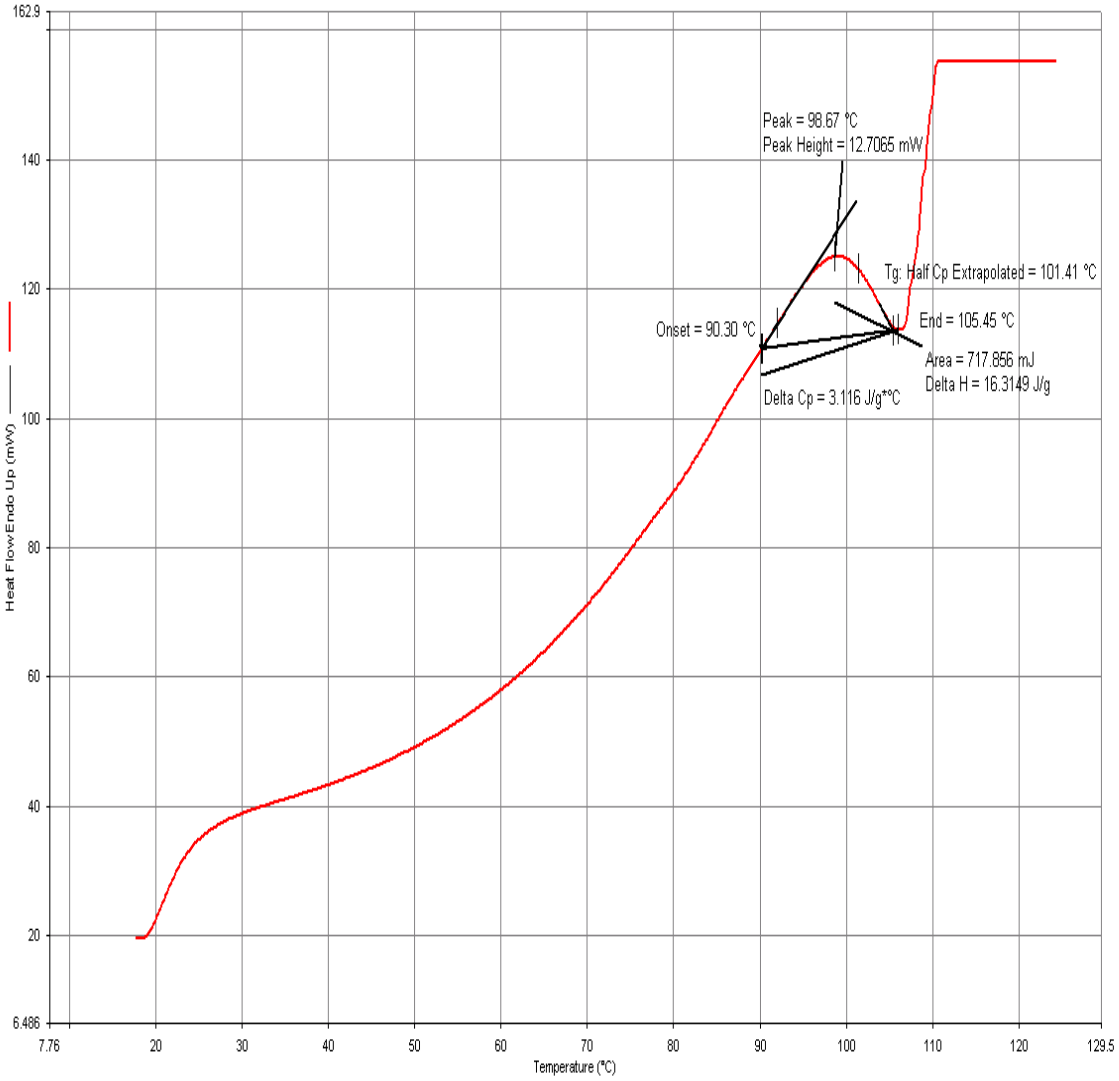


Figure 4.36. DSC thermogram of acid-modified *D. dumetorum* (Yellow cultivar) starch

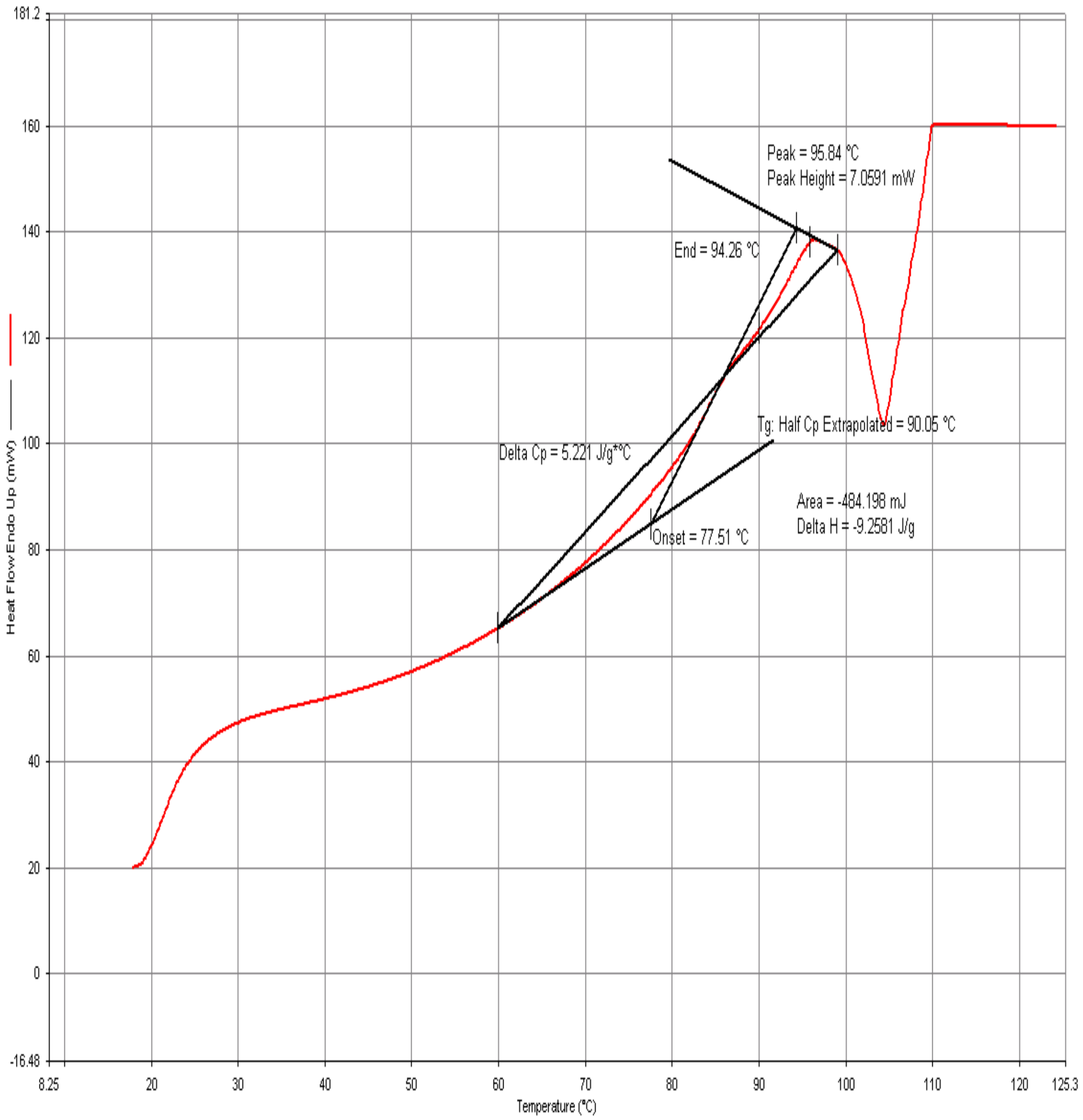


Figure 4.37. DSC thermogram of native *D.dumetorum* (Yellow cultivar) starch

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 General conclusions

Cocoyam and bitter yam gave high starch yield compared to conventional starch sources.

Evaluation of the physical, functional, physicochemical and thermal properties of native and modified starches from cocoyam and bitter yam cultivars showed that their intrinsic properties varied significantly with crop, cultivar and modification method.

The high lightness of native starches of NCe005, NCe010 and NXs003 were satisfactory for commercial application. The small and narrow granule sizes and range of the *Colocasia esculenta* accessions of cocoyam (except NCe010) and the bitter yam starches would make them applicable as texture modifiers, stabilizers and as surface encapsulation/carrier agents for materials like vitamins, colours, flavours, spices, seasonings and fats in industrial food systems. Their small sizes would also make them applicable in formulation of complementary/weaning food because of ease of digestibility. The low amylose contents of the native NCe001, NCe002, NCe003 and the white bitter yam would make them suitable substitute for waxy starches in the food industry as thickeners and stabilizers. Loss of viscosity of acid hydrolysed starches would particularly make them useful in applications requiring low bulk and softness. Starches from native NXs002, NCe005 and yellow bitter yam would be unsuitable in applications that require frozen storage and high anti-staling ability because of their high setback viscosities and therefore retrogradation tendencies. Highly soluble acid thinned starches could find usefulness in products demanding softness and transparency, like gum sweets or Arabic gums, instant pudding, cake frosting or pie-filling.

Starch from yellow bitter yam is recommended for use as a cold water swelling starch due to its high swelling power at relatively low temperatures. Starches with high swelling power include NCe010, NCe002 and NCe003 and could be useful as thickeners and stabilizers in various food systems. Starches from NCe004, NXs002 and white bitter yam could be useful in frozen products with low syneresis properties and as emulsifying agents due to their high WAC while starch from NCe005 could function as fat replacers, emulsifying and texture modifying agents due to its high OAC. Starches with higher transmittance or low opacity (starch from white bitter yam and all HMT and annealed samples) would be suitable for applications as confectionary sugars, non-dairy creamers, and in jams, jellies, candies, soups and sauces where high clarity is a desired quality parameter. Starches with high LGC (all HMT modified starches) will find applications in production of complementary/weaning or geriatric diets where low viscosity and bulk is important. Textural properties of some food products like pastries, jellies and gums may also be modified by addition of these starches. Acid-modified starches with low LGC (high gelatin power) may be applicable in processes as thickeners, stabilizers and gelling agents. Opacity is required in products like salad dressing which would make acid-modified starches suitable for such utilization. For industrial food application, starches with low syneresis (native and modified bitter yam starches) will be suitable in products for low temperature storage, pudding, custard and pie-fillings while starches from *Xanthosoma spp.* will not be suitable because of their low freeze-thaw stability. Native and modified bitter yam starches with high freeze-thaw stability may be used in production of low temperature-storage products, dessert, custard and puddings in which ageing, staling or syneresis are undesirable. On the other hand, all HMT with high syneresis may be useful in resistant starch production, and slowly digesting starch. High gelatinization peaks showed that the starches are resistant to thermal degradation

Exploitation of underutilised tubers like the cocoyam and bitter yam would provide interesting opportunity for globalisation of indigenous starches from developing country like Nigeria and could through value addition, increase the application of their native and modified starches in food industry where their specific functionalities are best suited. Data generated from this study could serve as a guide for selection and utilisation of starches from cultivars of cocoyam and bitter yam in specific industrial food application.

5.2 Recommendations

It is recommended that future research attention be focused on testing of the various native and modified starches from cocoyam and bitter yam in actual food applications at laboratory and pilot scale levels to establish their performance in real systems and thereby push them into the mainstream of agribusiness.

Promotion of starches from cocoyam and bitter yam (especially the *Xanthosoma spp.*), as currently practiced with cassava, could contribute to their wider application and utilisation as indigenous, readily available and economic alternative to the current sources of industrial starch.

5.3 Significant contributions to Knowledge

Through this study, the following are the contributions made to knowledge

- The physical, functional, physicochemical and thermal properties of starches from cocoyam and bitter yam were affected by cultivar and method of modification.
- A database of information on the effect of heat-moisture treatments, annealing and acid hydrolysis on properties of starches from cocoyam and bitter yam cultivars grown in Nigeria was provided
- The study provided information on innovative new and existing starch applications in food industry from indigenous alternative source of starch which could stimulate utilisation, diversification, income generation and foreign exchange savings.

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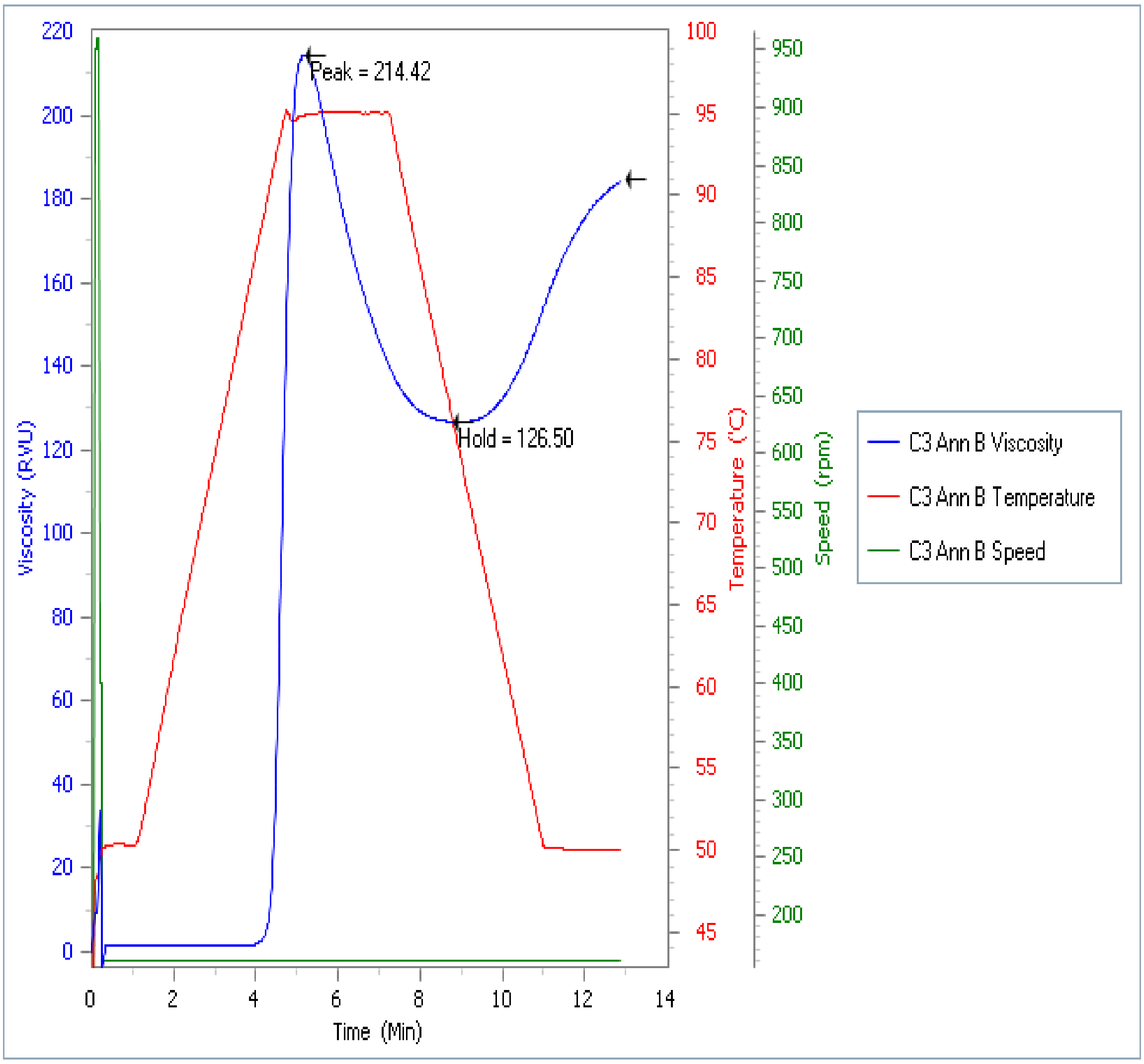
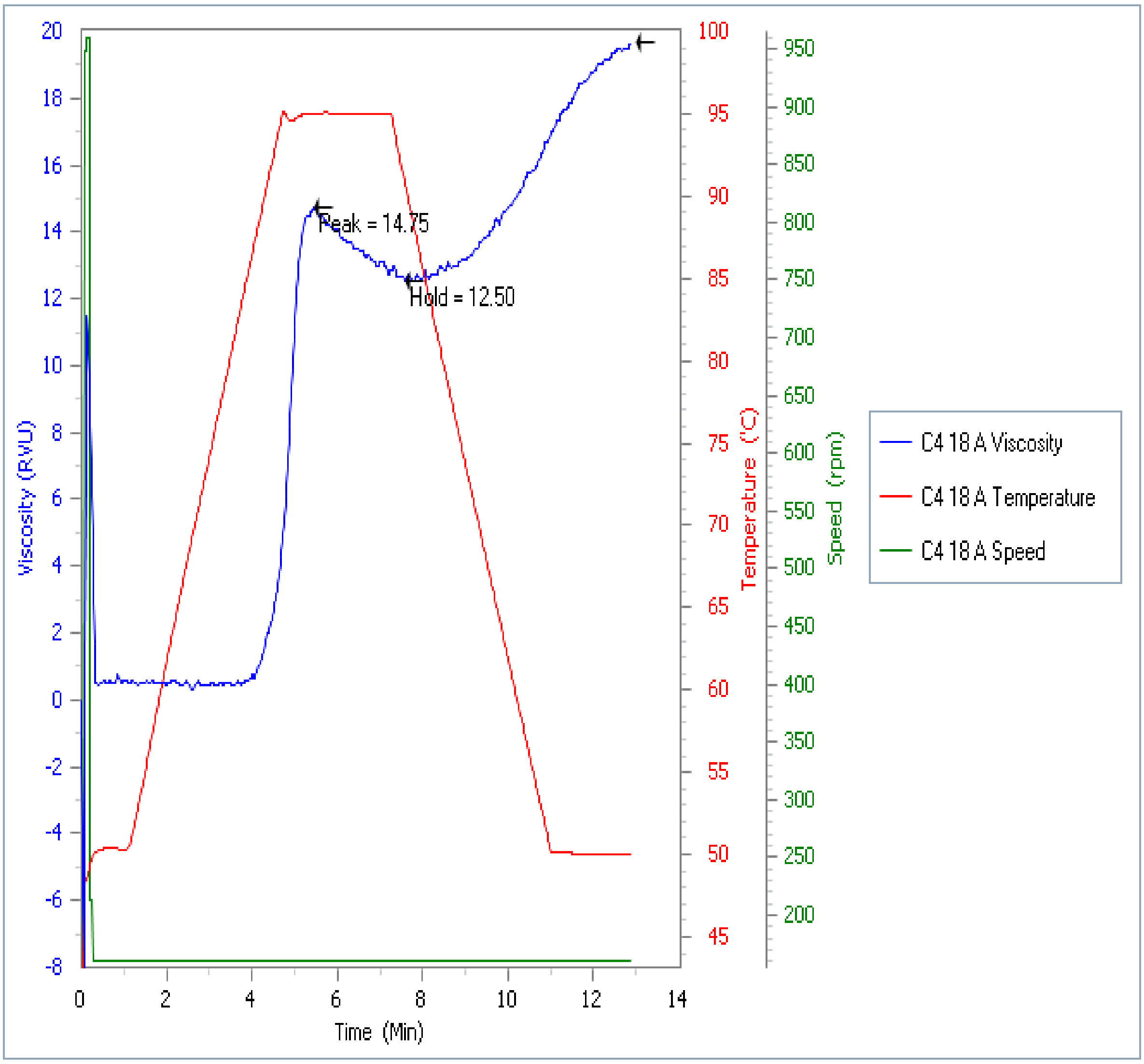
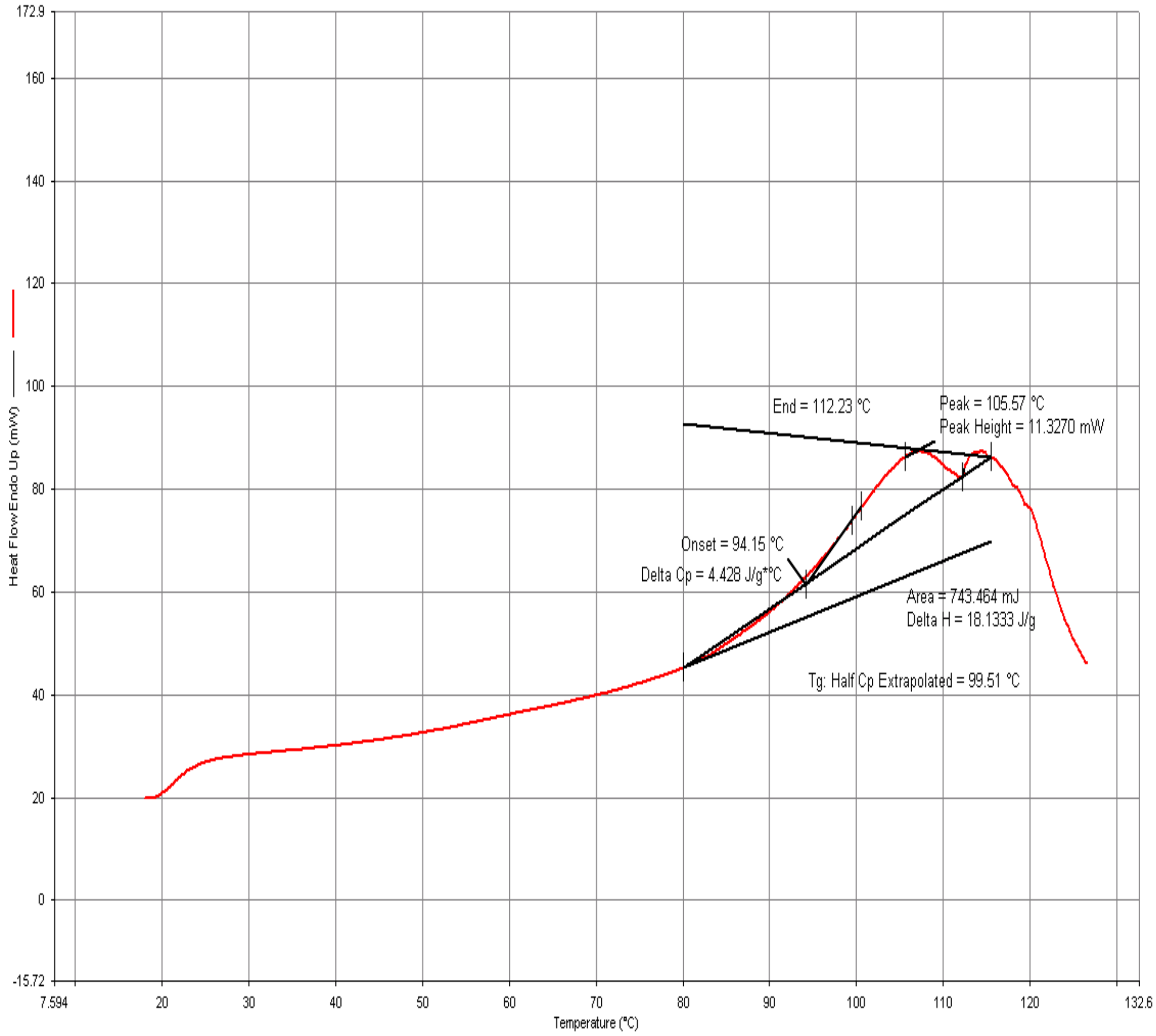
APPENDICES



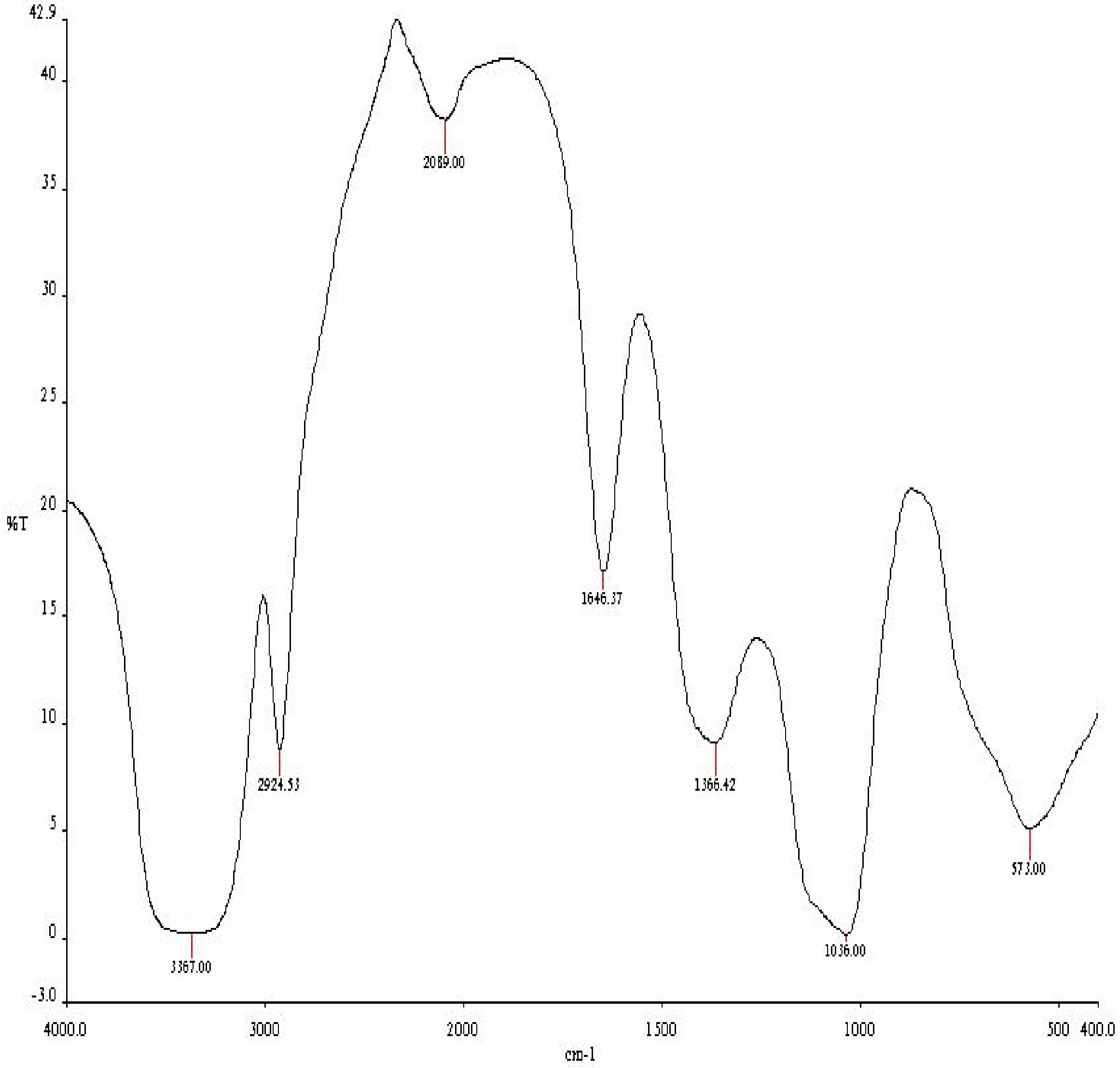
Appendix 1a. Pasting profile of starch from annealed NCe003



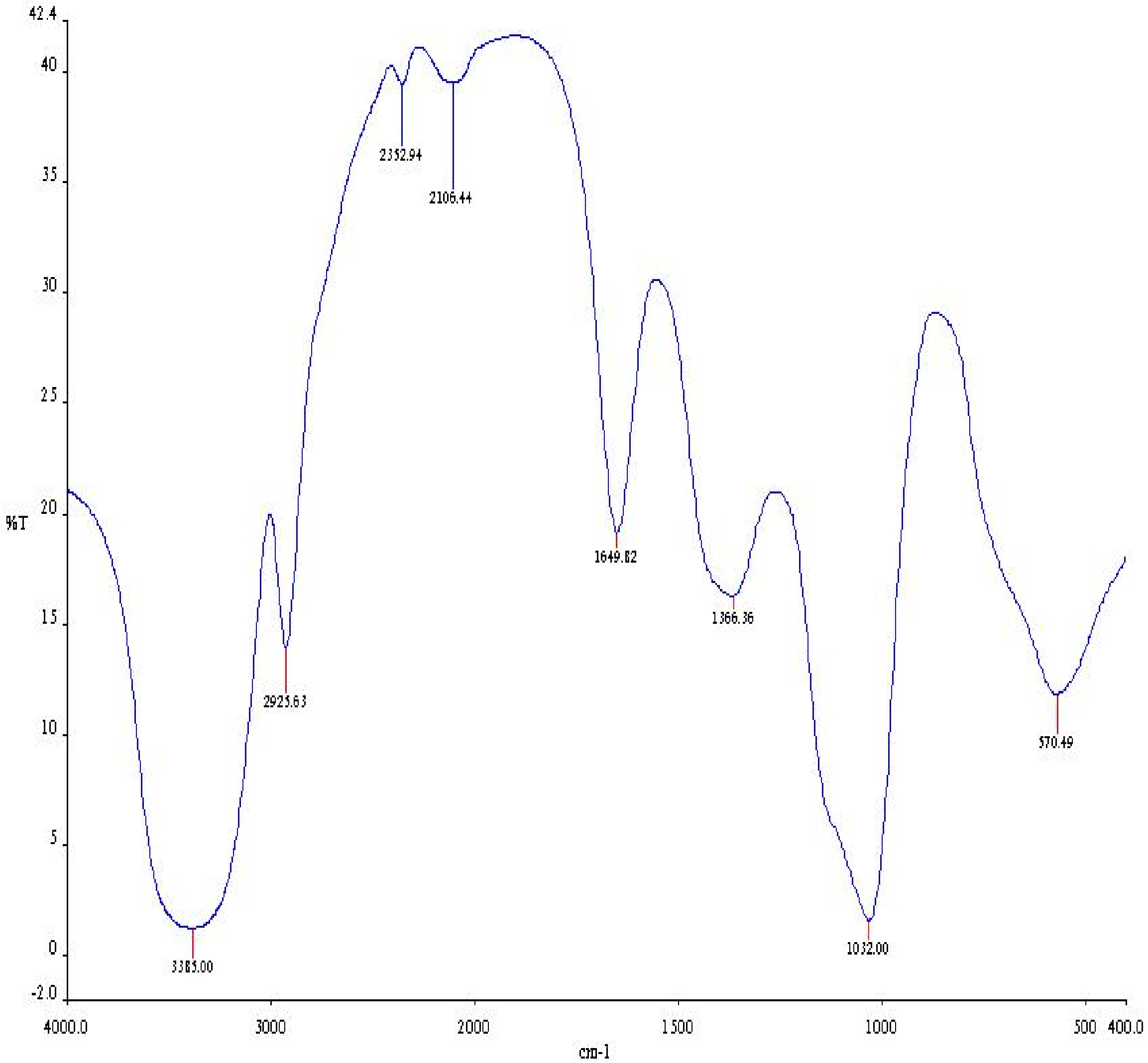
Appendix 1b. Pasting profile of starch from HMT18 NCe004



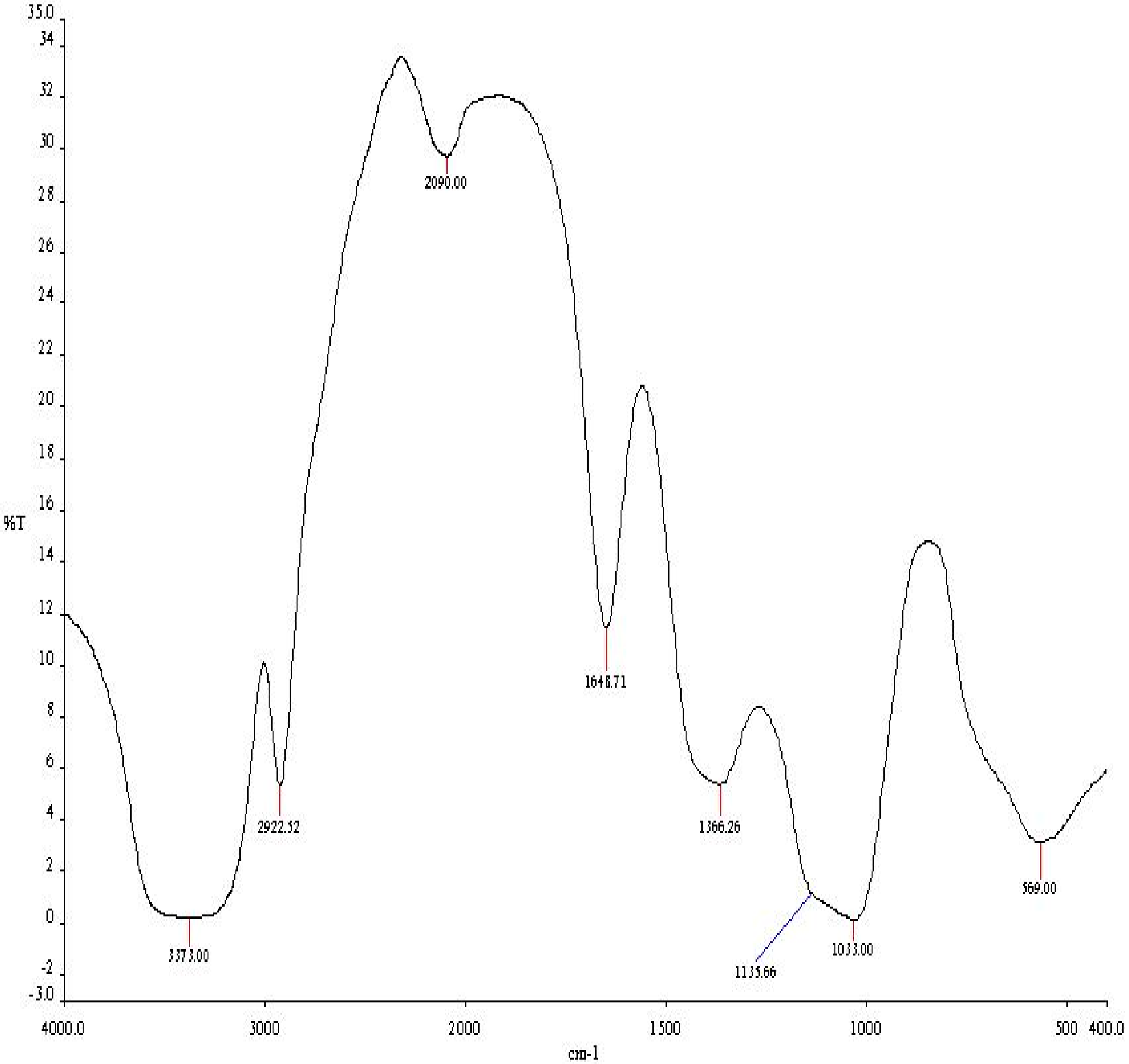
Appendix 2a DSC thermogram of starch from annealed white bitter yam



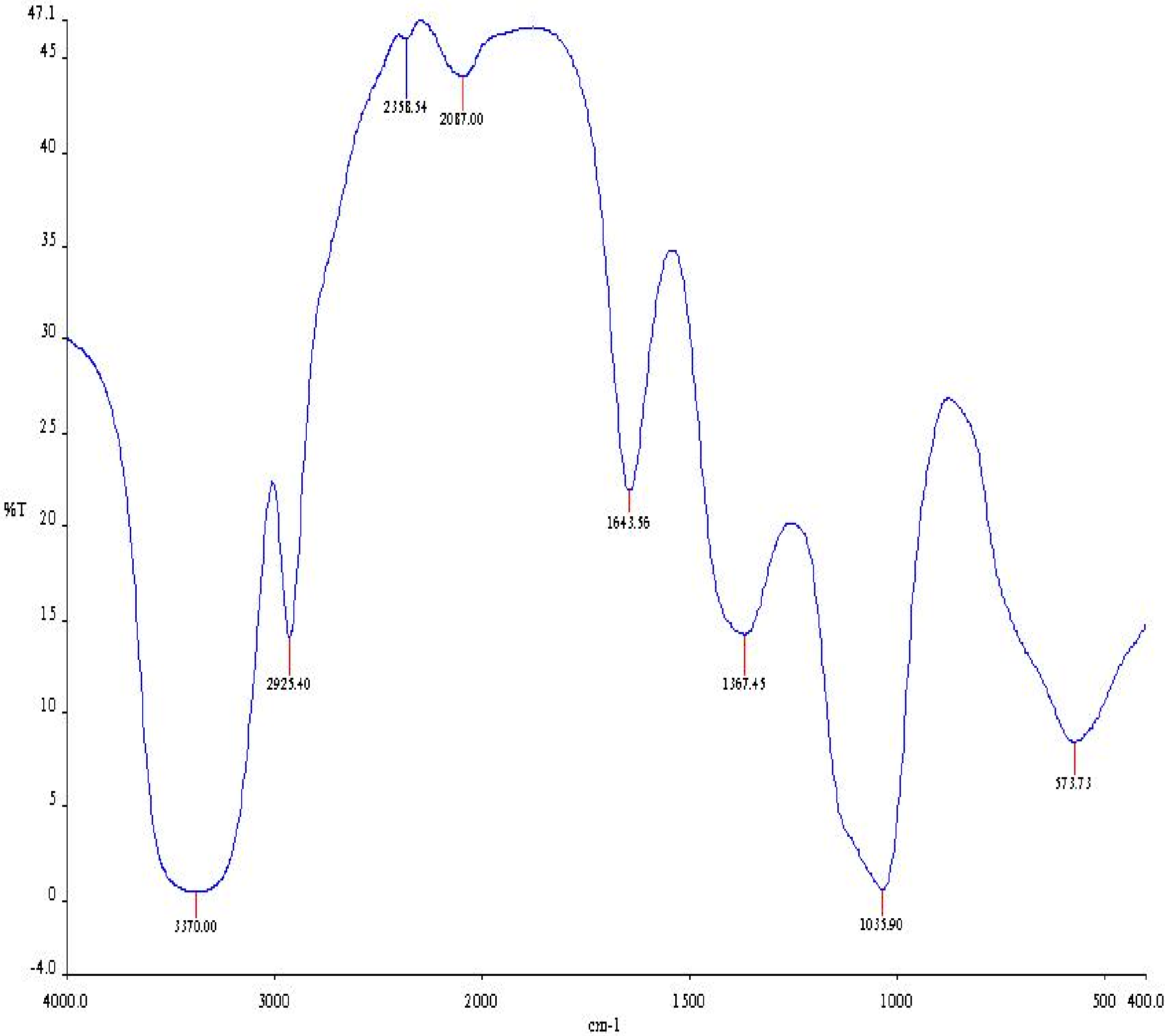
Appendix 3a. FTIR spectra of native NXs001 starch



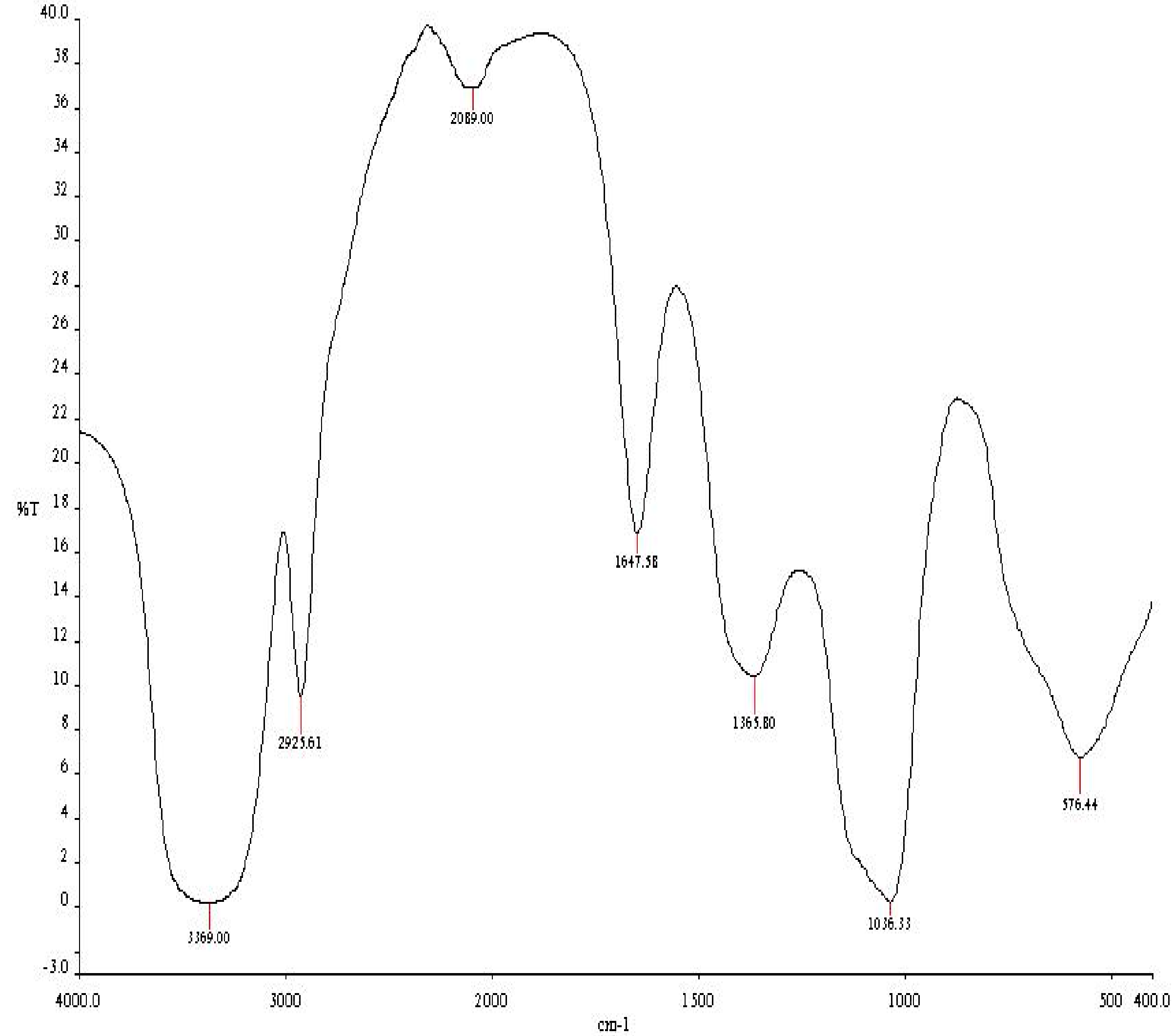
Appendix 3b. FTIR spectra of native NXs002 starch



Appendix 3c. FTIR spectra of native NXs003 starch



Appendix 3d. FTIR spectra of native yellow bitter yam starch



Appendix 3e. FTIR spectra of native white bitter yam starch

Post Hoc Tests

Homogeneous Subsets

Multiple Comparisons[a]

a. Crop = Cocoyam,
b. modification methods = HMT 27

Appendix 4a. Water Absorption Capacity WAC[a]

Duncan[b]

Cultivars	N	Subset for alpha = 0.05			
		1	2	3	4
NXs 003	2	.905000			
NXs 002	2	.980000	.980000		
NCe 001	2	1.070000	1.070000	1.070000	
NCe 002	2	1.145000	1.145000	1.145000	1.145000
NCe 004	2		1.275000	1.275000	1.275000
NCe 005	2		1.285000	1.285000	1.285000
NCe 010	2			1.310000	1.310000
NXs 001	2			1.315000	1.315000
NCe 003	2				1.420000
Sig.		.108	.052	.107	.076

Means for groups in homogeneous subsets are displayed.
Uses Harmonic Mean Sample Size = 2.000.

Appendix 4b. Amylose[a]

Duncan[b]

Cultivars	N	Subset for alpha = 0.05			
		1	2	3	4
NCe 001	2	10.105000			
NCe 003	2	10.180000			
NCe 002	2	10.875000			
NCe 004	2		16.636538		
NCe 005	2		18.011538		
NXs 003	2		18.210000		
NCe 010	2			24.710000	
NXs 001	2			25.780000	
NXs 002	2				37.075000
Sig.		.324	.062	.164	1.000

Means for groups in homogeneous subsets are displayed.

a. Crop = Cocoyam, modification methods = Native

b. Uses Harmonic Mean Sample Size = 2.000.

Appendix 4c. ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
DryMatter	Between Groups	375.430	10	37.543	120.056	.000
	Within Groups	3.440	11	.313		
	Total	378.870	21			
Yield	Between Groups	254.376	10	25.438	159.200	.000
	Within Groups	1.758	11	.160		
	Total	256.134	21			
Starch	Between Groups	776.806	10	77.681	42.902	.000
	Within Groups	19.917	11	1.811		
	Total	796.724	21			

Appendix 4d. Lightness L[a]

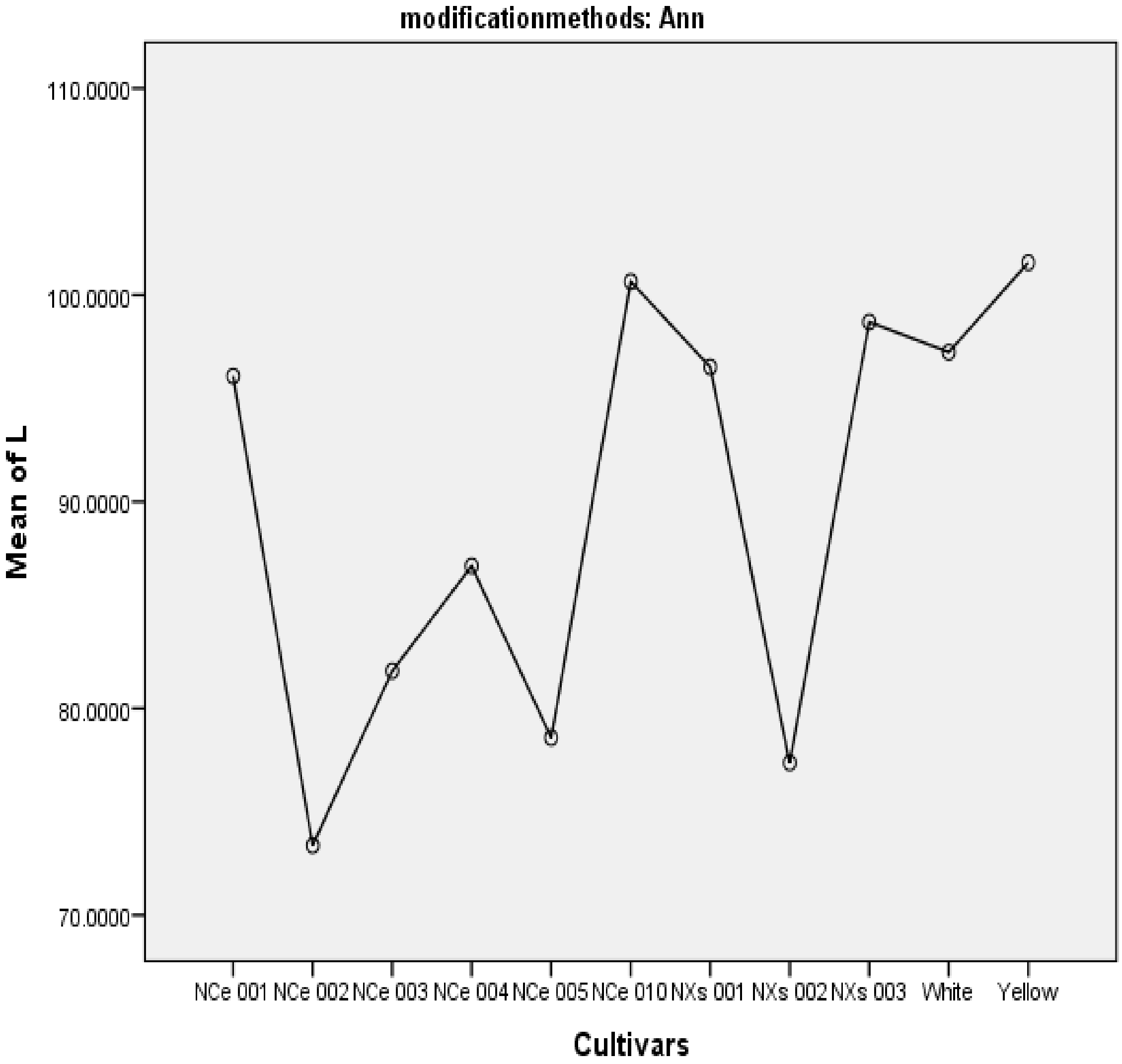
Duncan[b]

Cultivars	N	Subset for alpha = 0.05							
		1	2	3	4	5	6	7	8
NCe 002	3	67.8733							
NCe 003	3		78.4167						
NCe 004	3			80.4733					
NCe 005	3			81.4233					
White	3				88.6767				
Yellow	3					90.3200			
NXs 001	3					91.0300	91.0300		
NCe 001	3						92.0100		
NXs 003	3							94.3100	
NXs 002	3								97.1533
NCe 010	3								97.5500
Sig.		1.000	1.000	.218	1.000	.354	.205	1.000	.602

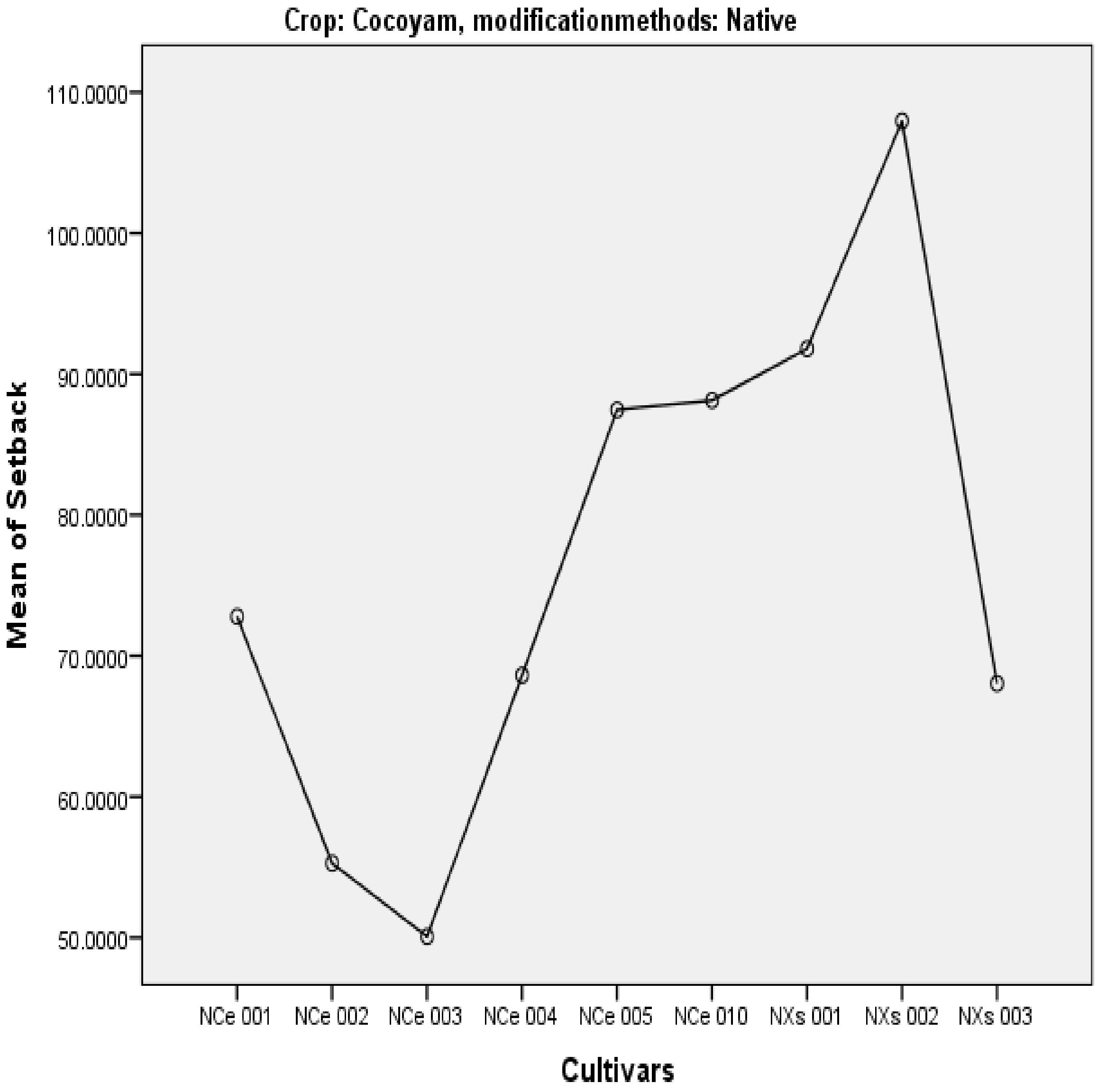
Means for groups in homogeneous subsets are displayed.

a. modification methods = Acid

b. Uses Harmonic Mean Sample Size = 3.000.



Appendix 5a. Mean plots of Lightness (L*) values for annealed starches of cocoyam and bitteryam



Appendix 5b. Mean plots of setback viscosities of starches from native cocoyam

Appendix 6a. Peeling of NCe002 corms in progress

Appendix 6b. Starch isolation from NCe005 and NCe002