Chapter 2

Review of Literature

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The amount of yams produced globally has doubled over the past 20 years, reaching about 60 million tonnes and a net worth of almost $12 billion worldwide. Nearly, 97 % of output comes from the underdeveloped countries, with more than 90 % production is in Western Africa **[91]**. Yam is four times more expensive to produce per calorie than cassava, with higher labour costs and poorer yields **[29, 57, 79]**. Despite these limiting factors, yams generate the most food per hectare and per season in low-technology farming areas **[60]**. Yams are essential for achieving food security in developing countries because they can last for 4-6 months at room temperature, unlike other root and tuber crops **[12, 58, 91]**.

There are 613 species of tuberous climbing plants in the genus *Dioscorea* (yams). Of these 613 species, seven to ten are grown on a considerable scale. Two of these-namely, *D. alata* and *D. cayennensis* (Lam. subsp. *cayennensis* and. subsp. *rotundata)* are of particular significance because they are the staple crops for more than 100 million people, primarily in Western Africa. *Dioscorea* species have also been widely employed as a source of steroidal precursors and in conventional medicine. However, research on yams and their use as a food crop and cash crop have been lacking **[71, 78]**. Despite their great yield, potential, high food and market values, and a variety of post-harvest storage and use choices **[11]**. The goals to prevent food insecurity, achieve sustainable development goals, and sustainable intensification of agriculture can be attained through value addittion of the crop.

Yams are significant staple foods because of their high starch content and potential supply of components for manufactured cuisines in many tropical nations. In root and tuber crops, starches are the main polysaccharide for storage, and these starches are semi-crystalline in structure. Because of their amylose and amylopectin ratio, root and tuber starches exhibit distinct physicochemical characteristics **[52, 107]**. According to **Cheetham and Tao [20]** along with the increase in the amylose level of maize starches, crystallinity dropped. The melting thermodynamic characteristics of starches were found to be inversely related to their amylose content **[69]**. The properties of the crystalline structure of starch granules have been revealed via X-ray diffraction patterns **[134]**. The majority of the starches in the root and tuber show a characteristic B-type X-ray pattern **[43]**. Gelatinization, retrogradation, solubility, swelling power, water-binding capacity, rheological behaviour, and pasting capabilities are the main physicochemical and functional characteristics of starches for food and non-food applications. The amylose level, granule shape, molecular structure, granule size distribution, and botanical source of native starches in the various sources are all connected with these characteristics. Starches from various origins exhibit different gelatinization behaviours due to differences in crystallinity, X-ray diffraction patterns, and amylose concentrations **[120]**. It has been noted that the amylose to amylopectin ratio, amylopectin weight, and amylopectin chain length all have an impact on the rheological characteristics of starch gel, which can reveal information about its viscoelastic capabilities **[42, 99, 119]**. Additionally, amylopectin structure was found to have a greater impact on rheological behaviours than amylose **[120]**. The distribution of branch chain length in amylopectin and amylose is connected to the pasting capabilities of starch. When amylose lipid complexes are formed, the setback viscosity of high-amylose starch was found to be low **[54, 119]**.

Factors such as granule size, crystallinity, the degree of interaction between starch chains (within the native granule), phosphorus content, amylopectin chain length distribution, amylose/amylopectin ratio, species, and cultivars affect the physicochemical properties, thermal stability, retrogradation rate and functional properties of starch. Native starches of roots and tuber are found to have poor functioning characteristics. Therefore, these starches must be modified to have qualities suitable for food applications. The functionality of starches used in the food business is currently changed chemically through cross-linking, substitution, and acid hydrolysis. However, chemical techniques for the modification of starches are prohibitively expensive. With contemporary cultural trends toward natural products, physical modification via hydrothermal treatment such as annealing and heat-moisture treatment would fit in and offer the ability to change starch functionality in a low-cost, safe, and environmentally beneficial manner **[49]**.

2.1.1 Isolation of yam starch

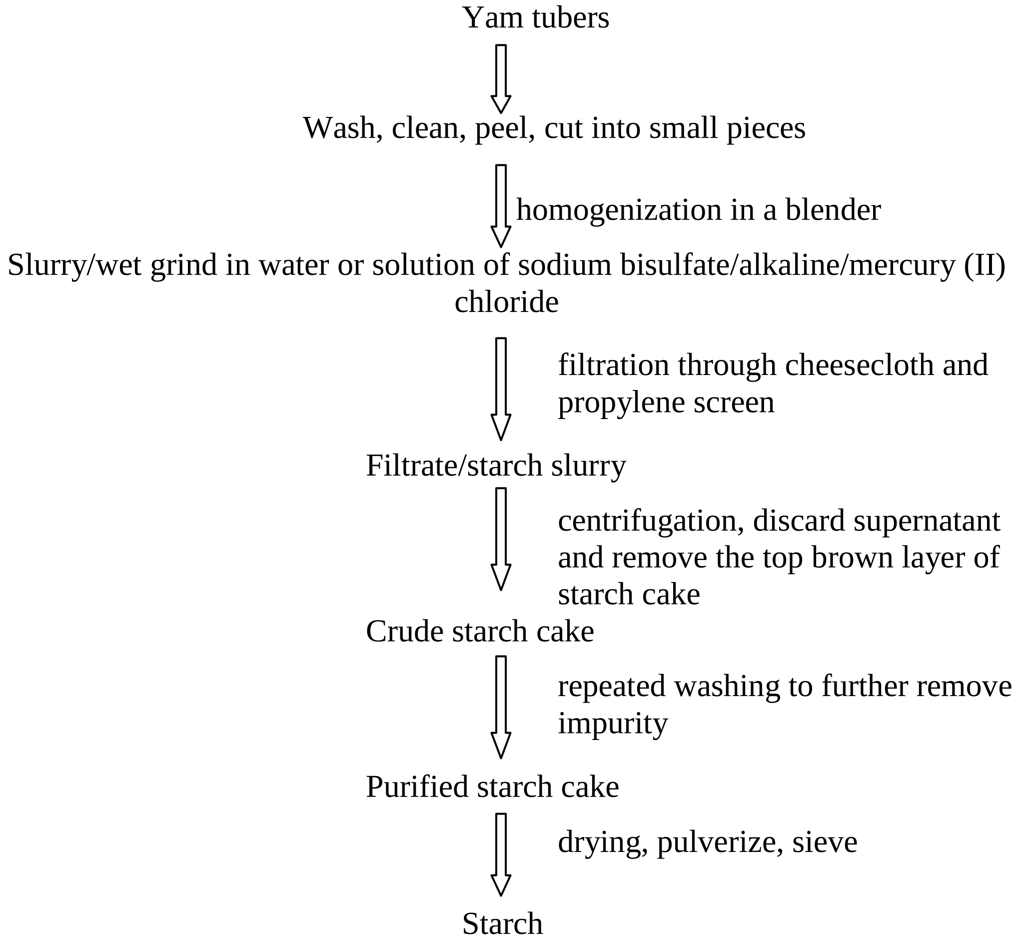

Fig. 2.1: Schematic flowchart showing the involved steps of starch isolation from yam tubers **[133]**.

Fig. 2.1 shows a schematic flowchart of the fundamental procedures for isolating starch from yam tubers. Briefly, the tubers are essentially washed, peeled, cut into small pieces, and mixed with water and sodium bisulfite solution (for instance, 0.075 %) or alkaline solution to obtain slurry using a blender **[8, 87, 96]**. To remove the impurities, the slurry is filtered, sieved, and allowed to stand for sedimentation or centrifuged. The obtained sediment is re-suspended in water for centrifugation and this washing process is repeated until a clean starch is visible. The starch thus obtained is then treated with a little sodium hydroxide solution (approximately 0.1 %), and washed several times with water before drying the resultant starch **[8, 87]**. In several investigations, microbial growth was inhibited during homogenization by using compounds like mercury (II) chloride (0.01 M), which is toxic **[133]**.

A study was carried out to isolate starch from *D. alata* by four different methods using water, pectinase, sodium hydroxide, and oxalic acid or ammonium oxalate solutions. The percentage of starch recovered from raw material was found to be higher for the method using oxalic acid or ammonium oxalate solution (62.92 %), followed by water (43.64 %), NaOH (42.73 %) and pectinase (42.59 %) **[28]**. Due to distinct structures and composition among various species of tuber, there can be certain variations in the methods used to extract starch from different species for a higher yield.

2.1.2 Composition of yam starch

The quantitatively minor presence of components such as protein, lipid, phosphorus content, and ash in starch granules can have a significant impact on the functionality of starch **[111]**. It has been shown that minor components of yam starch vary greatly in composition depending on the species (**Table 2.1**). The differences across the research on the composition of yam starch are most likely due to crop genetics and isolation techniques. The lower protein concentration often indicates a more effective starch extraction process **[14]**. Many researchers have reported that yam starches have lipid content less than 1 %, making them similar to other root and tuber starches, and lower than most cereal starches. The lipid content of the starches from yam can be higher than 1% due to the genotype or insufficient sample cleaning and the solvent employed can also affect the lipid content of the starch **[50]**. The extraction method should be described in each study to signify the lipid fractions because, for instance, an n-propanol-water mixture can extract the bound lipid in starch while a chloroform-methanol mixture can extract the unbound lipid fractions **[50]**. According to **Jiang et al. [54]** and **Zhou et al. [132]**, higher ash content (>0.5 %) typically indicates a less effective approach for purifying starch and a possibility to improve the extraction technique.

A significant part of starch is composed of amylose which is crucial to its qualities and applications **[111]**. Amylose content has been found to vary greatly between different genotypes of the same species as well as between different species (**Table 2.1**). Genotypes from several yam species had amylose levels ranging from 1.4 % **[88]** to 50 % **[97]**. *D. esculenta* and *D. dumetorum*, two of the most researched species, typically have lower amylose concentrations (<20 %) than *D. cayenensis-rotundata, D. alata, D. cayenensis* and *D. rotundata,* (> 20 %) **[9, 87]**.

Table 2.1: Composition of starch from diverse species of yam

Species name	Protein content (%)	Crude fat (%)	Crude fibre (%)	Ash (%)	Carbohydrate content (%)	Phosphorous content (%)	Amylose content (%)	Reference
Dioscorea dumentorum	0.13 ± 0.00	3.85 ± 0.01	12.93 ± 8.20	0.15 ± 0.01	74.65 ± 8.19	-	16.09 ± 0.18	**[31]**
	0.50 ± 0.03	0.52 ± 0.00	-	0.69 ± 0.01	86.49 ± 0.13	-	-	**[80]**
	0.68	0.08	-	0.02	-	-	16.6	**[9]**
Dioscorea rotundata	0.43 ± 0.01	0.45 ± 0.01	-	0.56 ± 0.03	85.36 ± 0.23	-	-	**[80]**
	1.23 – 1.36	0.39 – 0.44	1.08 – 1.13	1.03 – 1.09	86.02 – 86.61	0.024 - 0.035	22.86 – 23.16	**[6]**
Dioscorea alata	10.27	1.15	2.31	2.93	76.57	-	-	**[32]**
	8.40 – 10.46	1.62 – 2.41	3.33 – 3.53	2.48 – 3.53	70.88 – 73.90	114.65 – 211.63 (mg/kg)	12.42 – 16.11	**[83]**
	0.02 – 0.03	0.16 – 0.30	-	0.24 – 0.91	-	268.15 – 361.07 (ppm)	24.31 – 26.99	**[74]**
	0.19 – 0.35	0.09 – 0.11	-	0.08 – 0.38	-	-	25.3 – 27.4	**[9]**

	0.90 ± 0.16	0.02 ± 0.00	2.14 ± 0.12	0.06 ± 0.03	-	0.024 ± 0.001	25.77 ± 0.61	**[85]**
Dioscorea trifida	0.50 ± 0.01	0.12 ± 0.01	1.60 ± 0.10	0.007 ± 0.003	95.30 ± 0.10	-	-	**[27]**
Dioscorea bulbifera	0.00	0.31 ± 0.29	0.85 ± 0.19	0.19 ± 0.83	-	-	37.50	**[98]**
Dioscorea zingiberensis	0.54 ± 0.10	0.60 ± 0.14	0.07 ± 0.01	4.19 ± 0.47	-	-	23.62 ± 2.11	**[132]**
Dioscorea Odoratissima	5.37 ± 0.20	2.22 ± 0.12	2.07 ± 0.04	3.73 ± 0.02	70.48 ± 0.06	-	-	**[86]**
Dioscorea villosa	6.11 ± 0.25	0.45 ± 0.20	0.23 ± 0.01	0.40 ± 0.02	85.58 ± 0.20	-	57.52 ± 1.16	**[95]**
Dioscorea esculenta	1.2 ± 0.0 1	0.42 ± 0. 01	-	0.25 ± 0 .01	86.30 ± 1.11	-	-	**[101]**
	0.07 – 0.39	0.06 – 0.09	-	0.21 – 0.23	-	-	14.1 – 17.1	**[9]**
	1.20 ± 0.01	0.42 ± 0.01	-	0.25 ± 0.01	86.30 ± 1.11	-	-	**[101]**
Dioscorea cayenensis-rotundata	0.11 - 0.26	0.03 -0.10	-	0.04 – 0.26	-	-	25.2 - 28.8	**[9]**
Dioscorea pyrifolia	1.34 ± 0.11	0.00 ± 0.00	0.00 ± 0.00	0.88 ± 0.21	92.73 ± 0.48	-	-	**[103]**

Compared to other species, *D. hispida* typically has a higher content of amylose (39.3 %) **[115]**. It was also noticed that compared to other species, *D. dumetorum* and *D. esculenta* tend to have lower amylose contents.

It was also discovered that amylose mostly accumulated along the edges of granules, and amylose content increases along with an increase in the size of the granules **[48]**. Comparative analysis of different methods of determination of amylose in the same species has revealed different results. Thus, many factors such as the method of quantification, lipid content, agronomic practices, environmental factors, and harvesting period are also critical in determining the amylose content of starch.

The phosphorus content of yam starches can be related to both the starch itself and the methods used to measure it (such as spectrophotometric methods as opposed to atomic absorption spectroscopy) **[88]**. The latter makes direct comparisons between the findings of various investigations impractical. Inorganic phosphate, phosphate monoester, and phospholipids make up the majority of the phosphorus present in starch **[56]**. Comparative research on the phosphorus content of yam and other tuber starches is still lacking **[133]**.

2.1.3 Morphology of yam starch

Light microscopy, scanning electron microscopy, and laser light diffraction (LLD)-based particle size measurements have all been used to observe significant variation in the size and shape of starch granules isolated from diverse yam species or the same species (**Table 2.2**). It should be noted that the definition of the size changes as the shape of granules changes, and the exact values of the granule size depend on the measurement methods **[65]**.

The size of individual yam starch granules varies in the range from 1μ m (*D. esculenta*) to 90 μm (*D. alata*) **[28, 133]**. The majority of yam starches have a mono-modal size distribution and are simple granules (as opposed to compound granules) with minor cracks on their surface. The granule size of the same species has been shown to vary greatly with the method of size measurement. In a study, the average size of granules from nine genotypes of *D. alata* was found to be in the range of 28 to 40.25 μm by Light microscopy **[87]**.

Table 2.2: Morphology of yam starch

Species name	**Granule size (µm)**	**Granule shape**	**Method**	**Reference**
Dioscoreae zingiberensis	21.19 ± 0.04	Flattened ovoid	SEM	**[132]**
Dioscorea bulbifera	1.38 - 104.7	Triangular and flat	LM, SEM	**[19]**
Chinese yam	8 - 25	Elliptic, rough and polygonal	SEM	**[122]**
Dioscorea dumetorum	2.15 – 3.58	Polygonal	SEM	**[7]**
Dioscorea alata	-	Oval or ellipsoidal	SEM	**[70]**
	30–45	Truncated oval or spade	LM, SEM	**[50]**
	25.75 – 41.50	Oval, ellipsoidal, and round	LM	**[87]**
Dioscorea rotundata	-	Oval, spherical and irregular	SEM	**[70]**
	8.1 - 44.8	Polygonal, oval, and semi oval	SEM	**[68]**
Dioscorea opposita Thunb.	10 - 50	Round, elliptical or irregular	SEM	**[102]**
Dioscorea esculenta	3 - 10	Polygonal	LM, SEM	**[50]**
Dioscorea cayenensis	41.25 ± 3.66	Oval, ellipsoidal, and round	LM	**[87]**

By using light-scattering methods, a narrower range of starch granule size was measured for *D. cayenensis* and *D. rotundata* compared to *D. alata* **[35]**. The starch granules of *D. esculenta* and *D. dumetorum* are typically smaller in size than granules of other species. *D. dumetorum* granules can be as tiny as 0.8 µm **[77]**.

2.4 Properties of yam starch

2.4.1 Water and oil absorption capacity

Very few researches are available on the water absorption capacity (WAC) and oil absorption capacity (OAC) of starch derived from *Dioscorea* species. Heat-moisture treatment significantly affected the WAC and OAC of *D. alata* starch **[116]**. WAC (74.4 %) of native starches increased with oven heat-moisture treatment (OHMT) and autoclave heat-moisture treatment (AHMT) to 110.93–118.40 % and 109.07–135.47 %, respectively. WAC was found to increase with rise in the moisture content of HMT treatment, and the highest value of WAC has recorded for AHMT at 30 % and 35 % moisture. HMT improved the hydrophilicity of *D. alata* starches, thereby increasing the WAC. These outcomes were in line with past studies, where a higher capacity to absorb water after HMT was observed. Additionally, OAC (0.65 ml/g) of native starches increased with OHMT and AHMT to 0.66 and 1.20 ml/g, and 0.68 and 1.37 ml/g, respectively. **Adebowale et al. [3]** found a linear increase in WAC for heat moisture treated red sorghum starch compared to their native counterparts, indicating the hydrophilic inclination of starch along with an increase in the moisture content of treatment. **Babu and Parimalavalli [13]** hypothesized that an increase in the oil absorption capacity in HMT starches may be linked to the change of functional properties such as the lipophilic character of the granule surface and interior of starch due to HMT.

2.4.2 Swelling power and solubility

Swelling power (SP) and solubility (S) determination is a simpler method to reflect the gelatinization behavior of starch granules. They are often determined by heating a starch in water solution in a test tube in the temperature range of 50 to 95 °C for a predetermined amount of time (mostly 30 min) while shaking the tube periodically. The hot mixture is then cooled and centrifuged. The sediment and supernatant are separated, followed by drying of the latter to calculate the swelling power and solubility

[63]. The SP, S, and amylose leaching (AML) of different yam starches observed at a temperature ranging from 60 to 95 °C by many reports are presented in **Table 2.3**. Different species have displayed varying susceptibilities in SP and S to a range of temperatures (60 to 95 °C). Yam starch appeared to have less swelling and solubility than potato starch **[40]**. Moreover, a significant variation in the SP and S of yam was reported within the same species and among the species **[9, 55, 88]**.

Even though *D. dumetorum* and *D. esculenta* have smaller granule sizes and lower amylose content, no difference in the SP and S was observed at 50 and 90 °C in a comparative study between *D. esculenta*, *D. cayenensis-rotundata*, *D. dumetorum*, and *D. alata* **[9]**. This implies that substantial roles in swelling and solubility are played by factors other than amylose content and granule size. Few reports on the influence of environmental factors (e.g. harvesting period) in the swelling power and solubility of starch are also available **[88, 133]**.

A significant decrease in the SP and S was reported for the hydrothermally (HMT and ANN) treated starches from *Dioscorea opposita* compared to native starches **[129]**. The possible reason for decreased SP could be due to the presence of amylose and non-starch fractions like lipids which retards the SP of starch, and a lower amount of amylopectin, which facilitates the uptake of water **[1, 5]**. Solubility measures the amount of leached amylose from granules after heating, and the decrease in SP and S after HMT and ANN may be linked to the structural stability induced by increased amylose and amylopectin interactions **[126, 131]**.

Hydroxypropylation of starch increases the swelling and solubility of the starch granules **[37]**. *Dioscorea rotundata* starches exhibited a higher swelling power and solubility on hydroxypropylation, and the SP and S increased with the increase in molar substitution during hydroxypropylation **[61]**. This could be the result of the disruption of inter- and intramolecular hydrogen bonds and more access of water to the starch internal structures **[37, 61, 105]**.

Table 2.3: Swelling power (Sp) and solubility (S) of various yam starch

Temperature (°C)	**60**		**70**		**80**		**90**		**Amylose leaching (g/100 g)**	**Reference**
Species name	**Sp (g/g)**	**S (%)**	**Sp (g/g)**	**S (%)**	**Sp (g/g)**	**S (%)**	**Sp (g/g)**	**S (%)**		
Dioscorea hispida	-	-	-	-	-	-	15.6	9.92	15.8 (95)	**[114]**
Dioscorea dumetorum	3.60 - 7.90	29.00 - 33.50	4.20 - 8.30	40.50 - 53.50	10.25 - 14.10	95.00 - 96.50	17.30 - 26.10	122.00 - 132.50	-	**[4]**
	2.47 (55)	2.67 (55)	2.43 (65)	2.67 (65)	4.73 (75)	5.33 (75)	13.82 (85)	14.67 (85)	-	**[34]**
	15.1 (50)	12.2 (50)	-	-	-	-	13.7	12.4	-	**[9]**
Dioscorea alata L.	-	-	5.83 (75)	-	-	-	6.50 (95)	-	14.89 - 97.38 (75 - 95)	**[85]**
	2.33 (55)	3.33 (55)	2.15 (65)	2.67 (65)	5.15 (75)	13.33 (75)	8.77 (85)	8.67 (85)	-	**[34]**
	15.4 - 16.8 (50)	8.1 - 21.4	-	-	-	-	13.8 - 16.0	7.3 - 13.5	-	**[9]**

	-	-	-	-	9.49 - 13.80	2.98 - 6.68	-	-	-	**[82]**
Dioscorea rotundata	2.11 (55)	2.00 (55)	2.00 (65)	2.00 (65)	5.29 (75)	2.67 (75)	8.63 (85)	6.67 (85)	-	**[34]**
Dioscorea cayenensis	2.24 (55)	2.00 (55)	2.61 (65)	2.67 (65)	9.64 (75)	7.33 (75)	10.69 (85)	7.33 (85)	-	**[34]**
Dioscorea esculenta	14.8 - 16.1 (50)	7.1 - 16.5 (50)	-	-	-	-	13.9 - 14.8	7.3 - 12.5	-	**[9]**
Dioscorea cayenensis-rotundata	11.8 - 16.8 (50)	8.6 - 23.2 (50)	-	-	-	-	10.8 - 16.4	6.1 - 11.4	-	**[9]**
Dioscorea opposita	-	-	5.31	3.49	10.28	4.67	13.19	8.64	-	**[92]**
	-	-	-	-	7.80 - 11.10	7.41 - 11.40	11.10 - 12.00	7.80 - 11.70	-	**[102]**
	3.53	4.60	4.89	7.08	10.50	10.09	18.03	12.89	-	**[24]**
	-	-	-	-	-	-	10.79 - 30.34 (100)	7.84 – 14.55 (100)	-	**[21]**

2.4.3 Amylose leaching

Total amylose content, the degree of interaction between amylose-amylopectin (AM-AMP) and amylose-amylose (AM-AM), and the quantity of amylose lipid complex chains formed have an impact on the amount of amylose leaching **[44, 75]**. Amylose leaching was found to increase with temperature in all starches **[133]**. The HPSEC-MALLS-DRI system was used to examine the structure of the components that leached out from the granules of three species of yam (*D. alata*, *D. cayenensis-rotundata*, and *D. esculenta*) at 90 °C **[97]**. The leached fractions were found to be substantially smaller than the amylose and amylopectin fractions **[97]**. The possibility to entangle and get fixed with other molecules decreases with decreasing molecular size, thereby increasing the possibility to leach out during swelling.

2.4.4 Thermal properties

In general, starches are semi-crystalline structures and are insoluble in water. However, when starches are suspended in water, they get hydrated and swell slightly. These hydrated granules when heated at a specified temperature, more swelling of the granules takes place with the increase in diameter of the granules. When the temperature of heating is above the gelatinization temperature of the starch, the granules absorb more water and form a paste. This phenomenon of change of suspension of starch granules to paste is known as starch gelatinization. Thus, an endothermic process can cause the granules to expand when heated in water with simultaneous disorganization of starch structure **[127]**. Mainly, the decoiling of the double helix and melting of the crystalline areas of starch granules are two steps that take place in the gelatinization process.

DSC is critical for comprehending the thermal characteristics of yam starches and their potential uses. The starch of *D. pyrifolia* does not gelatinize below 70 °C which is desired for application in food such as dough and bread products **[103]**. The lower onset temperature (T_o) shown by yam starches (**Table 2.4**) makes it favourable where a gel is formed at a lower temperature with minimal energy for the manufacture of products, thereby, finding its application as a thickening agent in the food industry **[85]**.

Jiang et al. [54] studied the thermal properties of five yam species, viz, *Dioscorea alata*, *Dioscorea bulbifera*, *Dioscorea nipponica*, *Dioscorea septemloba*, and *Dioscorea opposita*. They reported a lowest T_o (68.10 ºC) for *Dioscorea opposita*, highest T_o (75.06ºC) for *Dioscorea septemloba*, and T_o in the order *Dioscorea opposite* < *Dioscorea nipponica* < *Dioscorea alata* < *Dioscorea bulbifera* < *Dioscorea septemloba*. The gelatinization enthalpy was found to be in the order *Dioscorea septemloba* < *Dioscorea nipponica* < *Dioscorea bulbifera* < *Dioscorea opposita* < *Dioscorea alata*. Several variables like the starch granule size, shape, amylose content, water-binding ability, composition, and internal arrangement have an impact on the starch gelatinization enthalpy values **[106]**. The amylose concentration, size, shape, distribution, water-binding ability of starch granules, internal organisation, and method of determination contribute to the variances in the gelatinization temperatures **[10, 54]**.

Another study made by **Yu et al. [129]** on hydrothermally treated Chinese yam starches revealed that HMT and ANN treatments increased the T_o, T_p, and T_c of the starches compared to native starches, and this could be attributed to the increased interactions of AM-AP, AM-AM, and more perfections of the crystalline area of starch granules **[104]**. However, a decrease in enthalpy (ΔH) was reported by the study, and this decrease may be linked to the disruption of amorphous regions of starch granules or the formation of fewer double helices **[129]**.

Lawal et al. [61] reported the thermal properties of hydroxypropylated *D. rotundata* starches, and found a decrease in T_o, T_p, and ΔH, which can be attributed to the decrease in the glass transition temperature of the granules due to decreased hydrogen bonding on hydroxypropylation **[37, 61, 105]**.

Wang et al. [118] studied the chemical modification of Chinese yam (*Rhizoma Dioscoreas Oppositae)* starch using STMP and STPP. No significant changes in the thermal properties of the cross-linked starches were reported.

Jayanthi et al. [51] reported a comparative study on the thermal properties of freshlycooked and freeze-dried starches from *D. alata* and *D. esculenta*. The onset temperature (T_o) and peak temperature (T_p) of freshly-cooked and freeze-dried starches of *D. alata* were found to be higher than the respective starches extracted from *D. esculenta.*

Table 2.4: Thermal properties of yam starch

Species name	**Starch to water ratio**	**T_o (⁰C)**	**T_p (⁰C)**	**T_c (⁰C)**	**ΔH (J/g)**	**Method**	**Reference**
D. opposita	1:2	68.4 - 71.5	72.4 - 74.4	76.8 - 78.2	8.46 - 14.14	DSC	**[102]**
	1:3	70.06 – 72.77	80.86 – 81.20	88.59 – 89.64	8.18 – 9.30	DSC	**[136]**
	30% (w/w)	84.12 - 88.59	94.07 - 99.18	101.22 - 108.55	13.44 - 23.35	DSC	**[135]**
D. trifida	-	32.09 - 34.79	90.02 - 90.56	136.24 - 136.49	6.17 - 6.29	DSC	**[100]**
D. bulbifera	1:2	69.94	74.77	96.95	18.19	DSC	**[19]**
D. alata	1:3	69.62	74.81	82.06	12.15	DSC	**[85]**
	20 % (w/w)	71.36 - 74.18	74.32 - 76.93	77.05 - 80.23	4.80 - 12.7	DSC	**[96]**
	3mg / 11µL	75.45 - 78.17	78.40 - 85.13	85.70 - 92.87	18.60 - 18.98	DSC	**[50]**
D. eculenta	3mg / 11µL	72.30 - 72.55	75.00 - 75.73	81.65 - 85.40	17.32 - 18.07	DSC	**[50]**
D. cayenensis rotundata	10mg / 50µL	69.9 - 76.9	-	-	13.7 – 16.7	DSC	**[9]**
D. zingiberensis	1:3	70.49	78.53	85.96	12.73	DSC	**[132]**

2.4.5 Pasting properties

The pasting properties of starch generally refer to the changes that occur in the starch as a result of the presence of heat and water. These changes affect the texture, digestibility, and end use of starch, so the study of these parameters is very crucial. Commonly, starch pasting properties are represented in terms of PT (peak temperature, °C), PV (peak viscosity, cP), BD (break-down, cP), SB (set back, cP), and FV (final viscosity, cP). Pasting properties depends on the starch properties such as starch origin **[135]**, cultivation area **[93]**, etc.

Different kind of treatments/modifications have different impacts on the pasting properties (**Table 2.5**). Drying time and temperature have significant effects on pasting properties **[30]**. Apart from the drying time and temperature, drying techniques also play a significant role in pasting properties **[66]**, so to obtain proper pasting properties selection of proper drying techniques of modified starches are very important **[59, 66]**.

Different types of physical treatment like ANN, HMT, ultrasonication, high-pressure processing, and ionic treatment play a significant role in pasting properties. **Yu et al. [129]** observed decreased trends of peak viscosity when Chinese yam starch was treated with HMT and ANN. **Suriya, Reddy, and Haripriya [113]** reported the significant effect of moisture content on the pasting properties of HMT-treated yam starch. **Wang et al. [117]** reported a decreased peak viscosity as the intensity of ionic radiation increased.

In a study on hydroxypropylated yam (*D. rotundata*) starch, a decrease in the peak temperature and an increase in the peak viscosity was reported **[61]**. The peak viscosity increased with the increase in the level of molar substitution during hydroxypropylation. These observations could be due to the increased penetration of water molecules to the starch internal structures **[37, 61, 105]**.

Chemical modification of Chinese yam (*Rhizoma Dioscoreas Oppositae)* starch using STMP and STPP was reported by **Wang et al. [118]** who reported a significant change in the pasting properties of the cross-linked starches. The crosslinked starches exhibited a lower swelling power and increased pasting temperature in the gelatinization of the starches. STMP is reported to be an effective crosslinking agent that increases the internal bonding forces in the starch granules **[114, 123]**.

Table 2.5: Pasting properties of yam starch

Species name	**Starch conc. (%)**	**PT (^{0}C)**	**PV (cP)**	**BD (cP)**	**SB (cP)**	**FV (cP)**	**Types**	**Reference**
Dioscorea opposita Thunb.	3 g in 25 ml d.w.	75.37	4226.67	1637.00	1065.33	3655.00	GY11	**[135]**
		79.85	4119.67	915.33	1823.67	5028.00	GY5	
		75.32	4114.00	1661.67	979.67	3432.00	GY2	
		76.50	5034.00	1106.67	1485.67	5413.00	GXPY	
		79.50	6145.67	2672.33	1060.67	4534.00	LCY	
		84.37	4679.33	933.00	2712.33	6458.67	SFY	
		83.40	5194.67	2209.00	725.33	3711.00	MPY	
		81.77	2405.33	1157.67	88.00	1335.67	SYPY	
		81.70	5558.00	870.33	2287.33	6975.00	ASY	
Yam bean tubers	3 g in 25 g d.w.	62.3	6783.8	5082.30	1190.7	-	Cultivated in Guangdong	**[93]**
		61.3	6783.50	5122.5	912.0	-	Cultivated in Sichuan	
Dioscorea opposita Thunb.	2 g in 25 ml d.w.	86.8	1880.5	146.0	574.5	2330.5	Native	**[92]**
		80.6	4934.5	1226.5	1958.0	5676.0	Octyl succinic anhydride yam starch	
		81.6	2772.0	1351.0	496.0	1924.5	Acetylated yam starch	
		-	85.5	50.5	12.0	41.0	Granular cold water soluble starch	

African yam bean (*Sphenostylis stenocarpa*)	15 g in 25 ml d.w.	76.90	292.67	115.33	146.50	323.83	Native	**[2]**
		78.85-82.95	238.00-279.42	43.67-61.33	115.08-134.00	314.50-352.08	HMT	
		75.15	277.75	107.50	191.67	361.67	Annealing	
Elephant foot yam (*A. paeoniifolius*)	3.5 g in 25 g d.w.	86.3	2591.6	2580.3	1270.7	3863.3	Native starch	**[112]**
		84.6	526	409	7.6	113.7	Oxidized starch	
		86.4	4120.7	1198.3	253	3184.3	Cross-linked starch	
		ND	16	6.3	7.3	15.7	Oxidized cross-linked	
		84.8	657	351	15.6	322.6	Cross-linked oxidized	
Elephant foot yam (*A. paeoniifolius*)	2.5 g in 25 ml d.w.	87.9	752.6	89.2	432.2	1090	Drying at 50^{o}C	**[59]**
		94.1	548	80	380	848	Drying at 60^{o}C	
		94.3	467	79	381	769	Drying at 70^{o}C	
Dioscorea opposita Thunb.	3 g in 25 g deionized water	86.43	4271	584	1200	4886	Native	**[124]**
		85.59-87.61	3807-4805	286-375	743-1582	4238-6012	Fermented	
Yam starch	6% starch	86.40	1077.67	96.33	837.67	1819.00	6% yam native starch	**[53]**
		92.37	288.00	20.33	140.00	407.67	6% yam starch + 0.2 CMCS	
		92.12	310.00	18.00	153.67	445.33	6% yam starch + 0.4 CMCS	
		92.58	291.00	18.00	142.33	415.33	6% yam starch + 0.6 CMCS	
Elephant foot yam starch	2 g in 16.6 ml d.w.	77.20	5386	3217.5	2551.5	7420.5	Control	**[108]**
		50.08	29.72	11.77	9.59	27.54	20% CA	

		63.99	24.43	8.42	11.48	25.6	40 % CA	
		67.89	26.53	12.37	10.31	27.39	60 % CA	
		60.06	47.55	20.02	6.34	35.37	20% CA+US	
		73.54	31.46	7.74	7.72	27.08	40% CA+US	
		52.01	28.95	13.86	4.56	25.7	60% CA+US	
Dioscorea opposita Thunb.	2.5 g in 25 g d.w.	-	3843.0	1307.0	1964.0	4500.0	Native starch	**[129]**
		-	3032.0	787.0	591.0	2836.0	HMT starch	
		-	2770.0	702.0	1874.0	3942.0	ANN-starch	
		-	3320.0	502.0	879.0	3696.0	Native flour	
		-	89.0	9.0	71.0	151.0	HMT flour	
		-	1570.0	29.0	521.0	2062.0	ANN flour	
Dioscorea opposita Thunb.	2 g in 16.6 ml d.w.	69.17	1876.33	841.00	440.33	1476.00	Native	**[117]**
		69.31	1706.00	809.67	366.00	1262.33	1.79 kGy	
		69.05	1536.00	837.67	310.00	1008.33	6.06 kGy	
		69.22	1355.33	788.33	259.00	567.00	10.07 kGy	
		68.88	1094.33	675.67	216.33	418.67	14.97 kGy	
Dioscorea opposita Thunb.	3 g in 25 ml d.w.	85.78	4860	389	1254	5725	Expansion stage native starch	**[136]**
		86.43	4271	584	1200	4886	Dormant stage native starch	
		86.66	1269	522	141	889	Expansion stage resistance starch	
		87.64	1046	856	-6	184	Dormant resistance starch	

Dioscorea opposita Thumb.	3 g in 25 ml d.w.	84.4	6492.5	2433.0	1736.0	5770.0	Native starch	**[66]**
		83.7	6526.5	2331.0	1641.0	5752.0	Freeze-drying pretreatment	
		85.5	6485.5	1626.5	3339.5	8135.5	Hot-air drying pretreatment	
		83.9	6493.0	2083.0	3037	7949.0	Subcritical dimethyl ether dewaterization pretreatment	
Chinese yam (*Dioscorea spp.*)	2.5 g in 25 ml deionized water	ND	8.6	14	61	129	Fresh	**[30]**
		90.4	2337	91	400	2646	Hot air drying 40 °C for 48 h	
		90.0	2771	234	612	3149	Hot air drying 50 °C for 36 h	
		87.9	3468	679	529	3317	Hot air drying 60 °C for 28 h	
		86.8	5319	1162	1422	5579	Hot air drying 70 °C for 24 h	
		84.9	4706	494	1398	5610	Hot air drying 80 °C for 20 h	
		81.9	4236	1379	1122	3979	Microwave freeze drying	
		87.1	3721	841	744	3624	Ultrasonically enhanced air-drying	
Elephant foot yam	3.5 g in 25 ml d.w.	86.93	3396.00	1366.00	1044.35	3072.29	Native starch	**[113]**
		88.06	1704.14	474.15	831.17	2063.97	HMT-15 % moisture	
		89.62	1958.28	349.07	1049.20	2658.47	HMT-20 % moisture	
		89.62	2956.51	396.11	1840.51	4400.10	HMT-25 % moisture	
		90.12	2974.08	420.20	1900.08	4456.66	HMT-30 % moisture	
		91.32	2891.24	243.14	1864.24	4514.48	HMT-35 % moisture	

PT (peak temperature,°C), PV (peak viscosity, cP), BD (break- down, cP), SB (set back, cP), FV (final viscosity, cP)

Singh and Sharanagat [108] reported that the pasting properties of elephant foot yam starch were reduced with the citric acid (CA) treatment and CA + ultrasonication (US) treatment. However, no significant ($p < 0.05$) reduction was reported in the US, which implies that US treatment did not have an additional effect on the pasting properties of CA-modified starch. Overall, citric acid content had a negative correlation with the pasting properties of yam starch **[108]**, whereas a positive impact on pasting properties was observed for the blend of carboxymethyl chitosan and yam starch **[53]**.

Sukhija, Singh, and Riar [112] observed the pasting properties of oxidized and cross-linked elephant foot yam starch. They observed lowered final and setback values for oxidized starch which may be due to the conformational rearrangement and reordering of structure and also the introduction of carboxyl and carbonyl groups in oxidized starches. As a result, the pastes were less prone to re-association tendency leading to lowered final and setback values **[112]**. The cross-linked yam starch showed no significant change in pasting temperature as compared to the native one, however, a significant reduction in the peak, trough, breakdown, final, and setback viscosities were observed **[112]**.

2.4.6 Freeze thaw stability

It is noted that starch-rich regions are formed in the matrix when a starch gel is allowed to be frozen, and partially unfrozen water remains in the matrix **[21]**. The starch chains begin to associate themselves to form thick filaments due to high solid concentrations in the matrix, and a separate phase is formed by the water molecules that form ice crystals. This behavior of the starch gels contributes to syneresis, which is a critical parameter to determine the retrogradation tendency and stability of a gel system **[73, 128]**.

Freeze–thaw stability (% syneresis) of starch gels from twenty-six botanical sources for the 1st, 3rd, and 5th Freeze-Thaw Cycle (FTC) was reported by **Srichuwong et al. [110]**. It was observed that an increase in the FTC increased the degree of phase separation and syneresis due to starch retrogradation, and it varied with species. The stability of starch gels of water and elephant yam was lost after the 1st FTC and the degree of syneresis was higher than 60 %. There was a subsequent increase in syneresis levels along with an increase in the number of FTC, and the degree of syneresis also increased. The increase in syneresis may be linked to the high retrogradation tendency of starch gels, and the retrogradation tendency can be affected by various factors such as granular size, amylose content, amylose–lipid complex formation, and amylose and amylopectin chain length **[130]**.

Oliveira et al. [85] observed an opposite phenomenon in *Dioscorea alata* starch gel and reported a decrease in the exudation of water with the retrogradation process. These changes may be linked to the reassociation and recrystallization of amylopectin fractions present in starch molecules that prevents the exudation of water during thawing **[62]**. Therefore the results supported the use of yam starch in chilled and frozen food products due to the stability of yam starch against thermal oscillations and freeze-thaw cycles **[85]**.

The native starch gel from white yam (*Dioscorea rotundata)* showed an increase in the syneresis levels with the increase in the number of FTC **[61]**. However, hydroxypropylation of starch decreased the level of syneresis and prevented the exudation of water till the 4th FTC. An increase in the molar substitution also decreased the level of syneresis of the starch gels, and exudation of water was not observed till the 6th FTC.

2.4.7 Rheological properties

Rheological properties of starch are generally associated with the study of deformation and flow behaviors responding to stress. In the presence of water, starch pastes show viscoelastic behavior. Various rheological approaches such as static rheological properties, dynamic rheological properties, frequency sweep test, amplitude sweep test, etc. have been used to characterize the viscoelastic properties of native and modified yam starches to understand their properties better. Dynamic rheological properties of different yam starches were studied by a few researchers **[53, 66, 92, 135].** The storage modulus (G′) implies the solid (elastic) characteristics, which gives an idea about the amount of energy retained by the yam starch during deformation. In contrast, loss modulus (G″) indicates the viscous property of the samples during shear and measures the viscous nature of the yam starch **[15]**. **Table 2.6** presents the findings of the studies conducted by researchers to measure the rheological properties of yam starches.

Table 2.6: Rheological properties of yam starch

Species name	**Modification type**	**Test method**	**Starch conc.**	**Results/observations**	**Reference**
Yams (*Dioscorea opposita* Thunb.)	Octyl succinic anhydride yam starch; Acetylated yam starch; Granular cold water soluble (GCWS)	Steady shear rheological; Dynamic viscoelasticity	20 g in100 ml	• Except GCWS starch, all starches showed shear-thinning behavior. • The flow indices of starch pastes were less than 1.00, which indicates all samples were pseudoplastic fluids. • During heating, G′ of the three starch pastes (except GCWS starch) increased significantly at a certain temperature to a peak value, and then decreased with continuous heating.	**[92]**
Elephant foot yam (*Amorphophallus paeoniifolius*)	HMT	Dynamic rheological properties; Frequency and amplitude sweep tests	500 mg in 2 ml	• Increased the G′ for modified starches as compared to native one. • The frequency range the G' takes precedence over the loss modulus ($G' > G''$), and $\tan(\delta)$ was less than 1.	**[15]**

Yam starch	Carboxymethyl chitosan modified yam starch	Steady shear flow tests; Dynamic viscoelasticity	6%	• The consistency index reduced with the addition of carboxymethyl chitosan. • The *n* value of all starches was less than 1, which indicated that it was a pseudoplastic fluid. • The *G'* and *G"* of carboxymethyl chitosan modified yam starch increased with increasing angular frequency.	**[53]**
Chinese yam *(Dioscorea opposita Thumb.*)	Different drying treatment	Steady flow rheological	3 g in 25 ml	• All the starch pastes showed pseudoplastic behavior as *n* values between 0.19 and 0.46. • Apparent viscosity sharply decreased with increasing shear rate, which implies all of them had shear-thinning behavior.	**[66]**
Yam *(Dioscorea opposita Thunb*)	Nine different starches	Dynamic rheological properties	0.1 g / ml	• The rheological properties were related to the structural properties of starch. • *G'* and *G"* increased with the increase in frequency for all yam starch gels. • All the yam starch gels showed pseudoplastic behaviour	**[135]**

During the analysis, as the yam starch granules continue to swell at above onset temperature, the elastic modulus (*G′)* increases with temperature. Therefore, the increase in granular swelling occurs at a temperature above the onset temperature **[15]**. **Barua et al. [15]** studied dynamic rheological properties, frequency, and amplitude sweep tests of HMT-treated elephant yam. They reported an increase in G′ for modified starches as compared to native ones and *G′* took precedence over the loss modulus ($G' > G''$) and *tan (δ)* was less than 1 in the measured frequency range.

During HMT, branched amylopectin initiated interaction with the amylose chains which may be responsible for increase in the elasticity **[15]**. During the cooling process, yam starch molecules start to realign, and diffusion of moisture molecules within granules begins. As it cools, partial recrystallization of amylopectin takes place along with the partial formation of helices by amylose and forms a hard cross-linked gel **[15]**.

2.4.8 Digestibility

Digestibility of starch is closely associated with the diet and physiological function of the consumer’s body, and higher starch digestibility is associated with some adverse health conditions like diabetes and obesity **[135]**. Consumption of native yam starch immediately upsurges the blood glucose level, which can have serious health impacts on diabetes and obese patients. Considering this scenario, some kind of yam starch may require modifications for which methodologies like physical, chemical, or enzymatic treatments can be reviewed **[16]**.

Digestion of starch is an important phenomenon, which comprises of three important phases. The starch digested within 20 and 120 min of digestion is referred to as rapidly digestible starch (RDS) and slowly digestible starch (SDS), respectively. The resistant starch (RS) denotes the fractions of starch which is not digestible after 120 min of digestion **[16, 17]**. RS, which slows down starch digestibility, acts as a health-beneficial compound for diabetic and obese patients **[18]**.

Types of starch, amylose content, and short-range molecular order, which alter resistant starch content, play a crucial role in the digestion process **[16]**. Hydrothermal treatments directly influence the digestibility of starch by the formation of SDS and RS and reducing the RDS.

Table 2.7: *In vitro* digestibility of yam starch

Species name	**Starch type**	**RDS (%)**	**SDS (%)**	**RS (%)**	**Enzyme used**	**Reference**
Yams (*Dioscorea opposita* Thunb.)	Native starch (NS)	-	-	43.71	α-amylase and amyloglucosidase for 16 h at 37 °C	**[45]**
	Dual enzyme-treated starch	-	-	33.91		
	Cross-linked carboxymethyl starch	-	-	40.22		
Elephant foot yam (*Amorphophallus paeoniifolius)* starch	Native starch	60	10	30	Amyloglucosidase (35 U/mg, 1.1 mg/mL for each sample) and pancreatic α -amylase	**[16]**
	Oven heated HMT starch	15	30	55		
	Microwave HMT starch	45	15	40		
	Autoclave HMT starch	55	15	30		
Elephant foot yam	Native starch	59.63 (mg/g)	9.94 (mg/g)	29.88 (mg/g)	Amyloglucosidase (35 U/mg, 1.1 mg/mL for each sample) and pancreatic α -amylase	**[17]**
	Oven heated HMT starch	14.18 (mg/g)	29.92 (mg/g)	54.98 (mg/g)		
	Microwave HMT starch	49.91 (mg/g)	14.8 (mg/g)	40.37 (mg/g)		
	Autoclave HMT starch	44.01 (mg/g)	15.87 (mg/g)	39.20 (mg/g)		

Elephant foot yam (*Amorphophallus paeoniifolius*)	Native	59.30	9.13	30.65	Amyloglucosidase (35 U/mg) and pancreatic α-amylase (50 U/mg)	**[18]**
	Ultrasonicated	68.18	6.90	24		
	Ultrasonication pretreated autoclave with 15 min	51.11	15.06	32.91		
	Ultrasonication pretreated autoclave with 30 min	47.66	14.62	36.5		
	Ultrasonication pretreated autoclave with 45 min	46.22	13.73	39.13		
Yam starch	6% yam starch	26.01	26.55	47.44	Porcine pancreatic α-amylase (8 U /mL), Amyloglucosidase (1×10^6 U /mL)	**[53]**
	6% Yam starch + 0.2 CMCS	18.99	36.99	45.90		
	6% Yam starch + 0.4 CMCS	16.38	34.74	48.88		
	6% Yam starch + 0.6 CMCS	30.69	4.05	65.26		
Chinese yam (*Dioscorea opposita Thunb)*	Native starch	69.99	14.37	15.64	Amyloglucosidase (180 U/mL) and porcine pancreatic α-amylase (290 U/mL)	**[129]**
	HMT starch	62.04	17.89	20.07		
	ANN-starch	65.43	16.69	17.88		
	Native flour	67.69	15.43	16.88		
	HMT flour	59.57	19.16	21.28		
	ANN flour	64.46	17.14	18.40		
Purple yam flour	100 % wheat flour	23.1	42	34.9	Porcine pancreatic 1600 U α-amylase and 40 U amyloglucosidase	**[67]**
	90% wheat flour+10% purple yam	22.9	41.7	35.4		
	80% wheat flour+20% purple yam	21.6	39.8	38.6		

	70% wheat flour+30% purple yam	21.4	37.4	41.3		
	60% wheat flour+40% purple yam	20.6	36.5	42.9		
	50% wheat flour+50% purple yam	20.6	38.1	41.3		
Yam *(Dioscorea opposita Thunb)*	GY11	3.37	1.17	95.46	2000 u of porcine pancreatic _-amylase and glucoamylase	**[135]**
	GY5	0.25	4.35	95.40		
	GY2	1.05	3.48	95.48		
	GXPY	0.70	1.87	97.43		
	LCY	1.47	4.24	94.28		
	SFY	0.50	6.06	94.35		
	MPY	1.00	3.85	95.15		
	SYPY	0.81	5.30	93.90		
	ASY	0.19	6.71	93.10		
Chinese yams (*Dioscorea opposita*) flour	Air-drying	2.76	16.73	44.46	75 U porcine pancreatic α-amylase and 70 U amyloglucosidase	**[22]**
	Sulfur fumigation-drying	1.41	3.77	61.16		
	Hot air-drying	16.80	16.98	34.13		
	Freeze-drying	3.78	21.15	39.02		
	Microwave-drying	3.92	23.13	24.56		

Yu et al. [129] treated the Chinese yam flour using HMT treatment and they found significant inhibition of *in vitro* digestibility with SDS and RS contents increasing by 3.73 % and 4.40 %, respectively.

Other physical treatments like ultrasonication treatment are responsible for the disruption of starch's internal structure and reduction in granular integrity, which increases the susceptibility to enzymatic hydrolysis. Ultrasonication- autoclave treatment promoted the formation of short amylose crystals resulting in the formation of the highest RS fractions **[18]**. Chemical modifications also affect the digestibility of starch. When carboxymethyl chitosan was added at concentrations of 0.2 and 0.4 %, the RDS content of the modified yam starches decreased significantly while the SDS content increased **[53]**.

2.5 Modifications of yam starch

Starch is the main component of yam (65.2–76.6 % dry basis), which can be a good source of carbohydrates **[135]** and have applications in the diverse area of food processing sector. However, native starch shows some disadvantages such as low solubility in water, low shear resistance, higher retrogradation tendency, poor processability, lower mechanical strength, less process tolerance under higher shear forces, higher digestibility, high viscosity, low thermal stability, etc., which limits its application in the food industry **[15, 92, 113]**. To increase the industrial applicability of yam starch, modifications to improve the properties are required. Most commonly, three methods of modifications, viz., physical, chemical, and enzymatic are being employed to modify starches **[26]** due to their efficiency and cost-effective nature **[113],** but physical or chemical processes have been studied extensively **[39]**.

Generally, starch modifications are being performed to improve viscosity, processing parameters, shelf stability, textural properties, particle integrity, appearance, solubility, workability and emulsification properties, etc. **[33]** of starch granules and can act as better functional components in food, cosmetics and pharmaceutical industries **[113]**. Recently, a different study has been conducted to modify the properties of the yam starches such as the digestibility (resistant starch such as RS3, RS4) **[16, 45, 53]**, water and oil holding capacity **[33, 45, 112]**, a viscosity **[53, 92]**, textural characteristics **[92]**, solubility **[16, 17, 92]**, swelling properties **[17, 45, 92, 112]**, morphology **[15, 33, 59,**

112], foam stability **[33]**, emulsification properties **[33, 92]**, densities **[33],** flowability / flowing properties **[15, 33]**, particles size **[15, 108]**, etc.

Apart from the physicochemical properties, some researchers have performed the yam starch modification to develop new bioactive starches with biologically active functional properties **[45]** such as positive effects on hypolipidemic **[45]**; enhancing small intestinal peristalsis **[45]**; positive effect on glycemic index **[16]**; controlling cholesterol and improving the anti-oxidant activity [64]; hypoglycemic and lipid-lowering properties **[22, 23]**; immunomodulator **[46]**; reduce cyclophosphamide on gut microbiota **[47]**; bioaccessibility as well as the biological properties such as antioxidant activity, hypoglycemic activity, anti-angiotensin I-converting enzyme (ACE) or anti-acetylcholinesterase (AChE) **[38]**; and reduced anti-nutrient factors **[124]**.

2.5.1 Physical modifications

Physical modifications have received considerable attention because of their low cost, safety, effectiveness properties, nominal waste production, and non-toxicity. Physical modifications being a green technique (without chemical reagents) to enhance the functional properties of starch, it has gained wide industrial acceptance **[36]**. Various physical modifications (**Table 2.8**) such as pre-gelatinization, hydrothermal processes like heat-moisture treatment (HMT) and annealing (ANN), ultrasonication, high-pressure processing, micronization, milling, microwave, osmotic pressure, blanching, soaking, cooking, ionization irradiation, pulse electric field, etc. have been used for the modification of yam starches **[36, 38, 94, 117]**.

The combined effect of heat and moisture that helps in the alteration of starch properties is known as hydrothermal treatment, and the term ANN and HMT are coined together to describe the hydrothermal process of starch **[126]**. ANN is a starch modification process in which starch is treated with both water and heat for specified time intervals by controlling the temperature between the glass transition (above) and gelatinization temperature (below) **[126]** in sealed or unsealed containers **[33]**. In the HMT process starch granules with low moisture content (10 to 35 %) are heated above the gelatinization temperature (80–140 °C) for the time period ranging from 15 min to 16 h **[15, 36]** with different types of heating source such as hot air oven, autoclave, microwave, etc. **[15]**.

The effectiveness of the hydrothermal processes depends on the process parameters such as moisture content, temperature, heating time, heating source, mode of heating, and the starch properties like botanical source, cultivation area, structure, amylose/amylopectin ratio, composition, packing properties of the granules, etc **[36]**.

Several studies have been performed on ANN for physical modifications of various starch, where ANN was used for better yam starch yield, flow properties, solubility, emulsification properties, relative crystallinity, functional properties, etc. **[2, 33, 126]**. Similarly, ANN treatment has been performed for the modifications of different types of yam starch such as African yam bean **[2]**; white yam- *Dioscorea rotundata* Poir, water yam-*Dioscorea alata* L., yellow yam-*Dioscorea cayenensis* Lam, white bitter yam- *Dioscorea domentorum* Pax **[33]**; Chinese yam-*Dioscorea opposita Thunb.* **[129]**; etc. HMT is one of the most prominent and promising physical treatments for modifying the structure-function properties of yam starches **[16]**, and has been performed for different types of yam starches such as elephant foot yam **[15-17, 113]**; African yam bean **[2]**; Chinese yam **[129]**; etc.

ANN and HMT are the most commonly performed techniques that showed effectiveness in modifying starch properties such as particles aggregation, surface modification, reduced particles size, enhanced elasticity, relative crystallinity, water absorption capacity, pasting properties, gelatinization temperature, maintaining the molecular integrity of starch, enthalpy, etc **[2, 15-17, 33, 113, 129]**. Apart from the physicochemical properties, ANN and HMT modification are also used for lowering the glycemic index, decreasing starch digestibility, and improving other functional properties **[36]**.

Apart from the hydrothermal treatment, treatments use different drying systems such as air-drying, sulfur fumigation-drying, hot air-drying, microwave-drying, and freeze-drying; and other treatments like ultrasonication, high-pressure processing, autoclave, blanching, cooking, soaking, electron-beam-irradiation has also been studied by researchers **[18, 22, 30, 66, 117]**.

Barua et al. [18] modified yam starch by treatment with ultrasonication and ultrasonication pretreated autoclaving. They reported the enhancement of water absorption capacity, swelling power, solubility, and also the resistant starch fractions of yam starch. Electron-beam-irradiation treatment was studied by **Wang et al. [117]** which reported a significant increase in the solubility and light transmission of yam flour. Ionizing irradiation treatment can increase the nutritional value and active ingredients of yam flour in a relatively short period **[117]**.

Drying treatment also plays a significant role in the properties of yam starch. Common methods followed for drying yams are air-drying, sulphur fumigation, freeze-drying, hot-air drying, microwave drying, and ultrasonically hot air drying **[22, 30, 66]**. Various drying treatments can cause changes in molecular structure resulting in changes in various functional properties such as solubility, swelling properties, gelatinization characteristics, pasting properties, rheological properties, and morphological properties, which makes the modified yam starch suitable for industrial application **[66]**. **Chen et al. [22]** observed that among all the flours dried by different drying techniques, freeze-dried yam flour showed potential scope for the development of lipid-lowering and hypoglycemic functional foods.

Cooking was also found to have a significant role in yam starch modification. **Gong et al. [38]** investigated the effect of different cooking methods which included normal pressure steaming, high-pressure steaming, normal-pressure boiling, high-pressure boiling, stir-frying in a wok, and microwaving on the properties of Chinese yam **[38]**. The authors reported an effect on the bioaccessibility of the bioactive components, and a significant loss of total soluble phenolic compounds and diosgenin content.

Quayson et al. [94] studied the effect of blanching and soaking on three varieties of yam from Ghana, and found a significant decrease in the non-enzymatic browning intensities for pre-soaked fried yam-KM and roasted yam-RKD, and the reducing power was also affected.

The effects of ultra-high pressure (UHP) treatment on the properties of starch have also been studied. UHP treatments, which are largely dependent on the magnitude of pressure and sources of starch, can modify the structure of starch granules and alter the functional properties **[121]**. **Wang et al. [121]** modified the pasting properties of yam starches by treating them with ANN and ultrahigh pressure.

Table 2.8: Physical modification of yam starch

Species name	**Physical modification type**	**Results/observations**	**References**
		Hydrothermal	
African yam bean (*Sphenostylis stenocarpa*) starch	Hydrothermal treatment ANN at 50 °C for 24 h incubation HMT at 100 °C for 16 h	Hydrothermal modifications increased the pasting temperature, water absorption capacity but reduced the solubility and swelling capacity.	**[2]**
White yam- *Dioscorea rotundata* Poir; Water yam-*Dioscorea alata* L.; yellow yam-*Dioscorea cayenensis* Lam; White bitter yam-*Dioscorea domentorum* Pax	ANN modification (1:2 w/v) heated at 50 °C for 24 h in sealed containers	Annealing increased the yield of all starches. Annealed yam starches showed better foam stability than citric modified and acid hydrolysed yam starches.	**[33]**
Elephant foot yam (*Amorphophallus paeoniifolius*)	HMT	Heat capacity increased with HMT. Modified starch granules exhibited higher gelatinization temperatures and lower gelatinization enthalpy.	**[113]**
Elephant foot yam starch (*Amorphophallus paeoniifolius*)	Hydrothermally modified Hot air oven, autoclave, and microwave treatments	Modification increases the resistant starch with significant increment of SDS content and reduction of RDS content.	**[17]**

Elephant foot yam starch (*Amorphophallus paeoniifolius*)	Hydrothermal treatment Hot air oven, microwave, and autoclave	Modified starch showed the lowest glycemic index, making it ideal for forming diabetic-friendly food products.	**[16]**
Chinese yam (*Dioscorea opposita Thunb.)*	HMT and ANN	Both HMT and ANN caused an increase of the gelatinization temperatures and a decrease of enthalpy.	**[129]**
Elephant foot yam starch (*Amorphophallus paeoniifolius*)	Hydrothermally modified Hot air oven, autoclave, and microwave treated	HMT increased the particle aggregations, surface roughness, particle size, higher presence of short amylopectin fractions. Increase in the elastic moduli after modification. An increase in gelatinization temperature.	**[15]**
Irradiation			
Yam (*Dioscorea opposita Thunb*.) flour	Electron-beam-irradiation	Significant increase in the solubility and light transmission of flour, but a significant decrease in the paste ability and swelling.	**[117]**
Drying and Blanching			
Chinese yams (*Dioscorea opposita*) flour	Drying -Air-drying, Sulfur fumigation-drying, Hot air-drying, Freeze-drying, Microwave-drying	Freeze dried yam showed as a potential source of hypoglycemic and lipid-lowering functional foods.	**[22]**

Fresh Chinese yam (*Dioscorea opposita)*	Blanching followed by drying	The protein and soluble amylose contents, solubility and swelling power of the blanching yams were lower than without blanching.	**[23]**
Chinese yam *(Dioscorea spp.)*	Drying treatments – hot air-drying, microwave freeze drying and ultrasonically enhanced hot air-drying)	Microwave freeze drying resulted in the greatest amylopectin degradation. Structural modifications with lower gelatinization temperatures, less enthalpy changes, increased pasting viscosities, higher starch digestion rate and digestibility after drying.	**[30]**
Ultrasonication			
Elephant foot yam starch (*Amorphophallus paeoniifolius*)	Ultrasonication (US) and US pretreated autoclave (AL) modified starch	Both the treatments enhanced the water absorption, swelling power, and solubility of yam starch. US-assisted AL treatment enhanced the resistant starch.	**[18]**
Yam tubers (*Dioscorea alata*) starch	Ultrasonication	Developed starch nanoparticles with thermally stable particles.	**[72]**
High pressure processing			
Yam starch	ANN and ultrahigh pressure	Dual modifications altered the pasting properties of starches, but had little effect on granular structures of starches.	**[121]**

	Cooking		
Yam (*Dioscorea opposite Thunb*)	Cooking methods (Normal pressure steaming , High-pressure steaming , Normal pressure boiling , High-pressure boiling , Stir-frying in a wok and microwaving	Cooking caused significant losses of total soluble phenolic compounds and diosgenin content but no changes in the allantoin content. The cooking methods affected the bioaccessibility of the bioactive components differently.	**[38]**
	Blanching and soaking		
Yam cultivars (KM, RKD and SO89)	Blanching and soaking	Pre-soaked fried KM and roasted RKD showed a significant decrease in non-enzymatic browning intensities. Reducing power was affected by the different pre-treatment and dry-cooking methods.	**[94]**

2.5.2 Chemical modifications

Chemical modification of polysaccharides includes modifications such as acetylation, phosphorylation, selenide, sulfated, carboxymethylation, etc. **[46]**; and chemical methods such as esterification, crosslinking, etherification, etc. can be used to modify yam starches **[92]**.

Sulfated polysaccharides, which contain sulfate groups on sugar units of the polysaccharides, include natural and synthetic sulfated polysaccharides based on the sulfated origin **[46, 47]**. A large number of studies have reported the biological importance of sulfated polysaccharides. For example, chlorosulfonic acid added for the production of sulfated Chinese yam polysaccharides enhanced the immunomodulatory activity of splenic lymphocytes **[46]**. **Huang et al. [47]** reported an increased digestive enzyme activity of colon contents and restored production of short-chain fatty acids in mice by using the sulfated derivatives of yam polysaccharide. Recently, synthetic sulfated polysaccharides have gained attention as they have the potential to be used for immunity enhancing, anti-inflammation, anti-tumor, and anti-oxidant activities **[46]**.

Octenyl succinic anhydride (OSA) is extensively used as an etherifying agent in yam starch modification. In OSA modification, a certain amount of yam starch suspension at a specified alkaline pH condition is treated with OSA solution for some specified time intervals followed by creating a slightly acidic condition using HCl solution **[92]**. After modification with OSA, the starch gains new physicochemical properties with excellent emulsifying properties due to the introduction of bi-functional groups (both hydrophilic and hydrophobic) **[92]**.

Oxidation of yam starch is one of the chemical modification techniques in which yam starches are oxidized using oxidizing agents such as sodium hypochlorite, calcium hypochlorite, hydrogen peroxide, ozone, TEMPO-mediated oxidation, etc. In the commercial process, starch is oxidized by using sodium hypochlorite as an oxidizing agent **[112]**.

Cross-linking is another commonly used modification method in which intra and intermolecular bonds are introduced at random positions of yam starch molecules, which strengthens the yam starch granules, improves the resistance to acid, heat, and shearing force, and also reduces the solubility and rupture properties. Commonly, sodium trimetaphosphate, sodium tripolyphosphate, epichlorohydrin, phosphoryl chloride, a mixture of adipic acid and acetic anhydride, and vinyl chloride are used as cross-linking agents **[112]**. **Sukhija, Singh, and Riar [112]** used sodium hypochlorite and sodium trimetaphosphate to develop chemically modified oxidized, cross-linked, and dual-modified starches (i.e. oxidized cross-linked and cross-linked oxidized yam starches), which resulted in improvement in paste clarity, solubility, pasting, and thermal characteristics without having any adverse effect on the surface structure of starch granules. Carboxymethyl-based cross-linked yam starch was used to develop hydrophilic groups incorporated starch with significant anti-hyperlipidemia activity **[45]**. Chemically modified oxidized, cross-linked, and dual (oxidized-cross-linked) starches were also used for the development of biodegradable film **[76]**.

Acid hydrolysis has been done extensively in the food processing sector to modify yam starches. Commercially, acid-modified starches are produced by hydrolyzing the yam starches with sulfuric or hydrochloric acid for a specified period at a temperature below the gelatinization temperatures of the starches **[81]**. The efficiency of acid hydrolysis depends on the acidity of the medium, starch types, duration of hydrolysis, and process temperature **[81]**. Cleavage of glucosidic bonds that are present between the monomeric units takes place during the acid hydrolysis of starch to yield the reducing sugar end group (d-glucose) of the starch **[81]**. **Falade and Ayetigbo [33]** performed acid hydrolysis of yam starch by suspending 300 g (dry basis) of native starch in 600 mL of 6 % (w/v) HCl solution at 27 ± 2 °C for 192 h without stirring. The acid modification changes the physicochemical properties of the starches without destroying their granule structure, thereby, yielding starch with increased solubility and gel strength, and decreased viscosity **[81]**.

Acetylated starch is an esterified starch produced by treating starch with acetic acid, which introduces a new CH_3CO group in the starch under some specified reaction conditions. Granular cold water soluble starch is another kind of chemically modified starch that is developed by treating starch with alcohol and alkali to improve the solubility of native starch in cold water **[92]**. **Qian et al. [92]** developed chemically modified starches such as Octyl succinic anhydride yam starch, acetylated yam starch, and granular cold water soluble (GCWS).

Table 2.9: Chemical modification of yam starch

Chemical modification type	**Species name**	**Results/observations**	**References**
Carboxymethyl	Chinese yam starch *D. opposite Thunb.*	Increase of the ratio of NaOH/anhydroglucose unit.	**[125]**
Acid hydrolysis (6% w/v)	White yam – *Dioscorea rotundata L*. water yam – *D. alata L*	Improved the disintegrant efficiency of the yam starches. Tablets containing starches incorporated extragranularly showed faster disintegration and lower tensile than incorporated intragranularly.	**[81]**
Acid hydrolysis (300 g of native starch in 600 ml of 6% w/v HCl solution at 27 °C for 192 h)	*Dioscorea rotundata* Poir; *Dioscorea alata* L.; *Dioscorea cayenensis* Lam; *Dioscorea domentorum* Pax	Loose and packed bulk densities and CIE *L** of modified starch increased significantly. Chemical modifications caused etching, fragmentation and roughening of some granules' edge	**[33]**
Cross-linked (Carboxymethyl starch yam starch suspension with NaOH at pH=11, followed by Na_2SO_4 and 2 ml of epichlorohydrin and 10 g monochloroacetic acid)	Chinese yam -(*Dioscorea opposita Thunb*.)	Modified starch increased the hydrophilic groups, with higher water-holding capacity, swelling power and paste clarity, with significantly anti-hyperlipidemia activity.	**[45]**

Oxidized, cross-linked and dual modified starches using sodium hypochlorite and sodium trimetaphosphate	Elephant foot yam (*Amorphophallus paeoniifolius*) starch	Resulted an improvement in paste clarity, solubility, pasting, thermal characteristics without having any adverse effect on the surface structure of starch granules	**[112]**
Palmitic acid	Yam (*Dioscorea pposita Thunb.)*	Palmitic acid-yam starch complex exhibited significant antioxidant activity and bile acid binding capacity with higher ability of controlling cholesterol and improving the anti-oxidant activity than native yam	**[64]**
Octyl succinic anhydride (OSA) yam starch, Acetylated yam starch, Granular cold water soluble (GCWS)	Yams (*Dioscorea opposita* Thunb.)	OSA and acetylated starch showed higher viscosity and thixotropy with better gel textural properties than native one, whereas GCWS starch showed higher solubility and swelling power. Enhanced the solubility and swelling properties of modified starch	**[92]**
Sulfated polysaccharide by chlorosulfonic acid-pyridine method	Chinese yam polysaccharide	Sulfated Chinese yam polysaccharide enhanced the immunomodulatory activity on splenic lymphocytes	**[46]**
Subcritical dimethyl ether dewaterization pretreatment	Chinese yam *(Dioscorea opposita Thumb.)*	Treated starch showed relatively lower color values, solubility, swelling power than native one	**[66]**
Sulfated derivatives yam polysaccharide	Yam polysaccharide	Modified starches increased the digestive enzyme activities of colon contents and restore the production of short-chain fatty acids in mice that were decreased by cyclophosphamide treatment.	**[47]**

Citric acid-modified starch was studied by **Falade and Ayetigbo [33],** and palmitic acid-yam starch complex, which exhibited significant antioxidant activity and bile acid binding capacity with a higher ability to control cholesterol and improve the anti-oxidant activity was studied by **Li et al. [64]**. **Ji et al. [53]** developed carboxymethyl chitosan-based modified starch for better digestibility.

2.6 Applications

Native yam starches have various application potentials in food processing sectors (**Table 2.10**). For example, due to the high proportion of amylopectin in yam starch, it can be used in crispy foods, salad dressings, and ready-made desserts **[135]**.

Yam starch-based food products with high nutritional values and low digestibility can be obtained by using various physical modifications such as HMT and ANN, and chemical modifications to modify starch, and can be a promising substrate in bakeries. Modified yam starch can be also used in various food products such as food concentrates, sauces, confectioneries, dairy, and brewed food products with enhanced nutritional quality, which makes the products more convenient for consumption by diabetes and obese patients **[17]**. Chemically modified starch such as cross-linked starch which has higher stability against swelling, high temperature, and high shear, can be used as a texturizer in sauces, soup, and gravy. Esterified starch such as OSA starch can be used as an emulsion stabilizer and thickener **[108]**.

Perez et al. [90] investigated the effect of two different types of starches “hawthorn” yam (*Dioscorea rotundata*) and “creole” yam (*Dioscorea alata*) on physicochemical and sensory properties of stirred-type yogurt. They have reported that yogurt with yam starch showed less syneresis (13.38 %) than yogurts developed with pectin. Finally, they concluded that yam starch could be used as a stabilizer, which can improve the physicochemical, sensory, and rheological characteristics of yogurt **[90]**.

Apart from the use of yam starch as food ingredients, they can be used to develop biodegradable edible films. Chemically modified (oxidized, cross-linked, and dual: oxidized and cross-linked) yam starches were used for the development of biodegradable film, which showed significant results on the film properties **[76]**.

Table 2.10: Applications of yam starch

Species	**Form**	**Use**	**Major Findings**	**References**
D. rotundata	Native	Pasta	Dietary fiber rich starch pasta with addition of brewers spent grain was produced by extrusion using a single-screw extruder.	**[109]**
D. trifida	Native and cross-linked	Edible film	Films made from native and cross-linked starches with glycerol addition had different thickness, color, deformation, and stress to puncture whereas cross-linked starch-based film had higher width and opalescence than that of native starch.	**[89]**
D. alata *D. rotundata*	Acid-thinned	Tablet formulation	The higher disintegrant efficiency of acid-thinned starch than native and corn starches is useful in paracetamol tablet formulation	**[81]**
D. oppositifolia	Acid-thinned	Tablet formulation	Acid-modified starch may be useful as tablet binders when fast dissolution and high bond strength are needed.	**[84]**
D. dumetorum	Native	Cosmetics and textile industry	They can be used as stabilizers in baking powder, aerosols, face powder, or dusting powder in cosmetic and textile industry because of its fine granule size distribution which provides required texture to the products	**[87]**

D. dumetorum	Native	Fat replacer, Stabilizer	The small granules of starches exhibit fat mimetic properties which produces textures desirable in frozen desserts, cookies and other low-fat and fat-free food formulations.	**[87]**
D. cayenensis-rotundata	Native	Pharmaceuticals	Disintegration of yam starch compacts was found faster than those of potato starch and its potential as thickening agent comparable to maize. Thus it is concluded that yam starch could be used as a pharmaceutical excipient.	**[137]**
D. rotundata, D. bulbifera	Native	Food applications	Highly swelling starches can be used as thickeners, binders and gelling agents in products such as jams and jellies, and in foods that require elasticity. It can be used for products that require aging, such as noodle soup and sauce.	**[87]**
Dioscorea alata L.	Native	Food industry	The yam starch exhibited a high whitish color, characteristic recommended for use in ice cream, concentrated juices, and sweets and could replace corn starch. Due to lower gelatinization temperature and good thermal stability against freezing and thawing cycles it can be applied to crunchy foods, salad dressings, and ready-made desserts, in addition to foods that require high processing temperatures, such as canned foods.	**[85]**

D. trifida	Native	Biodegradable films/ Coatings	The starch showed good physical properties to be used as a matrix for edible films. Films of blended purple yam starch, chitosan, and glycerol were developed and characterized, which indicated that it improved the shelf-life of apples when applied for 4 weeks and it could be a feasible coating to food products	**[27]**
D. trifida	Phosphate-modified starch	Edible packaging films	The physicochemical properties estimated in this study determine the high potential of biodegradable films as packaging materials in the food industry, considering the characteristics of the product to be packaged and the packaging requirements. Yam starch-based materials are also recommended for coatings where greater resistance is required.	**[41]**

Cheng et al. [25] developed essential oil and yam starch-based active antibacterial films, which could have potential applications as an active packaging film to extend the shelf life of food. A blend of purple yam starch, chitosan, and glycerol was used to develop biodegradable films, which were able to preserve the quality of apples for 4 weeks **[27]**. These results have shown great prospects for yam starch (both native and modified) in the food packaging industry as a new biodegradable coating.

Due to the fat mimetic properties exhibited by the small granule size of *D. dumetorum* compared with other species, it could find application as fat replacers (carbohydrate-based fat replacers) in foods and can produce texture desirable in frozen desserts, cookies, and other low-fat and fat-free food formulations. They can also be used as stabilizers in baking powder, aerosols, face powder, or dusting powder in the cosmetic and textile industries. Yam starches with high swelling capacity (*D. rotundata*, *D. bulbifera*) can be used as thickeners, binders, and gelling agents in foods. Retrogradation and syneresis tendency of the starches will be a disadvantage in frozen products but they can be utilized in products where retrogradation is the desired quality, e.g noodles, soups, and sauces. Diverse gelation properties of the starches could be used advantageously in different food applications, for example, those with high gelling ability could be used in foods such as jams and jellies and in foods where elasticity is desired **[87]**.

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