RHEOLOGICAL AND FUNCTIONAL PROPERTIES OF POTATO AND SWEET POTATO FLOUR AND EVALUATION OF ITS APPLICATION IN SOME SELECTED FOOD PRODUCTS

THESIS

SUBMITTED TO THE UNIVERSITY OF MYSORE, MYSORE

for the degree of

DOCTOR OF PHILOSOPHY

in

FOOD TECHNOLOGY

BY

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DECEMBER 2005
ACKNOWLEDGEMENTS

I express my sincere thanks and indebtedness to Dr. R.S. Ramteke for his guidance and constant support during the course of this investigation.

I am very grateful to Dr. V. Prakash, Director, C.F.T.R.I, for permitting me to carry out the work and submit the same in the form of thesis. I am thankful to him for his critical comments and valuable suggestions during course of this study.

I thank Dr. S. Rajarathnam, Head, Dept. of Fruit and Vegetable Technology and Dr. W.E. Eipeson and Dr. K.V.R. Ramana former Heads of the Dept. of Fruit and Vegetable Technology for their cooperation and encouragement.

With deep sense of gratitude I express my sincere thanks to Dr. R.N. Tharanathan, Additional Director, Department of Biochemistry and Nutrition, for the help rendered throughout the investigation, with his critical and invaluable suggestions. I am highly thankful to Dr. Manisha Guha, Department of Grain Science and Technology, Dr. S. Yella Reddy, Department of Lipid Science and Traditional Foods, Dr. S. Mahadevamma, Department of Biochemistry and Nutrition for their help during the course of this study. I thank Dr. K. Ragottama and Dr. S. Subramanian of Indian Institute of Science, Bangalore for helping me in carrying out X-ray diffraction and NMR studies. The help rendered by the staff, Central Instrumentation Facility and Services, for SEM, FT-IR, TPA and Colour measurement studies is sincerely acknowledged.

I am very much grateful to my colleagues Mr. A.S. Chauhan and Mrs. M.N. Rekha for their unstint support and cooperation. I also thank all the staff members of Dept. of Fruit and Vegetable Technology, who have helped me in some way or the other during the course of this study.
I would like to express my gratitude to my parents and my elder brother Murali Krishna, Assistant Divisional Engineer, State Electricity Board, Govt. of Andhra Pradesh for their constant support and encouragement. I am thankful to my wife Rupa for her patience, moral support and cooperation and my children Rajashekar and Rithvik who have adjusted themselves well despite my long hours stay in the laboratory.
Dedicated To

My Parents and Family Members
DECLARATION

I declare that the thesis entitled RHEOLOGICAL AND FUNCTIONAL PROPERTIES OF POTATO AND SWEET POTATO FLOUR AND EVALUATION OF ITS APPLICATION IN SOME SELECTED FOOD PRODUCTS submitted to the University of Mysore, Mysore, for the award of degree of DOCTOR OF PHILOSOPHY IN FOOD TECHNOLOGY is the result of work carried out by me under the guidance of Dr. R.S. RAMTEKE, Deputy Director, Department of Fruit and Vegetable Technology, CFTRI Mysore, during the period 2000-2005.

I further declare that the results of this work have not been submitted for the award of any other degree or fellowship.

Mysore
December 2005

(RAMESH YADAV AVULA)
ABBREVIATIONS AND SYMBOLS

% Percentage
θ Theta
°C Degree Celsius
ΔH Enthalpy
µl Microliter
~ Approximately
C Concentration
Dil Dilute
G gram
h Hours
DA Dalton
Mg Milligram
min Minutes
ml Milliliter
MW Molecular weight
Nm Nanometer
OD Optical density
rpm Revolutions per minute
RT Room temperature
Sec Seconds
TR Retention time
Ve / V0 Elution volume / Void volume
W Weight
w / v Weight / Volume
w / w Weight / Weight
Am Amylose
Ap Amylopectin
Glc Glucose
DF Dietary fiber
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP</td>
<td>Degree of polymerization</td>
</tr>
<tr>
<td>RS</td>
<td>Resistant starch</td>
</tr>
<tr>
<td>HD</td>
<td>Hot air dried</td>
</tr>
<tr>
<td>DD</td>
<td>Drum dried</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulphoxide</td>
</tr>
<tr>
<td>DNS</td>
<td>Dinitrosalicylic acid</td>
</tr>
<tr>
<td>TGO</td>
<td>Tris glucose oxidase</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>FT - IR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SD</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>SE</td>
<td>Standard error</td>
</tr>
</tbody>
</table>
Potato (*Solanum tuberosum* L) is a nourishing food that has sustained civilizations for centuries in South America and Europe. Potato production has significantly increased in recent years in many countries, particularly Asia where it has become more important as a food and industrial crop. In terms of the number of producing countries, potato is second only to maize. About one half of the world's potato production is being used as human food. Though India is the third largest producer in the world after China and Russian Federation, the per capita consumption of potato is only 14.8 kg/year. Over the past decades, there has been a steady increase in potato production in India, accompanied by unsteady markets frequently resulting in peak harvest gluts. India produced 25 million tonnes of potatoes during 2004-05. This record production has led to several post harvest problems, storage being the major one. Increasing potato production with inadequate, expensive and unevenly distributed refrigerated storage facilities in the country has resulted in frequent gluts in the market causing economic loss to the farmers and wastage of precious foods.

In developing countries like India, people are traditionally dependent upon cereals and are generally unaware of the nutritional value of potatoes. Therefore, it is essential that potato consumption is increased to sustain this increase in production and to ensure remunerative prices to the farmers as well. Under the existing circumstances, processing of the bulky perishable potatoes into various processed products is a viable option which can help extend the storage life, solve the storage problem, cater to the consumer preference belonging to different age groups and social strata and serve as a means to increase the supply in off seasons thus maximizing potato utilization.
Sweet potato (*Ipomoea batatas* L. Lam) is a nutritive vegetable, being an excellent source of vitamin A precursor, certain other vitamins and minerals, energy, dietary fiber and some protein. Sweet potato consists of about 70% carbohydrates (dry basis) of which a major portion is starch, which can be utilized as a functional ingredient in certain food preparations. For example, controlling the rate of heating during cooking activates endogenous amylolytic enzymes leading to conversion of a portion of starch to dextrins, which as an adhesive material could function as a binding agent in food products. India produces about 1 million tonnes of sweet potatoes in a year, most of which are consumed fresh. In spite of the fact that it is cheaper than other crops, this abundant resource is, however, still poorly utilized.

Processing of potato into flour is perhaps the most satisfactory method of creating a product that is not only functionally adequate, but also remain for an extended period without spoilage. Incorporation of potato flour into various products is reported. Different products can be prepared by incorporating potato flour with other flours using different methods of cooking such as baking, roasting, steaming, boiling and deep fat frying. Potato flour is used by baking industry and is incorporated in the baking of bread to retain its freshness. It also imparts a distinctive, pleasing flavour and improves toasting qualities. It can be used advantageously in crackers, pastries, yeast raised doughnuts, cake and cake mixes.

The dried and ground sweet potato is used as a supplement in puddings, gruel, etc. Starch manufacture is the main industrial utilization of sweet potatoes which has been used in the preparation of noodles, bakery foods, snack foods, confectionery products and for alcohol production and in brewing industries.

The functional properties of the flour are provided not only by the starch but also by other flour components. The limited data for flour functional properties are different from those of starch since extra constituents available in flour (non-
starch carbohydrates, protein, fat, etc.), restrict access of water into the starch granules. For eg. most of the pasting viscosities of flour were not correlated to that of purified starch.

In view of the increasing utilization of potato and sweet potato in composite flours for various food formulations, their functional properties are assuming greater significance. Such properties of plant foods are determined by the molecular composition and structure of the individual components and their interactions with one another. Modified / speciality flours in snack foods serve as functional ingredients, contributing to desirable attributes such as increased expansion, improved crispness, reduced oil pickup, and better overall eating quality. Starch-based coatings and adhesives can replace fat or oil in low fat baked snacks, while resistant starch provides high fiber nutritional claims for snack foods.

Several basic properties of flours of concern to food processors such as heat, shear and acid stability are improved by starch modification. Either one or combination of these characteristics is required in most food processes where the properties of unmodified starch are insufficient. Flour is prepared by dehydration methods such as drum drying. However, the properties of such flours were not reported to decide their suitability for specific product development. Acetylated starches are used by food industry because of the unique characteristics imparted by acetylation such as low gelatinization temperature, high swelling and solubility, and good cooking and storage stability. Enzyme treated flour though tend to show changes in its properties due to the breakdown of starch as a result of enzyme action, the functional and rheological properties of such flours were not studied earlier. Thus, information on the properties of processed, acetylated and enzymatically modified potato and sweet potato flours is scanty and is mostly related to the starches. Hence, the present investigation on modified flour from potato and sweet potato was undertaken and
the results obtained are consolidated in the form of a thesis having the following layout.

CHAPTER I presents a **General Introduction** of the subject with special reference to production, utilization, processing methods, modifications to change the nature of starch, viz. the functional properties (gelatinization, retrogradation and thermograms) and rheological properties (pasting viscosities) and usefulness. Finally the scope of the present investigation is also included.

CHAPTER II describes the **Materials and Methods** used in the present study. Detailed methodology of each of the experiment is given with procedures and data computation.

CHAPTER III, which is the major chapter, describes the **Results and Discussion** of the work carried out in this investigation.

Potato contained slightly more of starch and protein, whereas sweet potato contained, in addition more of fiber content. Potato and sweet potato flours were developed by drum drying and hot air drying methods. Addition of sulphur dioxide and subjecting to heat treatment during processing, arrested browning reactions whereby the resulting flours were more brighter compared to native flours. Acetylation of potato and sweet potato flours by acetic anhydride in the presence of NaHCO₃ as well as the process conditions, viz. incubation time, temperature and enzyme concentration, for enzyme modification by glucoamylase were standardized.

Scanning electron microscopic studies of native and treated potato and sweet potato flour samples showed that the starch granules were smooth, oval or spherical or irregularly shaped. Processing resulted in disappearance of granular surface and effected agglomeration of granules that formed into an aggregated mass comprising of several small granules. The acetylated flour samples
showed indentations of the granules, whereby the granules appeared as clusters / bunches. The penetration of glucoamylase was found to be more in sweet potato samples which was also evident by the release of more amount of reducing sugars as a result of breakdown of starch by glucoamylase.

Fractionation studies of potato and sweet potato flour samples by gel permeation chromatography on Sepharose CL 2B column showed considerable molecular degradation of starch in the modified samples.

The infrared spectra of starches of flour samples that originate mainly from the vibrational modes of amylose and amylopectin reflected the changes in molecular structure. Characteristic peaks appeared in the fingerprint region of the spectrum of native samples. Studies indicated the gelatinization of drum dried and hot air dried samples. The spectra of acetylated flour samples showed evidence of acetylation by the presence of the ester carbonyl group stretch at 1731 cm\(^{-1}\) (C=O). The shift in hydroxyl stretching band was observed in the enzyme modified samples as a result of modification.

Native flour samples of potato and sweet potato showed pasting curves, with very high peak, hot paste and cold paste viscosities. But the processed samples manifested low initial amyllograph viscosities, as they were already modified to a great extent as a result of processing. The paste viscosities of hot air dried sweet potato flour were found to be much lower than that of drum dried samples due to the further breakdown of its starch by the action of endogenous thermostable amylases. The high stability of drum dried and hot air dried samples during heating and cooling processes, demonstrates that these samples have possible uses in products requiring sterilization, such as baby food.

The acetylated potato and sweet potato flour samples showed least paste viscosities exhibiting restricted swelling of starch granules, due to the presence of substituent functional groups that weakened the associative forces. The
tendency of resistance to retrogradation of enzyme modified sweet potato flour samples was indicated by low setback viscosity.

The pasting viscosities of isolated starches from native and processed flour samples showed that the extra constituents available in flour restricted the access of water into the starch granules. Hence, the RVA pasting viscosities of isolated starches were much higher than that of flour.

The texture profile analysis of potato and sweet potato dough showed that the dough rheology was influenced by processing conditions, type of modification and moisture content. Among the modified samples, drum dried samples were more hard, springy, gummy and chewy, whereas the hot air dried samples were less cohesive, springy, gummy and chewy.

Thermal characteristics of flour samples, as measured by differential scanning calorimetry, revealed a broad endothermic transition temperature for both potato and sweet potato. X-ray diffraction studies showed that the native potato and sweet potato samples were characteristic of B-type and Ca, respectively, whereas the processed samples showed V-type diffraction patterns. $^{13}$C NMR spectral data corroborated with the linear α-1,4 glucan nature of these starches. The reduction in intensity of peaks was attributed to loss of crystallinity and debranching of the starch polymer.

Resistant starch (RS) levels of processed flour samples increased and it was more in the case of drum dried samples. Correlation between insoluble dietary fiber (IDF) and RS supported the idea that RS has contributed to the observed increment in the IDF fraction.

The effect of temperature on swelling power of differently processed potato and sweet potato flours indicated differences in the molecular organization within their starch granules; drum dried samples showing higher and acetylated
and enzyme modified samples showing lower swelling power. The higher solubility of drum dried samples could be attributed to a higher degree of macromolecular disorganization. Though acetylated and enzyme modified samples showed increase in their solubility with increase in temperature, the values obtained for them were found to be much lower than that of native flour. The enormous differences among the modified flour samples in their swelling and solubility patterns can thus form the basis for the functional properties that determine their suitability in product development.

Higher sediment volume of the processed samples was an indication of a greater degree of gelatinization of drum dried and hot air dried samples. The gel consistency of the samples which is proportional to the hydration power and sediment volume of the flour, was found to be higher in processed samples, more so in drum dried samples. The enzyme modified flour of sweet potato with highest cold paste viscosity among the treated samples, exhibited lowest gel consistency values. Excepting acetylated flour samples, the gel consistency of other modified flour samples of potato and sweet potato were correlated with their cold paste viscosities.

Both in their native as well as modified forms, sweet potato flour was better digested with glucoamylase than potato flour. The enzyme digestibility of the latter was improved by processing which involved cooking and high temperature drying, that led to gelatinization of starch and subsequent changes in its crystallinity. The acetylated flours showed poor digestibility indicating the influence of substituent groups on starch digestibility. The changes brought about by enzyme action facilitated better digestibility of enzyme modified flours.

The salient features deduced from this study are listed as Summary and Conclusion in CHAPTER IV. In brief, it may be concluded that structural, rheological and functional properties of modified potato / sweet potato flour were dependent on type of modification. The high stability of drum dried and hot air dried flours during heating and cooling processes, demonstrates their possible use in products requiring sterilization such as baby food. The flours showing low paste viscosities, i.e, physically treated and acetylated flours may be used in
formulations requiring high solids per unit volume. Enzyme modified flours with high paste viscosities act as good thickeners. The application of the above modified flours would ensure desirable levels of digestible starch in food products. Poorly digested flours may function as a source of dietary fiber or aid in weight control. Thus, the data can be used in designing food processing and preparation protocols in accordance with consumer requirements for potential application of potato and sweet potato flours in foods.

Finally, citation of literature references made use of in consolidating this work is listed in the last section, *Bibliography*. 
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1.1 Potato: Production and Distribution

Potato (Solanum tuberosum L) is a nourishing food that has sustained civilizations for centuries in South America and Europe. To the inhabitants of Peru and Bolivia, potato was the 'bread of life' for centuries. Potato production has significantly increased in recent years in many countries, particularly Asia where it has become more important as a food and industrial crop. In terms of production, potato is second only to maize, about one half of the world's potato production is being used as human food. The per capita consumption of potatoes is very high in European countries; in Belarus it is 653 kg / year and in Poland it is 467 kg / year. Though India is the third largest producer in the world after China and Russian Federation, the per capita consumption of potato is only 14.8 kg / year. Thus, there is plenty of scope for increasing the potato consumption in India although people are traditionally dependent upon cereals and are generally unaware of the nutritional value of potatoes.

The nutritional composition of potato is influenced by a large number of factors such as variety, fertilization, climate, and soil, etc. Dry matter content of potato varieties ranged from 15.4 to 23.1%. Potato varieties having 23 percent or more dry matter are classified as high dry matter varieties which are suitable for chips manufacture. Based on this classification, Indian potato varieties are medium dry matter varieties having dry matter content between 20-23%. Starch content of tubers determines the texture of the processed product and high starch content is associated with mealliness texture. Starch content varied from 12.3 to 18.3% among different potato cultivars. A variation in starch content from 14.7 to 18.8% was obtained by Swaminathan and Pushkarnath. The average chemical composition of potato tuber is depicted in Fig. 1.
Potato produces more carbohydrate, fiber and vitamins per unit area and time than other major food crops. Potato is a low energy food. The dry matter content in potato is 47.6 kg / hectare / day whereas in wheat and rice it is 18.1 and 12.4 kg / ha / day respectively (Fig. 2). Similarly potato contains 3 kg / ha / day of edible protein as compared to 2.5 and 1.0 kg in wheat and rice, respectively. The mineral content (kg / ha /day) of potato is 3.7 times more than that of wheat and 11.0 times more than that of rice³ (Table 1).
that of some food products of animal origin. Potatoes can supplement meat and milk products, improving their taste, lowering the total energy intake and reducing the cost of food. In view of shrinking cultivable area and increasing population, potato has a high potential to solve the problems of hunger and malnutrition in our country.

**Table 1. Mineral content of potato and other major crops**

<table>
<thead>
<tr>
<th>Crop</th>
<th>Minerals (kg)</th>
<th>Phosphorous (g)</th>
<th>Calcium (g)</th>
<th>Iron (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato</td>
<td>1.1</td>
<td>75.2</td>
<td>18.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Rice</td>
<td>0.1</td>
<td>22.9</td>
<td>1.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Wheat</td>
<td>0.3</td>
<td>63.5</td>
<td>8.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Maize</td>
<td>0.2</td>
<td>37.0</td>
<td>1.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Source: Ezekiel et al.3

The nutritional composition of potatoes is also very important for processing. All the potato varieties are not suitable for diverse forms of processing. The suitability of a variety for a particular process depends upon the nutritional composition such as the dry matter content, sugars, protein and other nitrogenous compounds. According to Potato Marketing Board, London5, tubers of cultivars having low dry matter content are suitable for canning and those with high dry matter content are good for processing into chips and other dehydrated forms. The ideal reducing sugar content for processing into chips is generally accepted to be 0.1% of tuber fresh weight with 0.33% as the upper limit, while for French fries the upper limit may be as high as 0.5%. According to a prediction equation for predicting chip colour, potatoes should not exceed 296 mg / 100g fresh weight1. Thus, the nutritional composition of potato plays a major role in deciding about the type of processed product prepared from potatoes.

Kufri Jyothi, Kufri Sutlej, Kufri Pukhraj, Kufri Badshah and Kufri Bahar are the main crop varieties for the Indo-Gangetic plains. Kufri Kanchan, Kufri Jyothi, Kufri Sherpa for Darjeeling hills and Kufri Megha for North Eastern hills of India (Fig.3). Recently Central Potato Research Institute (CPRI), Shimla, has developed and released two high dry matter varieties Kufri Chipsona - 1 and Kufri
Chipsona - 2 which are most suitable for chips and French fries processing. Different Indian potato varieties released by the CPRI were evaluated for the dry matter content and reducing sugars (Table 2).

![Map of India showing potato growing areas and suitability for processing](image)

**Fig. 3. Potato growing areas in India showing their suitability for processing**

**Table 2. Processing quality of Indian potato varieties**

<table>
<thead>
<tr>
<th>Varieties</th>
<th>Dry matter (%)</th>
<th>Reducing sugars (mg / 100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kufri Jyothi</td>
<td>18-21</td>
<td>106-275</td>
</tr>
<tr>
<td>Kufri Lauvkar</td>
<td>18-20</td>
<td>200-250</td>
</tr>
<tr>
<td>Kufri</td>
<td>18-20</td>
<td>250-325</td>
</tr>
</tbody>
</table>
Over the past decades, there has been a steady increase in potato production in India (Table 3), accompanied by unsteady markets frequently resulting in peak harvest gluts and consequent economic losses to the farmers. India produced 25 million tonnes of potatoes during 2004-05\(^7\). Indo-Gangetic plains, where the crop is harvested during February - March, contribute to about 90% of the total potato production in India\(^8\).

<table>
<thead>
<tr>
<th>Year</th>
<th>Production (mill. tonnes)</th>
<th>Area ('000 ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000 - 01</td>
<td>24.71</td>
<td>1340</td>
</tr>
<tr>
<td>2001 - 02</td>
<td>22.49</td>
<td>1222</td>
</tr>
<tr>
<td>2002 - 03</td>
<td>24.45</td>
<td>1250</td>
</tr>
<tr>
<td>2003 - 04</td>
<td>25.00</td>
<td>1370</td>
</tr>
<tr>
<td>2004 - 05</td>
<td>25.00</td>
<td>1400</td>
</tr>
</tbody>
</table>

Source: FAO\(^7\)

This record production has led to several post harvest problems, storage being the major one. Increasing potato availability with inadequate, expensive and unevenly distributed refrigerated storage facilities in the country has resulted in frequent gluts in the market causing economic loss to the farmers and wastage of precious foods. Therefore, it is essential that potato consumption is increased to sustain this increase in production and to ensure remunerative prices to the farmers as well. Under the existing circumstances, processing of the bulky perishable potatoes into various processed products is a viable option which can
help extend the storage life, solve the storage problem, cater to the consumer preference belonging to different age groups and social strata and serve as a means to increase the supply in off seasons thus maximizing potato utilization.

1.2 Status of Potato Processing

Processing is a fast growing sector within the world potato economy. Processing has also expanded in Western Europe and has been the focus of numerous initiatives in Eastern Europe and the countries of Commonwealth of Independent States (CIS). Processing has shown fast growth in developing countries, especially in Argentina, Columbia, China and Egypt. In the Netherlands and the USA, processing absorbs about 55 and 60%, respectively of the annual potato crop. However, industrial manufacturing of processed potatoes seems to be only in its infancy in most of the developing countries with the exception of China (12%), Korea DPR (6%) and Mexico (8%)\textsuperscript{1}.

In India, about 1000 tonnes of dehydrated potato products were produced for armed forces and the same quantity was canned; processing of potatoes constitutes less than 0.5% of the annual production. Plants have been established for producing chips and French fries. A number of processed products have been developed which include 1) fried products and other frozen products, 2) dehydrated products such as dehydrated chips, dices, flakes, granules, flour, soup or gravy thickener and potato biscuits and 3) canned potatoes, etc. With increasing production throughout the country, and inadequate storage facilities of potatoes, there occur greater proportions of wastage. Under such circumstances, the post harvest processing of the bulky, perishable, fresh tubers into dehydrated potato products, helps to extend the storage life, solve the problem of storage and serve as a means to increase the supply in off-seasons\textsuperscript{9}. Among such dehydrated products, potato flour is the oldest, commercially processed potato product\textsuperscript{10}. During the season, when potatoes are cheap, potato flour can be prepared and stored in air tight containers and used later during off-seasons in place of fresh potatoes\textsuperscript{1}. Processing of potato into flour is perhaps the
most satisfactory method of creating a product that is not only functionally adequate, but also remain for an extended period without damage.\textsuperscript{11}

Different products are prepared by incorporating potato flour with other flours using different methods of cooking such as baking, roasting, steaming, boiling and deep fat frying, etc.\textsuperscript{12} Nanda and Khanna\textsuperscript{13} reported that potato flour incorporated food products such as dalia, tomato soup, vegetable stew, khichri, sev, paratha, and upma were rated as very good and there occurred no deterioration in the appearance, colour, texture or taste of the product due to addition of potato flour. Potato flour is nowadays widely used in the food industries, specially baking industry in the preparation of bread and biscuits. Potato flour is incorporated in the baking of bread to retain its freshness. It also imparts a distinctive, pleasing flavor and improves toasting qualities. The generally accepted level of potato flour in the bread is 6%. It can also be used advantageously in crackers, pastries, yeast raised doughnuts, cake and cake mixes\textsuperscript{14}

Potato flour can be used as a base ingredient in several commercially produced snack foods such as tikkis in the fast food outlets, extruded products like papad as cottage industries and also in the preparation of idli and aloo-bhujia, etc. It is also used as a combined thickener - flavouring agent in products such as dehydrated soups, gravies, sauces and baby foods\textsuperscript{15}. Potato flour, used in the preparation of mash, gulab jamun, and paratha was more acceptable than those made with wheat flour alone\textsuperscript{14}. Storage studies and microbial safety of potato flour revealed that the flour can be kept safely in polyethylene pouches for six months without any spoilage.\textsuperscript{16}

The average composition of potato flour is given in Table 4. Potato starch contains 18-28% amylose and its starch solution do not form opaque gels though they thicken on cooling. The presence of low levels of phosphate ester groups in potato amylopectin is also responsible for increasing chances of hydration and minimizing association. Modification of potato starch is required in such cases to get desired properties in the starch based products. Modification of starch is
carried out such that the resultant pastes can withstand the conditions of heat, shear etc., associated with particular processing conditions and to introduce specific functionalities.

### Table 4. Composition of potato flour (g / 100 g)

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbohydrates</td>
<td>79.9</td>
</tr>
<tr>
<td>Protein</td>
<td>8.0</td>
</tr>
<tr>
<td>Fat</td>
<td>0.1</td>
</tr>
<tr>
<td>Moisture</td>
<td>8.0</td>
</tr>
<tr>
<td>Calcium (mg)</td>
<td>33</td>
</tr>
<tr>
<td>Iron (mg)</td>
<td>17</td>
</tr>
<tr>
<td>Ascorbic acid (mg)</td>
<td>19</td>
</tr>
<tr>
<td>Thiamin (mg)</td>
<td>0.4</td>
</tr>
<tr>
<td>Riboflavin (mg)</td>
<td>0.1</td>
</tr>
<tr>
<td>Niacin (mg)</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Source: Willard and Hix

1.3 Sweet potato: Production and Distribution

Sweet potato (*Ipomoea batatas* L. Lam) has played an indispensable role as a source of food in Asia and Pacific islands. More than 90% of the world's sweet potato is produced in these regions. In China, sweet potato is second only to rice and accounts for more than 80% (about 115 million tonnes) of the world's total production. India, Indonesia, and Philippines have the largest amount of land under sweet potato production. India produces about 1 million tonnes of sweet potato (Table 5) and different varieties are grown in various parts of the country.

### Table 5. Production of sweet potato in India

<table>
<thead>
<tr>
<th>Year</th>
<th>Production (mill. tonnes)</th>
<th>Area (‘000 ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000 - 01</td>
<td>1.11</td>
<td>114</td>
</tr>
<tr>
<td>2001 - 02</td>
<td>0.83</td>
<td>101</td>
</tr>
</tbody>
</table>
The major producing states include Orissa, Bihar, Uttar Pradesh and Madhya Pradesh (Table 6). The crop has limited production costs and does well even under marginal conditions (poor soils with limited water supplies). Among the world’s major food crops, sweet potato produces the highest amount of edible energy, per hectare per day.

**Table 6. Major producers (states) of sweet potato in India**

<table>
<thead>
<tr>
<th>State</th>
<th>Ave. Production ('000 MT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orissa</td>
<td>350</td>
</tr>
<tr>
<td>Uttar Pradesh</td>
<td>300</td>
</tr>
<tr>
<td>Bihar</td>
<td>150</td>
</tr>
<tr>
<td>Madhya Pradesh</td>
<td>40</td>
</tr>
<tr>
<td>Tamilnadu</td>
<td>30</td>
</tr>
<tr>
<td>Karnataka</td>
<td>25</td>
</tr>
</tbody>
</table>

Sweet potato roots are classified into two general types: dry-fleshed cultivars with mealy, light yellow or white flesh and the moist-type cultivars with soft, gelatinous, bright orange flesh. The average dry matter content is 30%, but varies depending on such factors as cultivar, location, climate, day length, soil type, incidence of pests and diseases and cultivation practices. Dry matter content varies from 13.6% to 35.1% in a number of sweet potato lines grown in Taiwan and from 22.9% to 48.2% in 18 cultivars grown in Brazil.

Sweet potato is a nutritive vegetable, being an excellent source of vitamin A precursor, certain other vitamins and minerals, energy, dietary fiber and protein. In addition, sweet potato consists of more than 80% carbohydrates on dry basis, of which a major portion is starch (Table 7).
Table 7. Composition of sweet potato roots (g / 100 g)

<table>
<thead>
<tr>
<th>Component</th>
<th>Value (g / 100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>71.0</td>
</tr>
<tr>
<td>Starch</td>
<td>20.0</td>
</tr>
<tr>
<td>sugar</td>
<td>2.4</td>
</tr>
<tr>
<td>Protein</td>
<td>1.4</td>
</tr>
<tr>
<td>Lipid</td>
<td>0.2</td>
</tr>
<tr>
<td>Dietary fiber</td>
<td>1.6</td>
</tr>
<tr>
<td>Ash</td>
<td>0.7</td>
</tr>
<tr>
<td>Calcium (mg)</td>
<td>29</td>
</tr>
<tr>
<td>Phosphorous (mg)</td>
<td>51</td>
</tr>
<tr>
<td>Iron (mg)</td>
<td>0.5</td>
</tr>
<tr>
<td>Magnesium (mg)</td>
<td>26</td>
</tr>
<tr>
<td>Potassium (mg)</td>
<td>260</td>
</tr>
<tr>
<td>Zinc (mg)</td>
<td>0.6</td>
</tr>
<tr>
<td>Copper</td>
<td>0.2</td>
</tr>
<tr>
<td>Vitamin A (mg)</td>
<td>0.01</td>
</tr>
<tr>
<td>Thiamine (mg)</td>
<td>0.08</td>
</tr>
<tr>
<td>Riboflavin (mg)</td>
<td>0.03</td>
</tr>
<tr>
<td>Niacin (mg)</td>
<td>0.6</td>
</tr>
<tr>
<td>Ascorbic acid (mg)</td>
<td>24</td>
</tr>
</tbody>
</table>

Source: Woolfe25

The starch content of fresh sweet potato roots varies between 6.9 - 30.7%. Starch as a component of sweet potato can be prepared to exhibit functional properties with potential utility in certain food applications. These properties can be developed by controlling the rate of heating during cooking which activates endogenous amylolytic enzymes of the sweet potato root to convert a portion of the starch to dextrins. Dextrins form an adhesive material that could function as a binding agent in food products.

Sweet potato contains many enzyme systems, which catalyse many synthetic and degradative processes within the tissues. The most important enzymes from the view point of quality in both cooked and processed roots are the amylases. The action of amylases on starch is illustrated in Fig. 4.
Fig. 4. Amylose and amylopectin degradation by the amylases

Beta amylase attacks the alpha -1,4 linkages within the amylose chain in a step wise fashion, starting at the non-reducing end, to give maltose, (and in case of amylose with an odd number of glucose units, a little maltotriose). Amylopectin is similarly hydrolysed, but as beta amylase is unable to hydrolyse or by-pass alpha -1,6 links, a high molecular weight limit dextrin remains unhydrolysed. Alpha amylase splits alpha- 1,4 links at random to form dextrins, after which these fragments are slowly hydrolysed to maltose.

Amylopectin on breakdown gives maltose and polysaccharide fragments called 'limit dextrins' (the enzyme is limited in its ability to hydrolyse, alpha - 1,6 bonds). Both the enzymes appear to contribute to starch break down during
cooking, and it is probable that by doing so they influence both sweetness and mouthfeel, an important quality attribute in the cooked roots\textsuperscript{20}.

Some 60\% of sweet potato production in China is used for feed or processed into starch\textsuperscript{21}. In Japan, and Korea also, sweet potatoes are used for starch extraction. Sweet potato has the advantage of being a good source of energy and an inexpensive source of carotene, ascorbic acid, niacin and thiamine. Sweet potato roots are one of the major food resources of carotenoids along with apricots, carrots and peaches. The significance of carotenoids is that some are converted into vitamin A. Beta-carotene has the highest (100\%) provitamin A activity, followed by alpha and gamma carotenes with 50\% activity. Orange fleshed sweet potatoes obtain their color through the presence of carotenoid pigments, with the flesh colour of the sweet potato root largely a function of the concentration of beta-carotene.

However, white sweet potato cultivars lack the presence of the three most important pro-vitamin A carotenes. The role of white sweet potatoes as source of vitamin A is restricted with only partial or no provitamin A activity. Although amounts of carotenoids present in sweet potato roots may be abundant, carotenoid content decreases over time with processing in both raw form and during heat treatment.

Sweet potatoes are substantial sources of ascorbic acid (vitamin C) and contain moderate amounts of thiamin (B1), riboflavin (B2) and niacin as well as pyridoxine and its derivatives (B6), pantothenic acid (B5) and folic acid. They have been reported to contain satisfactory quantities of vitamin E. A 130 g serving of sweet potato provides 320\% of the daily minimum requirements (DMR) for vitamin A, 70\% of the vitamin C, and appreciable quantities of thiamine, riboflavin, niacin, phosphorous, iron and calcium.

\textbf{1.4 Utilization of Sweet Potato}
In spite of the fact that it is cheaper than other crops, this abundant resource is, however, still poorly utilized. However, most sweet potato currently produced in developing countries are consumed fresh for various reasons. Firstly, as a living plant part that contains over 70% of water, the roots are very perishable and difficult to store. Secondly, sweet potato’s stigma as a poor man's crop limits its consumption. Thirdly, the high levels of sweetness and strong flavor found in some roots are not preferred by some consumers. However, In Japan, and Korea sweet potatoes are used for starch extraction and fermentation. Dried sweet potato chips are common in Taiwan. Table 8 gives the details of products produced in various countries.

Table 8. Processed products of sweet potato

<table>
<thead>
<tr>
<th>Country</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>Dried / fried chips, Noodles, Alcohol, Starch, Citric acid, Glucose and Fructose syrups, Monosodium glutamate, Amino acids</td>
</tr>
<tr>
<td>Japan</td>
<td>Alcohol, Starch, Noodles, Glucose and Fructose syrups, Candy, fried chips, Granules, Flour.</td>
</tr>
<tr>
<td>India</td>
<td>Flour</td>
</tr>
<tr>
<td>Philippines</td>
<td>Snack foods, Dried cubes</td>
</tr>
<tr>
<td>Taiwan</td>
<td>Noodles, Candy, Bread and Baked goods.</td>
</tr>
<tr>
<td>USA</td>
<td>Canned roots, Puree / Paste, Flakes, β-amylase</td>
</tr>
</tbody>
</table>

Starch manufacture is the main industrial utilization of sweet potatoes which has been used in starch noodles, bakery foods, snack foods, confectionery products and by the alcohol production and brewing industries\textsuperscript{22,23}. Chen et al.\textsuperscript{24} reported the use of dried and ground sweet potato as a supplement in puddings, gruel etc. Development of new and improved processed products from sweet
potato provides an excellent means of increasing the utilization of this high yielding, nutritious species.

As recent experience in China suggests, raw sweet potato roots can be processed into forms with a longer shelf life and characteristics more in keeping with latent demand and emerging utilization patterns. Options for sweet potato products are numerous, but based on recent diagnostic assessments carried out in developing countries, dried chips, starch, and flour were identified as among the most promising.

Sweet potatoes have been processed in various ways including dehydration by drum drying, the most effective means of preserving the crop. Sweet potato flour, a dehydrated product, can be used as i) a substitute for wheat flour to lower (bakery) costs and as such decrease imports of wheat flour, and ii) as an alternative market outlet for those selling the roots as raw material. Sweet potato flour has to be as white as pure wheat flour in order to maintain the original appearance of the products made. A substitution level of 10-15% for wheat flour on a dry weight basis is most acceptable. In addition to serving as a source of energy and nutrients (carbohydrates, beta-carotene (provitamin A), minerals (Ca, P, Fe, and K), sweet potato flour can add natural sweetness, color, and flavor to the processed food products. Baked goods can be made with higher proportions (10-100%) of sweet potato flour than bread. For example, in Papua, New Guinea, cakes made with 100% sweet potato flour has an acceptable taste, and in India, pancakes, puddings, and chapathis are made with 50% sweet potato flour. But a much wider range of products exist including doughnuts, biscuits, cookies, brownies, noodles, pies, breakfast foods, and weaning foods.

The possibility of utilizing wheat-sweet potato composite flours in breads and other baked goods has been investigated in several countries including Egypt, India, Israel, Korea, and Philippines. Sweet potato flour has also been used for its specific properties to form new products. In sweet potato flour,
carbohydrates account for the bulk of the flour, and range between 84.6% and 94.8% (on a dry weight basis). The total starch content varies between 57-90%. Woolfe\textsuperscript{25} divided digestible carbohydrates into starch and total sugars with levels of 87.5% and 12.5%, respectively. For the 44 varieties analyzed by Collado et al\textsuperscript{28}, starch content was found to be negatively correlated with fiber, total free sugar, and ash content. Reducing sugars in raw roots must be as low as possible (<2.0%) to prevent discolouration during processing.

The classification of sweet potatoes into moist and dry flesh is a very important quality factor in the industry. This property describes the mouth feel characteristics after baking and is independent of water content. The apparent viscosity was also a measure of moist mouth feel quality for sweet potatoes\textsuperscript{29}. The behaviour of carbohydrates in baked sweet potato roots as affected by curing and varieties has been investigated by Picha\textsuperscript{30}. Cooking processes account for marked changes in chemical composition and, consequently change in the nutritional value of cooked roots\textsuperscript{31}. Damir\textsuperscript{32} studied the effect of heat penetration during blanching and baking on some physico-chemical properties and on the ultrastructure of sweet potato roots.

Previous researchers have noted a lack of information on sweet potato flour quality. Generally controlling the quality of a product is based on the acceptability of the users and food legislation. For example, chemical and microbiological analyses are included in determining whether the flour conforms to food legislation. Peruvian law requires that flours from root and tuber crops do not show an alkaline reaction with phenolphthaleine and do not exceed maximum levels for humidity (15%), ash (2.5%), and acidity (0.15%)\textsuperscript{21}. Most suitable flour should have a high starch content, low acidity, low crude-fiber content, low ash content, and white colour. Acceptability was shown to depend on the organoleptic evaluation of the flour with colour, odour, and a high degree of whiteness being the most important quality factors, for its users (bakers, noodle manufacturers, etc.).
1.5 Properties of Potato / Sweet Potato Flour

Potato flour is prepared by drying the peeled slices in a hot air drier or by drying the cooked mash by a drum drier into flakes followed by grinding and sieving\textsuperscript{10}. Similarly, sweet potato flour can also be prepared by using the above procedures\textsuperscript{25}. By partly hydrolysing the starch component with alpha amylase, the drying characteristics of sweet potato mash have been improved, though the whiteness index of flakes decreased\textsuperscript{33}.

Sweet potato grated, sun dried and milled into flour has been produced by the Central Tuber Crops Research Institute, Kerala, India, and is now being marketed. It can be used to substitute part of the wheat flour used to make \textit{chapathis} and other baked goods\textsuperscript{25}. Flour quality depends both on good processing practices and prevention of deteriorative changes during storage. Most of the technical research on flour has focussed on the development of new products using flour rather than on efficient methods to produce and store the flour\textsuperscript{21}.

In view of the increasing utilization of potato and sweet potato in composite flours for various food formulations, their functional properties are assuming greater significance. Rheological and functional properties are physico-chemical properties, which give information on how a particular ingredient (e.g. starch, protein) will behave in a food system. Such properties of plant foods are determined by the molecular composition and structure of the individual component and their interactions with one another\textsuperscript{34}.

The functional properties provide a set of data, which gives information on the fields of application in food formulations\textsuperscript{35}. These can be used as a guideline in product development. Functional foods are assuming greater importance and have attracted the attention of food processors, marketers and consumers.

Most information on functional properties of potato and sweet potato refers to their starch instead of flour\textsuperscript{36}. The functional properties of flour are provided
not only by the starch but also by other flour components. The limited data for flour functional properties are different from those of starch since extra constituents available in flour (protein, fat, etc.), restrict access of water into the starch granules\textsuperscript{37}. For example, RVA pasting parameters of the flour, determined in the present investigation, were not correlated to the RVA pasting parameters of the purified starch. Hence, RVA pasting profile of the flour can not be used to indicate the pasting properties of the starch.

The crystalline order in starch granules is often the basic underlying factor influencing functional properties. Collapse of crystalline order within the starch granules manifests itself as irreversible changes in properties, such as granule swelling, loss of optical birefringence, loss of crystalline order, uncoiling and dissociation of the double helices, and starch solubility\textsuperscript{38,39}. High transition temperatures have been reported to result from a high degree of crystallinity, which provides structural stability and makes the granule more resistant towards gelatinization\textsuperscript{40}.

Gelatinization and swelling are descriptive terms for related events that occur when starch granules are heated in water. Gelatinization refers to the progressive disordering of the double helices, crystallites and larger ordered domains of amyllopectin. Swelling is essentially a property of the whole amyllopectin molecule, rather than parts of it, and amylose alone appears to be a diluent, while lipids (as complexes with amylose) strongly inhibit swelling\textsuperscript{41}.

The degree of starch gelatinization from fresh mixtures of sweet potato flour with water was found to be 50%. This indicates that processing the flour partially gelatinizes the starch\textsuperscript{42}. The temperature range over which gelatinization occurred, from onset to completion measured with DSC was from 69.9 to 92.9°C with a peak temperature ranging from 80.4 to 83.6°C\textsuperscript{43}. RVA visco-amylographs for 44 different genotypes in distilled water showed a mean peak viscosity (PV) of 156 RVU (ranging from 40 to 309 RVU).
Tester\textsuperscript{44} has postulated that the extent of crystalline perfection is reflected in the gelatinization temperatures. The gelatinization and swelling properties are controlled in part by the molecular structure of amylopectin (unit chain length, extent of branching, molecular weight, and polydispersity), starch composition (amylose to amylopectin ratio and phosphorus content), and granule architecture (crystalline to amorphous ratio). Enthalpy of gelatinization ($\Delta H_{\text{gel}}$) gives an overall measure of crystallinity (quality and quantity) and is an indicator of the loss of molecular order within the granule\textsuperscript{45,46}.

The temperature, and type of gelatinization (the swelling which takes place when starch granules are heated in water), swelling ability, hot paste viscosity, and gel forming properties of individual starches are important in determining their behaviour in food formulations. Starches fall into two major groups of crystalline organization, characterized by their X-ray diffraction pattern: an A-type pattern corresponding to a double crystalline structure with three relatively intense peaks, and a B-type with a single crystalline structure\textsuperscript{47}.

Digestibility of native starches among and within species have been attributed to the interplay of many factors such as starch source\textsuperscript{48}, granule size\textsuperscript{49}, amylose / amylopectin ratio, extent of molecular association between starch components\textsuperscript{50}, degree of crystallinity,\textsuperscript{51} amylose chain length,\textsuperscript{52} and amylose - lipid complexes\textsuperscript{53}. Potato and taro show the highest resistance to alpha amylase.

The texture of reconstituted dehydrated mashed potatoes has a major influence on consumer acceptance. Mullins et al.\textsuperscript{54} attempted to evaluate consistency and pastiness by measuring the diameter of a mashed potato ball falling upon a smooth surface from a given height. Smith and Davis\textsuperscript{55} used a modified L.E.E. - Kramer shear press to record the texture changes of reconstituted flakes, while Voisey and Dean\textsuperscript{56} and Voisey deMan\textsuperscript{57} measured torque and energy required to mix the reconstituted flakes. As stated by Ooraikul\textsuperscript{58}, most of these attempts actually measure overall textural quality, the
character of which is a complex combination of several attributes such as firmness, glueyness, and smoothness.

Henning et al.\textsuperscript{59} found no increase in molecular mobility up to 55°C in native potato starch. The onset of crystalline melting was observed at 60°C, and this increase was low until 63°C; above this temperature a high increase was observed. At 66°C, half of the molecules were already mobile, increasing to close to 80% at 68°C, while at 70°C no crystallite was left, i.e., all molecules were free.

Cording and Willard\textsuperscript{60} heated potato slices in water at 60 - 83°C before being cooked. A cooling step using water of less than 22°C for at least 14 minutes was inserted between precooking and final cooling steps in order to decrease pastiness and increase mealiness. These works showed that it actually promotes retrogradation of both extracellular starch and starch within the unruptured cell, thereby increasing mealiness, a required feature for good quality mashed potatoes.

1.6 Modified Flours

Several basic properties of flours of concern to food processors are improved by starch modification; among these are improved heat, shear and acid stability. Either one or combination of these characteristics is required in most food processes where the properties of unmodified starch are insufficient. The rapid growth of food technology, especially in the area of convenience foods, has resulted from this fact. Without the special rheological properties obtained by modifications, frozen, instant, dehydrated, encapsulated and heat serve foods and cold water swelling products would not be economically competitive.

The myriad functionality of starches today all but guarantees that - whatever the desired end result - a starch is available to meet the demand. However, for complex combination of applications, possible end - product
attributes and processing demands, guidance is needed to exploit this ingredient to the fullest.

Specialty flours in snack foods serve as functional ingredients, contributing to desirable attributes such as increased expansion, improved crispness, reduced oil pickup, and better overall eating quality. Starch-based coatings and adhesives can replace fat or oil in low fat baked snacks, while resistant starch provides high fiber nutritional claims for snack foods. The type of starches chosen will depend on their cost, availability, functionality and the quantity used\textsuperscript{61}. The knowledge on properties of modified flour will help in deciding the flour's suitability in product development. The thermal and mechanical stability and the low retrogradation pattern of flour are important characteristics useful for certain industrial applications.

1.6.1 Physical Modification

This method mainly involves heat. Potato/sweet potato flours are prepared by drying the peeled slices in a hot air drier or by drying the cooked mash by a drum drier into flakes followed by grinding and sieving\textsuperscript{10,25}. Drying results in lowering the moisture content of the product leading to reduced chances of microbial growth. The reduction in moisture content is accompanied by reduction in bulk, which facilitates storage, transportation and packaging. However, the characteristics of the flour prepared by the above methods will be altered due to the involvement of heat treatment.

Lamberti et al.\textsuperscript{62} studied the starch transformation during production and reconstitution of potato flakes. Changes in carbohydrates during cooking, baking and heat moisture treatment of sweet potato were reported by Damir\textsuperscript{32}, Kamolwan et al.\textsuperscript{63} and Susheelamma et al.\textsuperscript{64} Osundahunsi et al.\textsuperscript{65} compared the physico-chemical properties of sweet potato flour and starch including parboiled flour. The pasting viscosities of blanched banana and sweet potato flours were reduced compared to that of native samples. The pasting temperature (74°C-
95°C) of flours was greater than that of starch, depending on the variety and blanching process. Composition of starch and flour was found to affect swelling power and solubility. Red and white sweet potato cultivars have amylose content (32-34%) and exhibit a Ca type- X-ray diffraction pattern. Similar gelatinization characteristics were detected for both starches with onset temperature of 67°C and enthalpy of 10.5 - 11.0 J/g. Pasting properties of the white cultivar showed lower tendency for retrogradation.

1.6.2 Chemical Modification (Acetylation)

The most important reaction in the modification of food starches is the introduction of substituent chemical groups. These chemical modifications are of two types, monofunctional; di- or polyfunctional. The number of reaction groups determines the manner in which a chemical modifier will alter rheological properties. Monofunctional reagents react with one or more hydroxyl groups per sugar unit to alter the polarity of the unit, sometimes making it ionic, and markedly influence the rheological properties of the starch. In general, monofunctional substitution lowers the swelling (pasting) temperature, increases paste clarity, reduces gel formation and improves freeze-thaw and water holding properties. Monofunctional reagents most often used for food starch are acetic anhydride and propylene oxide. Acetic anhydride reacts to produce starch acetate (ester linkage).

Acetylated starches with low degree of substitution (DS) are widely used in food industries for many years because of the unique characteristics imparted by acetylation such as low gelatinization temperature, high swelling and solubility, and good cooking and storage stability. The acetylated starches are also less susceptible to retrogradation. It is thought that the amylose fraction which is mainly responsible for starch retrogradation, is modified and as a result is less susceptible to retrogradation. The physico-chemical properties of acetylated starches depend on their chemical structures, degree of substitution
(DS) and acetyl group distributions. Until now only a few publications dealt with structure features of acetylated starches.\textsuperscript{69,71,72,73}

Acetylation can influence the interactions between the starch chains through three possible mechanisms. 1) By simple steric hindrance preventing close association of chains to allow formation of hydrogen bonds, 2) by altering the hydrophilicity of the starch and thus affecting bonding with water molecules, or 3) by participation of the acetyl groups in improved hydrogen bonding with other starch chains. The observed effects of acetylation are consistent with an overall reduction in bonding between starch chains and a consequent increase in the ease of hydration of the starch granule\textsuperscript{74}.

It was reported that acetylated potato and sweet potato starches could significantly improve the quality of white salted noodle by replacing part of commonly used wheat flour\textsuperscript{75}. The different size granule fractions of potato and sweet potato starches were found to differ greatly in chemical compositions (e.g. amylose, phosphorous), gel properties, and processibility to starch noodles\textsuperscript{36}, acetic anhydride which react with the hydroxyl groups of the glucose moieties of both amylose and amylopectin populations present.

\subsection*{1.6.3 Enzymatic Modification}

In the \textit{in vitro} alpha amylolysis of different starch granules, the enzyme attack is rather restricted and is usually from outside inwards, i.e. exocorrosion\textsuperscript{76}. On the other hand, \textit{in vivo} the granules are subjected to cumulative actions of dilute acid (by gastric juices) and pancreatic alpha amylase, and as a result the granules are better digested. The enzyme from \textit{A. awamori} has been shown to have separate active site and raw starch adsorbability characteristics\textsuperscript{77}. The latter, in addition to its adsorption on to the granule, played a specific role in raw starch digestion. The granule degradation was mostly confined to pitting and surface erosion all over.
Most of the millet starches upon amylase digestion lost their characteristic polygonal shape and appeared spherical, indicating a preferential attack at these sites. Also some of the granules in the population restricted enzyme attack for reasons not clearly known yet. However, in vivo in addition to the stomach acidity, the intestinal microflora plays a crucial role in raw starch digestion, and the SEM analyses of the residual starch granules isolated from faeces and various other organs show characteristic degradation patterns\textsuperscript{78}.

In a recent study on the digestibility differences between legume and cereal starches, it was shown that all the three constituents, viz.. amylose, amyllopectin and intermediate fraction do play a crucial role, both qualitatively and quantitatively, for the overall in vitro digestibility differences\textsuperscript{79}. In the case of malted barley, the small (<5µm) granules were rather more susceptible to amylolysis than the large granules\textsuperscript{80}.

Action of porcine pancreatic and \textit{Bacillus subtilis} alpha amylases on native sweet potato starch was studied in comparison with the well known potato and cassava starches. Large differences in enzyme susceptibilities were observed when studied on 24h. Sweet potato starch was 53% hydrolysed, two times less than cassava starch. The level of hydrolysis was higher with porcine pancreatic amylase than with the \textit{Bacillus subtilis} amylase while initial hydrolysis rate was less\textsuperscript{81}.

The action of glucoamylase I and II (alpha - 1,4 - glucan glucohydrolase, E.C. 3.2.1..3 from \textit{Aspergillus niger} and the glucoamylase from \textit{Rhizopus niveus} on native wheat and corn starch granules was followed by scanning electron microscopy and by measuring the glucose released by enzyme attack. Glucoamylase I and glucoamylase II from \textit{R.niveus} attacked the granule surface relatively uniformly, resulting in large disc-like depressions. Glucoamylase II, while showing some disc-like depressions, produced small grooves (furrows) on the surface of the granule. Similar patterns were observed for both corn and wheat starch granules. Measuring glucose released indicated that hydrolysis by
these enzymes were nearly equal in extent and were about twice that by glucoamylase II\textsuperscript{82}.

Three crude glucoamylase preparations from \textit{Rhizopus} sp., \textit{Chalara paradoxa}, and \textit{Aspergillus} sp. K-27 were used to determine the digestibility of raw starches from eight sweet potato varieties. Granule sizes and amylose contents were also measured. The average granule sizes ranged between 10.5 and 14.2 $\mu$m. The amylose contents varied between 18.2 and 21.8\%. The hydrolysis rates for the raw starches by any of the three glucoamylases were similar\textsuperscript{83}.

Starch granules were observed by a scanning electron microscope in order to provide information concerning the types and extent of damage of the surface and internal structure of starch granules attacked by amylases. Granules resistant to the action of amylases, namely potato, and high-amylose maize starches showed shapes and surfaces similar to the intact granules after the action of either \textit{Rhizopus} glucoamylase or bacterial alpha amylase. Granules susceptible to amylases showed numerous pin holes on the surface layer and pores penetrated into the inner layers of the granules during the attack by amylases. In the case of alpha amylolysis, it is apparent that once the enzyme has penetrated into the inner layer of a granule, the layers are more readily attacked than the peripheral layers\textsuperscript{84}.

The enzymatically modified flour is useful adjunct in the manufacture of low energy and dietetic foods. Absorption of oil, emulsifying capacity, and the solubility of wheat flour were improved by enzyme modification\textsuperscript{85}. Modified flours are recommended for manufacture of low fat and low sugar wafers and other bakery products.

1.7 Scope of the present investigation
Though different workers have reported on the possible use of potato and sweet potato flours for product development, the properties of the flour desired for preparation of various products such as noodles, pudding, gravy, sauces, gruel, and bakery products vary. The swelling, solubility, gelatinization temperature, cold paste viscosity, gel consistency, etc., are important characteristics, if the flour has to be considered for product development. However, most information on functional properties refers to the isolated starch, instead of flour. The flour functional properties are different from those of starch, since extra constituents available in flour (non-starch polysaccharides, protein, fat, etc.), restrict access of water into the starch granules. The RVA visco-amylograph pasting parameters of the flour, determined in the present investigation, were not correlated to the RVA pasting parameters of the purified starch.

An attempt has been made in the present investigation to determine the functional - rheological properties of flour as affected by physical, chemical and enzymatic treatments. The extent of changes in starch as a result of processing / modification has also been investigated, since the accessibility of starch in flour is less to water and heat compared to an isolated starch. The relation between the functional properties of flour and the structural changes in their starches has also been established.

Textural quality, the degree of crystallinity and the double helical content (in the amorphous and crystalline domains) of tuber and root starches have not been thoroughly investigated. Consequently, the influence of these parameters on enzyme susceptibility, gelatinization, retrogradation and rheological properties could not be properly ascertained.

Furthermore, many researchers have used only one technique for determining gelatinization and retrogradation properties of tuber and root
starches. This approach is not sound, since various methods such as DSC, X-ray, NMR, FT/IR spectroscopy measure different properties of the material. A more advantageous approach may be to use these methods collectively to obtain a deep insight into the physico-chemical properties. There is thus, a need to carry out a systematic investigation on the properties of modified flours using a variety of analytical techniques and experimental conditions.

With a view to provide information on the properties of native, thermally processed, acetylated and enzymatically modified potato and sweet potato flours the studies were carried out with the following objectives.

I. Preparation of potato and sweet potato flours by physical (drum dried and hot air dried), chemical (acetylated) and enzymatic treatments.

II. Optimization of process conditions for acetylated and enzyme modified flours from potato and sweet potato.

III. Structural properties of modified flours by GPC, FTIR, SEM etc.

IV. Rheological and functional properties of differently treated flours of potato and sweet potato by RVA, TPA, DSC etc.

The rheological and functional properties have been investigated to find the potential application of potato and sweet potato flours in foods.
2.1 Materials

2.1.1 Chemicals

All the chemicals, organic solvents and acids used were of analytical grade. Sugar standards, pancreatic amylase (E.C. No. 3.2.1.1), amylglucosidase (E.C. No. 3.2.1.3), glucose oxidase (E.C.No 1.1.3.4), peroxidase (E.C.No 1.11.1.7), pepsin (E.C.No 3.4.23.1), β-amylase (E.C.No 3.2.1.2), are from Sigma Chemical Company, U.S.A. Termamyl (heat stable α-amylase) was from Novo, Denmark. Sepharose CL 2B and dextrans (T-10, T-20, T-40, T-500 and T-2000) were from Pharmacia fine chemicals, Sweden.

2.1.2 Raw materials

Potato (Solanum tuberosum L, var. Kufrijoythi) and the red skinned sweet potato (Ipomoea batatas L) were procured locally, cleaned under running tap water, surface dried.

2.1.3 General

a. All results are the average of not less than three experiments.
b. Double glass-distilled water was used for the preparation of reagents.
c. Distillation of organic solvents such as chloroform, methanol, ethanol, phenol, acetic anhydride and was done in an all-glass apparatus.
d. A Mettler AE-100 digital balance was used for weighing the samples.
e. Samples were incubated with enzymes in a shaking Julabo SW 20-100 °C thermostat water bath.
f. Either refrigerated Hermle-320K or Sigma 202-C bench top centrifuge was used for the centrifugation (10 min, 4000 g) of samples.
g. Boiling water bath temperature was maintained at 97°C unless otherwise stated.
h. All flash evaporation were done in a Buchi Rotavapor RE 120. Bath temperature was maintained at 40°C ± 1°C.
i. Shimadzu UV-160 A spectrophotometer was used to read the colour developed in all analytical determinations.
Samples were sonicated using Julabo USR sonicator for efficient dissolution.

2.2 Preparation of Flour
2.2.1 Native flour

Potatoes and sweet potatoes were peeled in an abrasive peeler (Model 547, Continental, New Delhi, India) and hand trimmed with knife, keeping them in water to prevent enzymatic darkening. Slices 2-3 mm thick were prepared from peeled roots with a dicing machine RG-400, AB Hallde Maskiner, Sweden and dried at 40±2°C, ground into powder and sieved through a 0.5 mm sieve (Fig. 5). The powder was packed in polyethylene bag and stored at 12°C till further use.

2.2.2 Drum dried flour

Cubes / dices (10 mm thick) from peeled potato / sweet potato were prepared as described at 2.2.1, steam cooked in a steam cooker, (Model 9143, Conrad Engelke, Hannover, Germany) at 85±2°C for 20 min, cooled to room temperature and made into a fine mash in a Hobart mixer. Sulphur dioxide (1000 ppm), whey protein concentrate (0.05%) and monosodium glutamate (0.05%) were added to the mash and mixed thoroughly. The mixture was dried in a double drum drier (DD), 60 cm width and 35 cm diameter (INH- 7831, Escherwyss, Ravenberg, Germany). The operating conditions were: steam pressure 6 bar, rotating at 3 rpm with a clearance of 0.3 mm. The sheets of dried potato / sweet potato were collected, crushed and milled in a hammer mill (APEX, Apex Construction Ltd., England) which is provided with a 0.5 mm sieve (Fig. 6).

2.2.3 Hot air dried flour

The cubes prepared as described at 2.2.1, were blanched in an open steam cooker at 85±2°C for 5 min, followed by soaking in water (1:2) containing 1000 ppm sulphur dioxide for 20 min. The sulphited cubes were drained, loaded in trays (6 kg/m²), and dried at 65±2°C in a batch type cross flow hot air cabinet.
drier (HD) for 7-8 h (Fig. 6). The flour was obtained by milling the dried cubes in a hammer mill (APEX, Apex Construction Ltd., England).

2.2.4 Acetylated flour

Acetylation of potato and sweet potato flours were carried out by three different methods to arrive at a suitable degree of substitution (DS) which was determined by FT-IR spectroscopy. Method 1 involved the wetting of 2 g native flour sample with 5 ml distilled water, stirring for 1 hr, adjusting the pH to 8.5 followed by addition of acetic anhydride (0.2 / 0.4 / 0.6 ml each), and 3% sodium hydroxide to maintain pH. The reaction was allowed for 15 min with continuous stirring, followed by addition of 0.5 N HCl to adjust pH at 4.5; centrifuged after repeated washings to remove alkali. The sample was dried at 40°C to 8% moisture and the degree of substitution, measured by FT-IR.

Method 2 involved the wetting of 2 g sample with 5 ml distilled water. Sodium hydroxide pellets (1 g) were added and mixed thoroughly. Acetic anhydride (2 / 3.5 / 5 ml) was added to the above mixture and kept at 40°C for 1 h. After repeated washings with water and alcohol, the sample (pH 7.0) was further dried at 40°C to 8% moisture. The degree of substitution of this acetylated flour was determined by FT-IR. Though acetylation took place in this method, the exothermic reaction in the presence of sodium hydroxide generated much heat that subsequently caused more froth formation during the reaction which resulted in overflowing.

In method 3, the flour samples (2 g), mixed with solid NaHCO₃ (1 g), were wetted with distilled water (1 ml). Acetic anhydride (4 ml) was added. The mixture was allowed for reaction for 2 h, at 40°C (Fig. 7). The reaction mixture was then washed thoroughly with alcohol, pH adjusted to 7.0 and dried at 40°C overnight.

2.2.5 Enzyme modified flour

To the flour samples (1 g) in acetate buffer (pH 4.6, 6 ml) was added glucoamylase (from *Rhizopus* mold, 21100 units / g solid) at three different levels
(1, 2.5 and 5%) (20 U mg\(^{-1}\) flour). The reaction mixture was incubated at 60°C for 90 min (potato flour) and 120 min (sweet potato flour). The incubated samples were centrifuged (Fig. 8). The sediment after centrifugation was collected, washed with alcohol repeatedly, dried and stored at 12°C for further analysis and the supernatant analysed for its reducing sugars content.

2.3 Reducing sugars by DNS Method\(^{88}\)

To the sample or standard (1.0 ml, 100 - 1000 µg glucose), 1 ml of DNS reagent (1 g of dinitrosalicylic acid and 30 g of sodium potassium tartarate in 0.4 N NaOH) was added and heated for 15 min in a boiling water bath. After cooling, 3.0 ml of double distilled water was added and the absorbance was measured at 530 nm. The calibration curves were constructed using glucose as standard.

2.4 Starch Isolation

Starch was isolated from fresh tubers / roots and the processed flours by water steeping method\(^{89}\). For deproteinisation, the crude starch was suspended in aqueous medium at pH 9.0 (by adding dilute NaOH) for 15 min with gentle stirring. The suspension was centrifuged and excess alkali was removed by repeated water washings. It was further deproteinised by stirring with 0.1M NaCl-toluene (10:1,v/v), for 2 h, thrice and later centrifuged. Excess NaCl was removed by repeated water washings and finally the starch sediment was dried by the solvent exchange method\(^{90}\).
Slicing

Shade drying (40°C)

Milling of dried slices

Native flour

**Fig. 5. Preparation of Native flour**

Potato / Sweet potato

Peeling

Dicing

Blanching / Cooking (5/20min)

Cooling
Fig. 6 Preparation of Thermally processed flours

Native flour (Potato / Sweet potato)

Addition of NaHCO₃

Wetting

Addition of Acetic anhydride

Washing of reaction mixture

Alcohol washing
Fig. 7. Preparation of Acetylated flour

Native flour (Potato / Sweet potato)
  ↓
Addition of acetate buffer
  ↓
Addition of glucoamylase
  ↓
Incubation at 60°C
  ↓
Washing of reaction mixture
  ↓
Alcohol washing
2.5 Proximate Composition

2.5.1 Moisture content

The flour sample (2 g) was taken in a preweighed porcelain crucible, was dried to constant weight at 105°C for 14 h. Loss in weight was taken as the moisture content of the sample.

\[ \% \text{ Moisture} = \frac{\text{Weight loss (g)} \times 100}{\text{sample weight (g)}} \]

2.5.2 Protein

Solution a: 40% NaOH in distilled water.
Solution b: 2% boric acid (10 g boric acid crystals in 500 ml of hot distilled water)
Solution c: Bromocresol green indicator solution (2-3 drops)

Sample (1 g) was taken in a 100 ml long necked micro-Kjeldahl flask and 25 ml conc. H₂SO₄ was added. It was digested on a hot sand bath till the white
fumes appeared and the sample finally became clear and colourless. It was allowed to cool and diluted to 100 ml with water.

The digestion mixture (5 ml) was taken in a conical flask, 10 ml of solution b and a few drops of bromocresol green indicator were added. Sodium hydroxide (10 ml) was added to make the digest alkaline and steam distilled for 15 min. The tip was rinsed with a little distilled water and the contents titrated against N / 70 HCl. Protein content was calculated by N₂ x 6.25.

2.5.3 Fat

Fat content was determined by extracting 5 g of sample with petroleum ether (B.P. 40-60°C) using soxhlet apparatus for 16-18 h. The residual ether was removed from the extracted sample by evaporation. The extracted fat was then dried and weighed.

2.5.4 Determination of starch

Sample (0.5 -1.0 g) was taken in a conical flask and dispersed in 50 ml water. Termamyl (0.1 ml, heat stable α-amylase) was added and then kept in a boiling water bath for 10 min. After cooling, acetate buffer (pH 4.6) was added to 0.05 M concentration and equilibrated at 60°C. To this glucoamylase (50 mg) was added and incubated in a shaking water bath at 60°C for 2 h. The solution was filtered and made up to a suitable volume and the liberated glucose was determined by the TGO method. The glucose value multiplied by a factor, 0.9 gives the starch content.

2.5.5 Glucose by Glucose oxidase method

Tris- glucose oxidase reagent: Glucose oxidase (2000 units, 125 mg) was taken in a 100 ml standard flask and 50 ml Tris buffer (61 g of Tris dissolved in 5N HCl (85 ml) was diluted to 1 L with water and the pH was adjusted to 7.0) was added and mixed well. Peroxidase (0.5 ml of 0.1% aqueous solution) and O-dianisidine (0.5 ml, 10 mg/ml in 95% ethanol) were added. The volume was made up to the mark with Tris buffer, filtered and used.
Aliquot (0.5 ml) of the sample, digested with glucoamylase / α-amylase was mixed with Tris-glucose oxidase reagent (3 ml) and incubated at 37°C for 60 min. The reaction was stopped by placing the tubes in a boiling water for 5 min. The purple colour developed was read at 420 nm against a reagent blank. Standard curve was prepared by using D-glucose (10-50 µg).

2.5.6 Ash

Five grams of the sample was transferred to a silica crucible and charred on a heater. Thereafter, the silica crucible was kept in a muffle furnace at 600°±15°C for 2 h. The crucible with ash content was then cooled in a desiccator and weighed accurately to a constant weight.

2.5.7 Phosphorous content

Flour sample (1 g) was weighed into a preweighed silica dish and carbonized, after adding a little ethanol for wetting, over a direct burner flame. After the smoking ceased, the sample was incinerated in a muffle furnace at 550°C for 4 h into a white ash, samples not yielding white ash were treated with dil. HNO₃ (1:2, 1 ml) and evaporated to dryness on a water bath, returned to furnace and ignited further to white ash. The inner sides of the dish were washed with 29% HNO₃ (1ml), mixed well, covered and kept at 105°C for 30 min for conversion of phosphorous to orthophosphoric acid. The solution together with washings were transferred quantitatively into a 10 ml volumetric flask and the volume was made up to the mark, mixed well and filtered. To an aliquot (3 ml) of this solution (in a 10 ml volumetric flask) were added dil. HNO₃ (29%,1 ml), ammonium vanadate* (0.25%, 1 ml) and ammonium molybdate** (5%, 1 ml) reagents, mixed well and the solution was made up to the mark. The absorbance of the coloured solution was later (after 2 h) read at 460 nm against a reagent blank. Standard curve was prepared by dissolving 0.4390 g KH₂PO₄ in water (1 L) to obtain 10 mg phosphorous per 100 ml.

*Ammonium vanadate was prepared by dissolving the compound, 2.5 g in boiling water (600 ml), cooled to 60°C, and adding conc. HNO₃ (20 ml) and finally diluted to 1 L with water.
Ammonium molybdate was prepared by dissolving the compound (50 g) in warm water (900 ml) and then dilution to 1 L.

\[
\% \text{ Phosphorous} = \frac{P \times \text{Dilution volume} \times 100}{\text{Aliquot volume} \times \text{Sample weight in g} \times 1000}
\]

2.5.8 Total carbohydrates

a. Aqueous phenol solution: Phenol (5 ml) was mixed with water (95 ml).

b. Standard aqueous glucose (0-25 µg) solution

To 0.5 ml sample, 1.8 ml of conc. sulphuric acid was added directly to the mixture with a wide tipped pipette and was shaken vigorously, tubes were immediately transferred to ice - cold water bath. Then 0.3 ml of 'a' was added and mixed. The tubes were allowed to cool at room temperature for about 20 min and the colour developed was read at 480 nm.

2.5.9 Determination of dietary fiber

Reagents required: (a) 4N HCl, (b) 4N NaOH, (c) 0.1 sodium phosphate buffer, pH 6.0, (d) 95% ethanol, (f) acetone and (g) 78% ethanol.

Enzymes used: a) Pepsin, b) Pancreatin, c) Termamyl and d) Amyloglucosidase.

Fat was twice extracted from the sample by treating with methanol: chloroform: petroleum ether (1:1:1) at refluxing temperature. To the defatted samples (1 g) suspended in sodium phosphate buffer (25 ml, 0.1 M, pH 6.0), Termamyl (100 µl) was added and the flask was covered with aluminium foil and kept in a boiling water bath for 15 min. Samples were cooled, distilled water (20 ml) was added and the pH was adjusted to 1.5 with HCl and incubated with pepsin (100 mg) at 40°C for 60 min with continuous agitation. The contents were cooled, distilled water (20 ml) was added and the pH was adjusted to 6.8 with NaOH. They were again incubated with pancreatic amylase (100 mg) at 40°C for 60 min after cooling, the pH was adjusted to 4.5 with HCl and the solutions were
filtered through a pre-weighed sintered glass crucible (porosity G2) containing 0.5 g dry Celite as a filter aid. Samples were washed with 2x10 ml of distilled water.

a. Residue (Insoluble fiber): The residue was washed with 2x10 ml of 95% ethanol and 20 ml of acetone, and dried (crucibles) at 105°C to constant weight (D₁). Later it was incinerated at 550°C for 6 h and weighed after cooling in a desiccator.

b. Filtrate (Soluble fiber): To the combined filtrates and water washings, 95% ethanol was added (3 vol). Polysaccharides were allowed to precipitate for 1 h and filtered through a dry and weighed crucible containing 0.5 g Celite as filter aid. The precipitate was washed successively with 20 ml each of 78% ethanol, 95% ethanol and acetone. The crucibles were dried at 105°C overnight and weighed after cooling in a desiccator (D₂). They were then incinerated at 550°C for 6 h and weighed after cooling in a desiccator (I₂).

c. Blank: Insoluble and soluble blank values (B₁ and B₂) were obtained by running the experiment without sample.

\[
\frac{D₁ - (I₁ - B₁)}{W} \times 100
\]

% Insoluble dietary fiber =

\[
\frac{D₁ - (I₂ - B₂)}{W} \times 100
\]

% Soluble dietary fiber =

W - Sample weight (g)
D - Weight after drying (g)
I - Weight after incineration (g)
B - Weight of ash free blank.

2. 5.10 Resistant starch\textsuperscript{98}

Lipid extraction was done by treating the flour (50 g) with chloroform: methanol : petroleum ether (1:1:1, v/v) for 30 min at room temperature with constant stirring. (This treatment was done twice). It was filtered through Whatman filter paper and dried.
Samples (1 g each) suspended in distilled water (10 ml), were treated with Termamyl (heat stable α - amylase, 100 µl) for 45 min at boiling water bath. The samples were cooled, centrifuged and the supernatant was discarded. To the residue phosphate buffer (10 ml, 0.08 M, pH 6.0) was added, stirred well for 5 min and the pH was adjusted to 6.0 by adding NaOH (0.275 N) or HCl (0.325 N). The protease solution (100 µl), prepared just before use (10 mg protease in 1 ml 0.08 M, pH 7.5 phosphate buffer) was added and the solutions were incubated for 35 min at 37°C, with continuous agitation. Samples were centrifuged, supernatant discarded and to the residue acetate buffer (0.1 M, pH 4.6, 3 ml) was added, mixed well and pH was adjusted to 4.6 by adding NaOH or HCl. Amyloglucosidase solution (6 mg in 0.6 ml acetate buffer, pH 4.6) was added and incubated for 35 min at 60°C with continuous agitation. The samples were cooled and centrifuged. Supernatant was discarded and the residue (crude RS) was washed thoroughly for 4-5 times with water and freeze dried.

A freshly prepared 2 M KOH solution (5 ml) was added to the crude RS sample (1 g), stirred continuously for 30 min at room temperature, and neutralized by adding 2 M HCl. Samples were then centrifuged and to the supernatant, acetate buffer (3 ml, 0.1 M, pH 4.75) was added and the pH was adjusted to 4.75 by adding either NaOH or HCl. The solution was again treated with amyloglucosidase (2 mg in 0.2 ml) at 60°C for 35 min. Samples were cooled and centrifuged. From the supernatant, aliquots were taken and glucose was estimated by the TGO method94. The RS was calculated as glucose (mg) x 0.9.

2.6 Total Amylose Equivalent

Total amylose equivalent of samples was determined by a combination of the methods of Juliano99 and Sowbhagya & Bhattacharya100. 100 mg sample was mixed with 1 ml alcohol and 10 ml NaOH (1 N) and kept overnight. It was later boiled and and the volume was made up to 100 ml. Petroleum ether (7 ml) was added to 20 ml of above dispersion. After suctioning out the ether, carbon
tetrachloride (7 ml) was added and 5 ml from the top aqueous layer was collected. To this, distilled water (50 ml), acetic acid (0.1N, 1 ml) and Iodine solution (2 ml) were added, and the volume made up to 100 ml. Standard amylose solution (100 mg amylose) was also prepared as above. O.D was taken at 630 nm for both standard and sample, with a blank containing no sample.

Total amylose Equivalent = \[
\frac{R \times a \times 1 \text{ ml}}{A \times r \times 5 \text{ ml}} \times 100
\]

- \( R \) = Reading of sample solution
- \( A \) = Reading of standard amylose
- \( a \) = Amount of standard taken
- \( r \) = Amount of sample taken

2.7 Colour Values

The colour measurements of the flours were carried out using a Colour Measuring System (Model Lab Scan-XE, Hunter Associates Laboratory Inc. USA). A glass cell containing the powdered flour was placed above the light source and covered with a white plate and \( L, a, b \) values were recorded.

2.8 Pasting Behaviour

The pasting profile was determined using Rapid Visco Analyser (Model RVA-4, Newport Scientific Pvt Ltd., Australia). The sample (2 g, 14% moisture basis) was mixed with distilled water (25 ml) in aluminium sample holder can and cooked by heating at a rate of 6°C / min, held at 95°C for 5 min, and cooled (6°C / min) to 50°C and then held for 2 min. The parameters measured were: peak viscosity (PV in cP) i.e., the highest viscosity of the paste during the heating phase; hot paste viscosity (HPV) i.e., the viscosity at the end of the heating phase at 95°C; cold paste viscosity (CPV) i.e., the viscosity at the end of the cooling phase; break down (BD) viscosity (PV-HPV) and set back (SB) viscosity (CPV-HPV).
2.9 Swelling and Solubility

Swelling power and solubility patterns were determined as described by Schoch\textsuperscript{101}, with modification as per the method of Unnikrishnan and Bhattacharya\textsuperscript{102}. Flour (500 mg), was suspended in water (25 ml) for 30 min at different temperatures (30°C to 96°C). At each temperature interval, contents were centrifuged (2000 rpm for 15 min), the clear supernatant was carefully drawn off by suction into a porcelain dish and evaporated to dryness on a steam bath followed by vacuum oven drying at 105°C for 4 h and weighed. The insoluble residue was also weighed. The percentage of solubles and swelling power was calculated as mentioned below.

\[
\text{Solubility (on db)} = \frac{\text{Weight of soluble starch}}{\text{Weight of starch (g)}} \times 100
\]

\[
\text{Swelling power} = \frac{\text{Weight of residue}}{\text{Weight of starch (g) (100 - \% solubles)}} \times 100
\]

2.10 Gel Consistency

The gel consistency values of native and processed flours were determined as per the method given by Cagampang et al.\textsuperscript{103} and Perez\textsuperscript{104}.

The sample (100 mg. db) was wetted in a test tube (16x 150 mm) with 0.2 ml of 95% ethanol containing 0.025% thymol blue and dispersed in 2 ml. of 0.2 N KOH. The tube was heated in a vigourously boiling water bath for 8 min. The samples were then cooled at room temperature for 5 min., followed by cooling in an ice - water bath for 20 min. and then laid down horizontally for 1 h. The longer the gel travels, the lower is its consistency.

2.11 Sediment Volume

Sediment volume of potato and sweet potato flours was determined according to the method of Bhattacharya and Ali\textsuperscript{105}. 2 g (db) flour was taken in a 50 ml. glass stoppered measuring cylinder and 40 ml. of 0.05 N HCl was added
with gentle shaking. The cylinder was stoppered and the slurry was mixed by repeated inversions. A drop or two of amyl alcohol was added on top to disperse the froth and the cylinder was left undisturbed. The sediment volume was read after 4 h. Mean of three replicates was reported.

2.12 In-vitro digestibility

Flour (50 mg), suspended in sodium acetate buffer (pH 4.8, 0.05 M, 4ml) was gelatinized, cooled to 60°C and incubated with glucoamylase (50 units) for 30 min. The enzyme was inactivated by heating the digest in a boiling water bath for 10 min. The mixture was centrifuged (5,000 rpm for 15 min) and the residue was washed with water. The supernatent was made upto 15 ml with all washings and analyzed for released glucose by the TGO method.94

2.13 Texture Profile Analysis

Instrumental texture evaluation was carried out using a Universal Testing Machine (Texture Analyser, Model LR- 5K, Lloyd Instruments Ltd., England), equipped with a 1000 N load cell and a 35 mm cylindrical probe. The flour sample (50 g on d b) is kneaded for 4 min by adding water to make into a dough of 46, 47.5 and 49% moisture content each. The dough is kept for 20 min, covered with a wet cloth. The dough is cut into dices with a die of 20 mm depth and making it tight (without intercellular spaces) with the help of a roller pin (sheet maker). The sample is kept on closed condition covered with a wet cloth for another 10 min. A cross head speed of 50 mm min$^{-1}$ was used to compress the central area of dough samples to 80% of their original height. Samples were placed centrally beneath the probe in order that the probe is with a consistently flat surface at all times. Each sample was compressed twice in a reciprocating motion to give a two-bite texture profile curve. A range of values, to three decimal places, for textural attributes were extracted from the resulting curve. The parameters that could be derived from the curves included: hardness (N), cohesiveness (ratio), springiness (mm), gumminess (N), chewiness (N - mm) and adhesiveness (N).
2.14 Differential Scanning Calorimetry

DSC (differential scanning calorimetry) was carried out with Mettler DSC-30 (Mettler Toledo, Switzerland) instrument, equipped with STARe software. The PT - sensor was calibrated using Indium. Samples (20 mg) were accurately weighed, mixed with water (1:3 w/w) and were taken into standard aluminium crucibles. The crucibles were crimped and heated from 20-100°C for all flour samples at a scanning rate of 10°C / min. An empty crucible with pierced lid was used as a reference. Minimum of two measurements were performed for each sample. Both gelatinization temperature and enthalpy values of flour samples were obtained.

2.15 Gel Permeation Chromatography (GPC)\(^{106}\)

Sepharose CL-2B was packed into a glass column (1.7 x 92 cm) and equilibrated with the running eluent (water) overnight. The sample (10 mg), dispersed in DMSO (1 ml), was applied over the column bed and eluted by the descending method with water containing 0.02% sodium azide, at a constant flow rate (18 ml / h). Fractions (3.0 ml) were collected and an aliquot (0.5 ml) of the fraction was analysed for total sugars (O.D. at 480 nm).\(^6\)

2.15.1 Molecular weight determination\(^{107}\)

The approximate molecular weight (MW) of the starch was determined from a calibration curve prepared for standard dextrans (T-10, T-20, T-40, T-70, T-500 and T-2000) of known molecular weight on the same GPC column. The void volume (\(V_0\)) was determined by using a predialyzed blue dextran (5 mg / 0.5 ml water). The molecular weight values were computed from the standard plot of log MW vs. \(V_e/V_0\), where \(V_e\) was the elution volume of the respective fractions.

2.16 X-ray diffraction\(^{108}\)

X-ray diffraction patterns were determined using an EG-7G solid state germanium liquid N\(_2\) cooled detector Scintag XDS-2000 instrument equipped with a \(\theta-\theta\) goniometer at 25 mA and 30 kV. The starch samples were powdered to pass through a 189 \(\mu\)m sieve and kept for saturation with distilled water in a
desiccator overnight. The samples were exposed for 5 h to Co-K$_\alpha$ filtered radiation ($\lambda$ 1.54184 nm). Diffractograms were scanned from 5-40° at a diffraction angle of 2θ.

2.16.1 Determination of Crystallinity Index\textsuperscript{109}

The crystallinity index (CrI) was determined according to the method proposed for cellulose and applied to starch, by using the equation:

$$\text{CrI} = \frac{I_{110} - I_{am}}{I_{100}} \times 100$$

2.17 \textsuperscript{13}C NMR studies\textsuperscript{110}

\textsuperscript{13}C NMR spectra of starch samples dissolved in DMSO (Dimethyl sulfoxide) -d$_6$ - D$_2$O solution (85%) were recorded at a probe temperature of 80°C in a Bruker AMX-400 spectrometer, Germany, at 100 MHz. The spectra were obtained from 8000 scans in the pulsed FT mode using tetramethylsilane as the external standard.

2.18 Infrared spectroscopy

IR spectra were recorded in KBr discs on a FT-IR spectrometer (Model SPECTRUM-2000, Perkin Elmer, USA) under dry air at room temperature. Approximately 4 mg of dried flour sample was blended with 100 mg of potassium bromide (IR grade) and about 40 mg of the mixture was then used to prepare a pellet.

2.18.1 Determination of degree of acetylation (DS)\textsuperscript{111}

The DS was determined by considering the OH band at 3450 cm$^{-1}$ as a reference. The DS was defined from the ratio of absorbance: (A1733 cm$^{-1}$/ A3450 cm$^{-1}$).
2.19 Scanning electron microscopy

Samples were mounted on metallic stub, gold coated (~ 100 Å) with sputter coater (Polaron Sputter Coat System, Model 5001, England) and viewed under SEM 435 VP (Leo 40 Electron Microscopy Ltd. Cambridge, UK) at 10 kV.

2.20 Statistical analysis

The data were subjected to statistical analysis using the method of Akhnazarova and Kafarov\textsuperscript{112}. 
3.1 General

Potato and sweet potato constituting the staple foods in many developed countries, are an important source of starch and other dietary carbohydrates. Due to their perishable nature, their conversion into a shelf stable product like flour will be useful in the preparation of several products like bakery, noodles, sauce, soup, etc., besides serving the purpose of their availability during off seasons. The flour being starch rich, exhibit functional properties which will decide its suitability in specific product formulations. However, the properties may be influenced by the method of preparation, severity of heat treatment, type of chemical modification, the presence of other components such as fiber, protein, etc. The changes in structural characteristics of starches occurring as a result of modification / treatment may also be responsible for bringing specific functionality to the flours.

Most information on functional properties of potato and sweet potato refers to their starch instead of flour. The functional properties of flour are provided not only by the starch but also by other flour components. The limited data for flour functional properties are different from those of starch since extra constituents available in flour (non-starch polysaccharides, protein, fat, etc.), restrict access of water into the starch granules. For example, RVA visco-amylograph pasting parameters of the flour, determined in the present investigation, were not correlated to the RVA pasting parameters of the purified starch.

With a view to investigate the rheological, functional and structural characteristics of potato and sweet potato flour developed by different processing methods i.e, (i) physical, (ii) chemical and (iii) enzymatic treatments, the flours were prepared by drum drying and hot air drying (physical treatment), which are commonly used by the industry and chemical (acetylation) and enzymatic (glucoamylase) modifications of native flour by optimizing the process conditions. The proximate composition of native potato and sweet potato flours is given in Table 9.

Table 9. Proximate composition of potato and sweet potato flours*
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<thead>
<tr>
<th>Characteristic</th>
<th>Potato</th>
<th>Sweet potato</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein</td>
<td>9.1 ± 0.1</td>
<td>6.6 ± 0.1</td>
</tr>
<tr>
<td>Fat</td>
<td>0.3 ± 0.02</td>
<td>1.0 ± 0.07</td>
</tr>
<tr>
<td>Total carbohydrates</td>
<td>75.3 ± 1.0</td>
<td>73.0 ± 0.6</td>
</tr>
<tr>
<td>Starch</td>
<td>67.8 ± 0.6</td>
<td>63.5 ± 0.5</td>
</tr>
<tr>
<td>Amylose</td>
<td>22.8 ± 0.3</td>
<td>21.6 ± 0.2</td>
</tr>
<tr>
<td>Total dietary fiber</td>
<td>10.6 ± 0.3</td>
<td>17.5 ± 0.2</td>
</tr>
<tr>
<td>Ash</td>
<td>3.0 ± 0.1</td>
<td>1.0 ± 0.06</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.5 ± 0.01</td>
<td>0.1 ± 0.01</td>
</tr>
</tbody>
</table>

*Dry weight basis, SD±, n=3

### 3.2 Drum dried flour (DD)

Potato and sweet potato mash prepared from peeled, diced and cooked potato / sweet potato containing anti-browning agent, whey protein concentrate and monosodium glutamate to improve mouth feel was subjected to double drum drying. The speed of the drum was maintained at 3 rpm (Fig. 9). The ribbon like dried material was collected and size reduction was done in a hammer mill, provided with a sieve (500 µm). The experiment was repeated thrice and the mean colour (L, a, b) values of drum dried potato and sweet potato flour are given in Table 10. Compared to native samples, bright coloured flour was obtained by drum drying due to the inhibition of browning reactions by heat treatment and addition of sulphur dioxide.

### 3.3 Hot air dried flour (HD)

The dried cubes / dices prepared from peeled, blanched and sulphited potato / sweet potato were subjected to cross flow hot air tray drying with a tray capacity of 6 kg / m². The dried cubes were ground in a hammer mill provided with a 500 µm sieve (Fig. 10). The colour values of hot air dried (HD) flour are given in Table 10.
A. Potatoes

B. Peeling of potatoes  
C. Peeled potatoes  
D. Dicing / cubing

E. Steam cooking  
F. Mashing  
G. Drum drying

H. Flakes and Flour

Fig. 9. Preparation of drum dried potato flour

Table 10. Colour values of Potato and Sweet potato flours
<table>
<thead>
<tr>
<th>Sample</th>
<th>L</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato -N</td>
<td>71.1±0.1</td>
<td>2.0±0.02</td>
<td>17.1±0.1</td>
</tr>
<tr>
<td>DD</td>
<td>85.4±0.2</td>
<td>-2.0±0.01</td>
<td>11.4±0.1</td>
</tr>
<tr>
<td>HD</td>
<td>82.3±0.1</td>
<td>-1.5±0.01</td>
<td>9.9±0.05</td>
</tr>
<tr>
<td>Sweet potato- N</td>
<td>75.8±0.2</td>
<td>0.2±0.01</td>
<td>15.0±0.1</td>
</tr>
<tr>
<td>DD</td>
<td>83.7±0.1</td>
<td>-2.6±0.01</td>
<td>12.7±0.1</td>
</tr>
<tr>
<td>HD</td>
<td>80.2±0.1</td>
<td>-1.6±0.01</td>
<td>11.7±0.1</td>
</tr>
</tbody>
</table>

N: Native, DD: Drum dried, HD: Hot air dried flour; SD±, n=3

HD flour was relatively less brighter than DD flour as the product was the result of dehydration for longer period compared to drum drying. ‘L’ value of the modified flour samples gives the extent of difference / deviation in lightness / brightness from the control (L~100), which clearly showed DD flour was more nearer to control than the HD flour. The large differences between L, a, b, values of native flour and DD / HD flours were mainly due to browning reactions which had occurred in the latter in the absence of heat treatment and browning inhibitors.

Fig. 10. Physically modified flours
(I. Potato dices and flour (HD) and II. A. Sweet potato roots, B. HD dices, C. HD flour, D. DD flakes, and E. DD flour)

3.4 Acetylated flour
The most important reaction in the chemical modification of food starches is the introduction of substituent groups. These chemical modifications are of two types, monofunctional and di- or polyfunctional. Monofunctional reagents react with one or more hydroxyl groups per sugar unit to alter the polarity of the unit, sometimes making it ionic, and markedly influence the rheological properties of the starch. Monofunctional reagents most often used for food starch are acetic anhydride and propylene oxide. The former reacts to produce starch acetate (ester linkage)\(^{67}\). Acetylated starches with low degree of substitution (DS) possess unique characteristics such as low gelatinization temperature, high swelling and solubility, and good cooking and storage stability.\(^{68,69}\) Acetylated starches are also less susceptible to retrogradation. It is thought that the amylose fraction which is mainly responsible for starch retrogradation, is modified and as a result is less susceptible to retrogradation\(^{70}\). The physicochemical properties of acetylated starches depend on their chemical structures, DS and acetyl group distributions. Few publications dealt with structure features of acetylated starches.\(^{71,72,73}\)

Studies on acetylation of potato and sweet potato flours were carried out and the degree of substitution was determined to select an appropriate method to carry out further investigations. Method I was found to be unsuitable for acetylation of potato and sweet potato flours. Though methods 2 and 3 yielded acetylation, method 3 was found to be more appropriate for larger batches wherein NaHCO\(_3\) was added in place of NaOH to overcome the problem encountered with the commonly used method\(^{87}\). The acetylated sample was dried at 40°C (Fig.11).
In Fig. 12 are given the FTIR spectra of potato and sweet potato flours acetylated by three different methods as described in 2.2.4. These spectra provide evidence of acetylation in flour samples by the presence of the ester carbonyl group stretch (C=O) at 1731 cm\(^{-1}\) and corresponded to 0.6 ml (method 1), 5 ml (method 2) and 4 ml of acetic anhydride (method 3), respectively. Table 11 shows the DS obtained for the above described acetylated flour samples.

**Fig.12. FT-IR spectra of potato (1,3,5) and sweet potato flours (2,4,6) acetylated by different methods**
Table 11. Degree of substitution of acetylated flours

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method - 1</th>
<th>Method - 2</th>
<th>Method - 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato flour</td>
<td>0.02±0.001</td>
<td>0.36±0.02</td>
<td>0.29±0.01</td>
</tr>
<tr>
<td>Sweet potato flour</td>
<td>0.04±0.001</td>
<td>0.39±0.01</td>
<td>0.35±0.02</td>
</tr>
</tbody>
</table>

SD± n=4

3.5 Enzyme modified flour

During *in vitro* alpha amylolysis of different starch granules, the enzyme attack is rather restricted and is usually from outside inwards, i.e. exocorosion\(^{77}\). On the other hand, *in vivo* the granules are subjected to cumulative actions of salivary amylase, dilute acid (by gastric juices) and pancreatic alpha amylase and intestinal microflora and as a result the granules are better digested.

The granule degradation was mostly confined to pitting and surface erosion all over. Some researchers have shown 'onion-type' layering of the granules\(^{78}\). Information on the properties of structural and functional properties of potato / sweet potato flours when subjected to enzymatic modification is rather scarce. In order to determine the characteristics of enzyme modified flour, the native flour samples were subjected to glucoamylase action and the reducing sugars produced as a result of breakdown of starch were estimated. Table 12 gives the reducing sugars produced by breaking down of starch by glucoamylase at different levels of concentration and duration (incubation time). The production of reducing sugars decreased with increase in incubation time, especially at 2.5 and 5% enzyme concentration levels, which may be due to product inhibition reaction.

Table 12. Reducing sugars in enzyme modified flours

<table>
<thead>
<tr>
<th>Incubation time (Min)</th>
<th>1% Enzyme</th>
<th>2.5% Enzyme</th>
<th>5% Enzyme</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P</td>
<td>SP</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>SP</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>SP</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>----</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>30</td>
<td>6.2±0.2</td>
<td>10.2±0.1</td>
<td>9.0±0.1</td>
</tr>
<tr>
<td>60</td>
<td>6.5±0.1</td>
<td>10.4±0.2</td>
<td>6.6±0.1</td>
</tr>
<tr>
<td>90</td>
<td>7.0±0.15</td>
<td>10.8±0.2</td>
<td>6.3±0.1</td>
</tr>
<tr>
<td>120</td>
<td>7.5±0.2</td>
<td>15.0±0.1</td>
<td>6.3±0.2</td>
</tr>
<tr>
<td>SE</td>
<td>0.02</td>
<td>0.12</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Considering the optimum concentrations of enzyme for production of sizeable quantity of reducing sugars, potato and sweet potato flours modified by enzyme at 1% level and incubated for 90 min and 120 min, respectively were selected for carrying out further investigations (Fig. 13). Fig. 14 shows the physically, chemically and enzymatically modified flour samples of potato and sweet potato.

![Fig. 13. Enzymatically modified flours of A. Potato, B. Sweet potato (1.Native, 2. Enzyme modified)
3.6 Scanning electron microscopy (SEM) studies

3.6.1 Potato flour

Scanning electron microscopy (SEM) studies of differently treated potato flour samples were undertaken to determine the changes in the morphological features of their starch granules. Scanning electron micrographs of raw and modified samples are shown in Figs 15 and 16.

Native starch has oval, spherical and irregularly shaped granules of 6-60 µm size, while in drum dried (DD) and hot air dried (HD) samples, the granular appearance totally disappeared. Processing also resulted in agglomeration of granules that formed into an aggregated mass comprising of several small granules. The size of each such agglomeration of granules was found to be more than 100 µm. The agglomeration of small granules was more pronounced during drum drying. Overall, the morphological features of DD and HD starch granules resembled each other, though process conditions and severity of heat treatment differed.

Disruption of the granules indicated gelatinisation of starch in both the drying processes. However, the DD samples showed more of ruptured granules that exposed the internal surface. The release of amylose during processing...
would have resulted in hollowness of the processed samples, especially the drum dried samples, whereby the granules appear to be broken open (Fig. 16).

Fig. 15. SEM of modified potato flours
(1. Native 500 x, 2. DD 200 x 3. HD 200 x, 4. Acetylated 500 x, and 5. Enzyme modified 1000 x)
This may also have led to better hydration of DD and HD samples that determined the pasting viscosities. The inner portion of some of the granules appear terraced or step shaped (Fig. 16 B) which conforms to the layered internal structure of starch granule. Tamaki et al.\textsuperscript{113} postulated that if starch granule is a pearl string, in which pearl is the crystal and string is amorphous, and heat treatment brings about drastic movement at string, then the string is disrupted and pearl is liberated.

![Fig. 16. SEM of agglomerated granules of processed potato flours (A.Drum dried, B. Hot air dried, 500 x)](image)

The acetylated samples showed indentation of the granules as a result of modification, whereby the granules appeared as clusters / bunches (Fig. 15). The fusion of starch granules in acetylated samples could be attributed to the introduction of hydrophilic groups to the starch molecules, which resulted in increase of hydrogen bonding\textsuperscript{86}. Therefore, starch molecules, coalescing together resulted in fusion of granules. The fragmentation of the granules would have taken place during the process of indentation. The cavities observed in some granule indentations would have originated from deformation caused by other granules and / or constituents. The fragmentation and the presence of substituents in acetylated samples would have influenced the crystallinity of the starches which, inturn would have decided their altered functional properties.

The enzyme modified samples of potato flour have shown slight surface erosion in all the granules. Few granules of native flour treated with
glucoamylase showed surface terraces, which are exposed edges of layered internal structures in some granules (Fig. 15). However, a large proportion of starch granules of potato attacked by the enzyme did not show the outer striated or the inner shell structure on the same granule. The enzyme attack manifested itself in only superficial surface erosion of the granules. This might probably be the result of the overall composition per se of potato starch and / or due to the poor adsorption of glucoamylase onto the granule surface.

3.6.2 Sweet potato flour

SEM studies corresponding to the starch granules of raw and modified sweet potato flour show considerable structural differences (Fig.17). Raw starch granules are round, spherical of 4-26 µm size, while in modified samples the granular characteristics totally disappeared.

The morphological features of DD and HD samples revealed similar type of changes as described in the case of potato flour samples. The entire granule population seems to be clustered to form an aggregated mass comprising of several small granules, more so during drum drying. At 200 x magnification, the size of agglomerated DD granules ranged from 70-80 µm (smallest) to 80-220 µm (largest), whereas it ranged from 40-60 to 80-130 µm in HD granules (Fig. 17). Chen et al. 22 reported that the noodle quality was determined by the source and size of the starch granules.

The disruption of the granules indicated complete gelatinization of starch in both the drying processes. The flat surfaced granules in DD samples were more conspicuous due to the flattening of clustered granules between the rollers during drum drying process.
Indentations of acetylated flour sample and exo-corrosion of enzyme modified samples were noticed. The penetration of glucoamylase was found to be more as the granules showed serrated surface and breakage of outer layer in some granules (Fig. 18). This was also evident by the release of more reducing sugars as a result of amylolysis of sweet potato samples (Table 12).
3.7 Fractionation Studies by Gel Permeation Chromatography (GPC)

3.7.1 GPC profiles of potato flour

The flour samples, solubilized in dimethyl sulphoxide (DMSO), were subjected to GPC on Sepharose CL-2B to check for their homogeneity. GPC on Sepharose CL-2B fractionates molecules in a way opposed to that of hydrodynamic volume. It is a versatile technique to separate neutral polymers based exclusively on differences in their molecular weight values. It is commonly used for the separation of starch components. Amylose, amylepectin as well as the intermediate fraction have wide variations in their elution volumes (Ve), and accordingly they have different molecular weight values. The latter is deducible from a pre-calibrated GPC column (Fig. 19).
Fig. 19. Pre-calibrated curve for determination of molecular weight.

GPC of native flour comprised two major peaks which were obtained at tube numbers 17 and 35. The first peak corresponds mainly to amylopectin and its molecular weight was found to be $60.2 \times 10^5$ Da (Table 13). This first distribution area is presumed to consist of amylopectin that eluted first because the time lag for starch to be eluted is related to molecular size.\textsuperscript{114}

**Table 13. GPC fractions of modified potato flours**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbohydrate* (%)</th>
<th>Molecular weight (10^5) Da</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fr-I</td>
<td>Fr-II</td>
</tr>
<tr>
<td>Native</td>
<td>78.1</td>
<td>21.9</td>
</tr>
<tr>
<td>Drum dried</td>
<td>57.2</td>
<td>31.6</td>
</tr>
<tr>
<td>Hot air dried</td>
<td>62.8</td>
<td>37.2</td>
</tr>
<tr>
<td>Acetylated</td>
<td>62.3</td>
<td>37.7</td>
</tr>
<tr>
<td>Enzyme modified</td>
<td>61.3</td>
<td>38.7</td>
</tr>
</tbody>
</table>

*Total carbohydrates (%) in Fr-I + II + III = 100
The fraction - II, generally considered as amylose entered the gel and was eluted over a wide range. The degraded products in the modified flour samples entered the gel and were eluted in Fraction-II and III, thereby increasing the proportion of carbohydrates in these fractions. The recovery of carbohydrates in the chromatographed fractions ranged between 82% and 96.6% with a mean of 89.3%.

Fig. 20 shows typical chromatograms of native and processed potato flour samples. Table 13 shows data on the proportion of carbohydrates (absorption at 480 nm) at fractions I, II and III and their corresponding molecular weights. It could also be seen from Table 13, that the carbohydrate content in Fraction-I of the total starch in all the modified flours decreased with consequent increase of Fraction-II and III. Further, among the flour samples, the degradation of Fraction I was maximum in the case of DD flour. It appeared that the high molecular weight branched molecules (Fraction-I) of native flour were more prone to degradation, due to their large molecule size with many branch points that become vulnerable to degradation under severe conditions and thermal forces.

**Fig. 20. GPC pattern of physically modified potato flours**
(N:Native, DD:Drum dried and HD: Hot air dried flours)
It could be noted from Fig. 20 that the peak of the fraction-II of all modified samples eluted at a slightly lesser elution volume than that of native flour. The shift of Fraction-II peak towards the higher molecular weight side increased more in DD sample. The formation of linear oligosaccharides in DD and HD potato flours may be the reason for the reduction in the intensity of the first peak and increase of subsequent peaks.

Both acetylated and enzyme modified samples showed two peaks each at the same tube numbers indicating similar molecular weight obtained as a result of modification, though the fractions differ in their carbohydrate content (Table 13).

![GPC pattern of modified potato flour](image)

**Fig. 21 GPC pattern of chemically and enzymatically modified potato flours**

Hence, starch in treated potato flour samples was degraded to lower molecular weight components during the modification process as evidenced by GPC
studies. Upon fractionation, the content of carbohydrate of high molecular weight fraction decreased, with a proportionate increase in the lower molecular weight carbohydrate fractions. Among the modified flour samples, molecular degradation was maximum in drum dried sample as can be seen in Fig. 20.

3.7.2 GPC profiles of sweet potato flour

The GPC profiles of sweet potato flour, fractionated through Sepharose CL 2B column are shown in the Figs. 22 and 23. The major peak was obtained in void volume and the second fraction was eluted later. The degradation of starch led to the formation of low molecular weight first fraction with proportionate increase in the subsequent fractions (Table 14).

![Fig. 22. GPC pattern of physically modified sweet potato flours](image-url)
The degraded products of acetylated and enzyme modified samples entered the gel and were eluted as Fractions II and III (Table 14). Excepting enzyme modified samples, others showed three peaks. The

![Fig. 23. GPC pattern of chemically and enzymatically modified sweet potato flours](image)

**Table 14. GPC fractions of modified sweet potato flours**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbohydrate (%)</th>
<th>Molecular weight ($10^5$) Da</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fr -I</td>
<td>Fr - II</td>
</tr>
<tr>
<td>Native</td>
<td>77.3</td>
<td>22.7</td>
</tr>
<tr>
<td>Drum dried</td>
<td>21.4</td>
<td>27.5</td>
</tr>
<tr>
<td>Hot air dried</td>
<td>25.8</td>
<td>22.1</td>
</tr>
<tr>
<td>Acetylated</td>
<td>28.6</td>
<td>15.6</td>
</tr>
<tr>
<td>Enzyme modified</td>
<td>22.3</td>
<td>77.7</td>
</tr>
</tbody>
</table>

*Total carbohydrates (%) in Fr-I + II + III = 100
information on iodine binding nature of GPC fractions, lamda max of iodine -
polysaccharide complexes and aggregation of degraded molecules will be useful
for further understanding on starch degradation.

3.8 Infrared spectroscopy studies

3.8.1 Potato flour

Interpretation of the IR absorption bands was made in the light of earlier
investigations.\cite{115,116}. The infrared spectra of potato flour samples exhibited bands
that originate mainly from the vibrational modes of amylose and amylopectin (Fig.
24), which have been shown to be sensitive to changes in molecular structure,
such as starch chain conformation, helicity, crystallinity and the retrogradation
processes.\cite{117,118} The O-H (3000-3600 cm\(^{-1}\)) stretch, C-H (2800-3000 cm\(^{-1}\))
stretch, the skeletal mode vibration of the glycosidic linkage (900-950 cm\(^{-1}\)) in
infrared spectra are clearly seen for all the modified samples. The changes in
intensity of some FTIR bands and band ratios as a function of modification could
be seen in Fig. 24.
The changes in absorption spectra of DD and HD flour samples were mainly due to gelatinization of their starch during processing. These samples were thus found to be sensitive to changes in the range 900-1200 cm\(^{-1}\). Starch gelatinization plays an important role during processing of starch products. Gelatinization behaviour varies with the differences in composition and structure\(^{119}\). The changes in the crystallinity of modified samples reflected their respective bands around 1640 cm\(^{-1}\). Native potato sample showed band at 1648 cm\(^{-1}\) whereas the intensity of DD and HD samples decreased more compared to the other modified samples, DD being with lowest intensity (1640 cm\(^{-1}\)), indicating more changes in its crystallinity. Therefore variations in the crystallinity of different starches could be observed as this band was attributed to the water absorbed in the amorphous region of starch granules and also to the crystallinity of starch.

The change in IR absorbance at 1020 cm\(^{-1}\) (C-O-H bending and deformation) and 1640 cm\(^{-1}\) (O-H related vibration) indicates the rupture of the inter- and intra- molecular hydrogen bonds and hydrophobic bonds of starch, and formation of intermolecular hydrogen bonds between starch and water accompanying the phase transition in DD and HD samples. Absorbances at 1150, 1080 and 1020 cm\(^{-1}\) are more sensitive to the conformational changes.
during processing, indicating that the short range order and helicity changes when crystallinity and molecular orientation are lost\textsuperscript{120}.

An extremely broad band due to hydrogen bonded hydroxyl groups (O-H) appears at 3403 cm\textsuperscript{-1}, which is attributed to the complex vibrational stretches associated with free, inter- and intra-molecular bound hydroxyl groups that make up the gross structure of starch. The sharp band at 2926 cm\textsuperscript{-1} is characteristic of C-H stretches associated with the ring hydrogen atoms. Intensity changes in C-H stretch range could be attributed to the variations in the amount of amylose and amylopectin present in starches\textsuperscript{121}.

The degree of substitution (DS) for a starch derivative is defined as the number of hydroxyl (OH) groups substituted per D-glucopyranosyl structural unit of the starch polymer. Since each D-glucose unit possesses three reactive hydroxyl groups, the maximum possible DS value is 3. The yield of recovered material was slightly higher than the initial sample due to the addition of substituted groups. Therefore, the reactions to form acetylated starches can be controlled with high accuracy by adjusting the molar ratio of the reagent and catalyst in the reaction mixture, in order to obtain the desired DS value.

The IR spectra provided evidence for acetylation by the presence of the ester carbonyl group stretch at 1731 cm\textsuperscript{-1} (C=O). The strong band at 3403 cm\textsuperscript{-1} (hydroxyl groups) of native sample (Fig.24) decreases in intensity after the acetylation reaction as the number of hydroxyl groups present diminishes. Intensity of this band was found to be decreased in all the modified samples compared to native sample. Detection of these structural changes in starch that are due to chemical modifications is an important industrial necessity in order to determine quality of modified starches\textsuperscript{122}. Weakest hydroxyl stretching band at
3345 cm\(^{-1}\), was observed in enzyme modification. The bands in the fingerprint region associated with C-O stretching (1083, 1030 cm\(^{-1}\)) decrease in relative intensity to those associated with the C-H stretch.

3.8.2 IR studies of Sweet potato flour:

The bands corresponding to different stretches (O-H; C-H; COO and C-O) are given Fig. 25. The pattern of changes in sweet potato samples almost resembled those of potato samples excepting a few variations. For eg. decreased intensities of 2800 - 3000 cm\(^{-1}\) (C-H stretch) and 1600 cm\(^{-1}\) (COO group), bands.

Wave numbers (cm\(^{-1}\))
3.9 Pasting properties (RVA studies)

3.9.1 Potato flour

Pasting properties of potato flour which indicate the extent of molecular degradation / changes and degree of paste viscosity and stability of starch were determined with Rapid visco analyser (RVA). Results from RVA amylograph test included peak viscosity (PV), hot paste viscosity (HPV), cold paste viscosity (CPV), breakdown viscosity (BD) and setback viscosity (SB).

The pasting curves of native and modified flours are given in Fig.26. The native flour has shown a pasting curve, typical representative of unprocessed raw starch product with a very high peak, hot paste and cold paste viscosities. The pasting properties and viscosity of flours high in starch content can to a large extent be attributed to the starch in the flour.

Native potato flour showed unrestricted swelling, exhibiting maximum viscosity (PV) at a relatively shorter period of heating. As the temperature increased, the starch granules swell and increase the viscosity of the starch paste until the peak viscosity (PV) is attained. A higher peak viscosity corresponds to a higher thickening power of starch. Though the viscosity of the flour increased rapidly with increase in temperature, i.e PV, it decreased during the holding period at 95°C (HPV), due to granule fragmentation. The granules being fragile, the viscosity falls gradually with time of heating.
Peak viscosity of DD and HD samples were 328 and 363 cP compared to 803 cP of that of native flour. The starch granules were probably completely gelatinized as a result of processing and no further swelling occurred during the heating cycle in RVA apparatus. Both DD and HD samples manifested low initial amylograph viscosities and the values did not increase significantly even when held at 90°C (HPV) compared to that of native flour, indicating DD and HD flours have been modified to a considerable extent as a result of processing.

Fig. 26. Viscoamylograms of potato flours
The peak viscosity at any concentration is an important distinguishing feature of a starch. High paste viscosities are desirable in flours used as thickeners\textsuperscript{123}. The hot paste viscosity measures the tendency of the paste to breakdown during cooking, and a high value is preferred / required for industrial purposes\textsuperscript{124}. The changes in breakdown values (PV- HPV) of DD and HD flour samples reflect changes in crystallinity, swelling and extent of amylose leaching. The amylose molecules being randomly dispersed, can orient themselves in parallel fashion to form aggregates of low stability, leading to gel formation\textsuperscript{125,126}.

On cooling the paste to 50°C (CPV), there was an increase in viscosity, indicating the tendency of starch to associate or retrograde. The setback (CPV - HPV) or retrogradation value was lower in DD sample compared to HD sample. When hot starch pastes are cooled, the extent of increase in viscosity is governed by the retrogradation tendency of the starch. This behaviour is largely determined by the affinity of hydroxyl groups of one molecule to another. A low set back value indicates a non-cohesive nature of starch, which is useful in many industrial applications. A high setback value is useful when the starch is to be used in products, which require a high viscosity and paste stability at low temperature\textsuperscript{127}.

The high stability of DD and HD flours during heating and cooling processes, demonstrates that these samples have possible uses in products requiring sterilization such as baby food. This is especially important since the viscosity of most commercial native starches decrease during these processes\textsuperscript{128}. Viscosity is important when processed flours become the basis for infant foods where calorie density is critical or drinks where consistency is an important acceptability consideration.
The acetylated potato flour showed least peak viscosity (21 cP) showing restricted swelling of starch granules, due to the presence of substituent functional groups. The viscosity values obtained after isothermal holding at 95°C (HPV) were much lower than PV values.

The tendency towards setback or gel formation has been minimized in the chemically modified starches due to the presence of functional groups which prevents starch chains from associating. Further, partial depolymerization that has occurred during the process of modification would also have resulted in low setback. There was no marked increase in the apparent viscosity of acetylated samples, on cooling, which revealed that the starch was already sufficiently degraded during acetylation, resulting in negligible increase in cold paste viscosity. Esterification of starch hydroxyl groups to give acetate groups results in reduced pasting temperatures due to weakening of associative forces.\textsuperscript{129}

The high pasting values of enzyme modified flour (Fig. 26) show that the starch molecules are strengthened as a result of modification to resist breakdown of paste. Further, enzyme modified samples exhibited resistance to retrogradation as indicated by low setback value than that of native flour.

The thermal and mechanical stability and the low retrogradation pattern shown by enzyme modified flours are important characteristics useful for baked and frozen products. The high stability ratio of starch was correlated to hardness of cooked noodles\textsuperscript{130}. The variability of functional properties of enzyme modified flour is also attributed to starch and protein moieties. Starch with a higher peak viscosity is desirable for making food products such as jelly and binders. Use of enzyme modified flour is recommended for manufacture of low fat - low sugar wafers and other bakery products. Enzyme modified flour showed improvement in the emulsifying and oil absorption capacity\textsuperscript{85}.

\textbf{3.9.2 Pasting behaviour of sweet potato flour}
The pasting behaviour of modified samples of sweet potato flour differed from that of native flour. Though the pasting viscosities of modified sweet potato flour samples showed similar trend as those of potato flour, the paste viscosities of HD samples of sweet potato were found to be much lower than that of DD samples (Fig 27). This was due to further breakdown of HD starch by the endogenous amylases present in them in addition to the thermal degradation, as the drying temperature (65-70°C) was most favourable for the activity of amylases. The gel fractionation studies of sweet potato samples by GPC also confirmed the higher breakdown of starch in HD sample, compared to DD samples.

Fig. 27. Viscoamylograms of modified sweet potato flours
3.9.3 Pasting behaviour of isolated starches

To determine the extent of differences between the values of pasting viscosities of flour samples and that of starches isolated from them, DD and HD flour samples of potato and sweet potato were selected; starch was isolated from them and subjected to determination of their pasting behaviour by RVA (Fig. 28)

![Viscoamylograms of starches](image)

Fig. 28. Viscoamylograms of starches A. Potato and B. Sweet potato (NS: Native starch, DS: Drum dried starch, HS: Hot air dried starch)

The pasting viscosity values of flour were found to be different from that of starches isolated from them. It appeared that the extra constituents available in flour (protein, fat etc.) restricted the access of water into the starch granules, whereby lower viscosities were obtained for flour samples (for eg. native potato flour / starch: PV 287 / 3439, HPV 264 / 3173, and CPV 366 / 4376 cP). Hence, the RVA pasting viscosities of the flour were not correlated to the RVA pasting profile of its isolated starch.

3.10 Dough Rheology
The science of rheology is devoted to the study of flow and deformation. Viscosity and consistency (parameters of fluids) are differentiated from the texture (parameter of solids) on the basis of amount of the force required to initiate flow.\textsuperscript{131} A typical force-distance curve represents the first and second bites (Fig. 29). The 'pip' is an indication when every time the cross head commenced a downward stroke. The parameters that were derived from the curves are as follows: Hardness, cohesiveness, springiness, gumminess, chewiness and adhesiveness.

![Typical texturometer curve](image)

**Fig. 29. Typical texturometer curve**

**3.10.1 Dough rheology of Potato flour**

The textural attributes of potato dough prepared from differently treated flour at three different levels of moisture content are presented and the typical curves of the flour samples as influenced by moisture content are given in Figs. 30 and 31. A moisture range of 46-49\% (46, 47.5 and 49\%) was selected based on the preliminary studies with different levels of water to obtain a consistent dough.

Mean hardness values, i.e the force necessary to deform the sample between the molar teeth, ranged from 8.1 N to 12.1 N in native to 8.7 N to 37.1 N
in doughs prepared from modified flours. Native sample was less harder than the
other modified samples at all moisture levels studied. The DD flour sample
yielded the highest mean scores, followed by enzyme modified flour. Among the
modified flours, the dough prepared from acetylated flour showed lesser
hardness values at 46 and 47.5% water levels. Hardness values of potato dough
decreased with increasing water levels in all the samples.

Cohesiveness values indicated the strength of the internal bonds that
made up the body of potato dough. Mean cohesiveness (%) scores ranged from
0.03 - 0.13; 0.03- 0.13 and 0.02 - 0.14 for the flour samples at 46, 47.5 and 49%
moisture levels, respectively. The dough prepared from DD flour samples yielded
the highest mean scores for each treatment.

The enzyme modified samples did not differ much from native samples in
its cohesiveness. The HD flour samples were found to be significantly less
cohesive than all other flour samples. Cohesiveness values of flour samples did
not change much with increase in moisture level.

Springiness is the rate at which the deformed material goes back to its
undeformed state once the deforming force has been removed. Springiness
scores ranged from 1.0 - 4.0; 1.1 - 3.8 and 0.8 - 3.6 mm for samples added with
46, 47.5 and 49% moisture levels, respectively (Figs 30, 31).

Excepting drum dried dough, other dough samples were not much
different from each other in their springiness, whose values ranged from 0.8 -1.7.
Drum dried dough showed greater springiness values, which decreased with
increase of water content and the values ranged from 3.6 to 4.0. Though all the
dough samples showed a decrease in springiness with increase in water level,
the dough from enzyme modified flour showed a slight increase in its springiness
values. The lower values of elasticity / springiness of acetylated and enzyme modified samples may be due to the reduced exudation of amylose which prevented the swelling and solubility. With reduced leaching of amylose, the elastic quality of dough is diminished as the starch molecules could not establish enough junctions of adequate size to give an elastic net work.

Gumminess is the energy needed to disintegrate a semi-solid food to make it ready for swallowing. Gumminess values of potato doughs prepared from differently treated potato flour samples at 46, 47.5 and 49% levels ranged from 0.7 - 4.7 N; 0.6-3.5 N; and 0.2 - 3.2 N, respectively. However, dough samples from DD, acetylated and enzyme modified flours showed significantly greater gumminess values compared to native samples, DD sample yielding the highest value. The dough made with HD flour was found to be least gummy. With increase in moisture levels, the dough samples showed a decrease in their gumminess values.

Chewiness is a measure of the length of time required to masticate a solid food until it is ready for swallowing. Chewiness values of the dough samples at three different moisture levels ranged from 0.9 - 18.8 N-mm; 0.7 - 13.1 N-mm; and 0.2 - 11.4 N-mm, respectively. The dough from drum dried sample yielded the highest values and was about 13 times more chewy than the native sample. The dough from hot air dried flour was least chewy amongst the dough samples studied.

The acetylated and enzyme modified samples showed slightly higher values than native samples. Within a given sample, the results showed that the dough samples were found to be more chewy at 46%
moisture level than at higher moisture levels i.e, the chewiness values of dough samples decreased with increase of water (Fig. 30).

Fig. 30. Texture profile analysis of potato dough of physically modified flours at 46, 47.5 and 49% moisture levels (A. Native, B. Drum dried, C. Hot air dried)
Adhesiveness is the work required to overcome the attractive forces between the surface of the food and the surface of other materials with which food comes into contact. The values ranged from -0.5 to 1.9 N; -1.0 to 2.0 N and -1.2 to 2.6 N for the samples with 46%, 47.5% and 49% moisture levels, respectively. The dough prepared from native flour showed more adhesiveness values compared to modified samples. Excepting the dough samples of native and enzyme modified flour, the adhesiveness values decreased with increase in water. The reduction in adhesiveness values was more significant in acetylated samples with increase in moisture levels.

Dough rheology (Texture profile analysis) showed that DD sample was more hard, springy, gummy and chewy, whereas, HD flour was less cohesive, springy, gummy and chewy than the other modified samples. The gelatinization temperature, amylose / amyllopectin ratio, crystallinity of starch granules would have influenced some of these properties.

The pre-gelatinized (DD / HD), acetylated and enzyme modified samples have altered dough rheology. Drum dried sample being more thermally degraded and gelatinized, showed improved textural characteristics. Enzyme modified and acetylated samples also brought improvements in textural properties. Hot air dried flour was comparable with native flour in its dough rheology, which may be due to the retrogradation of starch that took place during the drying process.
Fig. 31. Texture profile analysis of potato dough of chemically and enzymatically modified flours at 46, 47.5 and 49% moisture levels (A. Native, B. Acetylated, C. Enzyme modified)
Therefore, the dough rheology of modified potato flour was influenced by processing conditions, type of modification in addition to the factors discussed earlier. The textural properties vary with change in water content, thereby highlighting the importance of moisture content and provides guidelines for successful operation of processed products' development.

Both transparency and overall acceptability of noodles were significantly correlated with cohesiveness values of texture profile analysis (TPA)\textsuperscript{132}. Low cohesiveness of noodles may result from insufficient release of amylose due to strong internal bonds, resulting in low solubility and swelling power during cooking\textsuperscript{133}. Cohesiveness by TPA is a useful technique which could be used to rapidly screen starch samples before conducting a more laborious sensory evaluation\textsuperscript{134}.

Hardness, cohesiveness and gumminess are measures of different aspects of intermolecular forces between the starch granules / molecules and swollen granules in the dough. The decrease in cohesiveness and gumminess is attributed to lower granule swelling power and decreased amylose leaching, as a result of increased granule internal stability\textsuperscript{135}.

3.10.2 Dough rheology of sweet potato flour

The dough rheology of differently treated sweet potato flour exhibited similar features as that of potato. The TPA studies revealed higher values for sweet potato samples compared to potato flour samples in all the textural attributes studied (Figs. 32 and 33).
Fig. 32. Texture profile analysis of sweet potato dough of physically modified flours at 46, 47.5 and 49% moisture levels (A. Native, B. Drum dried, C. Hot air dried)
Fig. 33 Texture profile analysis of sweet potato dough of chemically and enzymatically modified flours at 46, 47.5 and 49% moisture levels (A. Native, B. acetylated, 3. Enzyme modified)
Significant rise was noticed in chewiness values of HD flour of sweet potato samples. The values were found to be much higher than acetylated and enzyme modified samples, though lesser than DD samples. It reveals further break down of starch in HD samples that resulted in resistance to retrogradation unlike HD samples of potato.

3.11 Differential scanning calorimetry (DSC)

3.11.1 Potato flour

DSC has been extensively used to study the gelatinization or melting characteristics of crystalline forms of starch. DSC is useful in understanding the phenomenon of starch gelatinization and retrogradation, particularly to know about gelatinization temperature (GT) range, the nature of lipid - amylose complex, and retrograded starch. Essentially DSC analyses the changes in hydrogen bonding, occurring between the hydroxyl groups of adjacent starch molecules, throughout the process of heating and cooling.

The gelatinization endotherm obtained by DSC gives an overall measure of the progressive loss of long, medium and short range order in starch granule crystallites, as they are gradually heated in excess water. The amount of heat required to gelatinize the starch is termed as enthalpy (ΔH). GT is a qualitative index of the crystalline structure, whereas ΔH is a quantitative measure of the order.\textsuperscript{136,137} The temperature at which starch gelatinizes is given as T onset (To), T peak (Tp) and T conclusion (Tc).

Thermal properties of modified potato flour samples, measured by DSC, differed significantly. Endotherm peaks of native flour samples appeared between 77 - 92°C (Fig. 34). The transition temperatures (To, Tp and Tc), ΔH gel of different flour samples are summarized in Table 15. The differences in transition temperatures may be attributed to the differences in granular structure, amylose content and gelatinization temperature between the starches.\textsuperscript{138}
A typical DSC endotherm for gelatinization of native flour was obtained (Fig. 34). The DD and HD flours did not show any gelatinization endotherm when heated up to 100°C, which confirmed the changed nature of starch granules as a result of processing. Gelatinization enthalpy depends on a number of factors such as crystallinity, intermolecular bonding, etc. Biladeris et al.\textsuperscript{139} and Leszkowiat et al.\textsuperscript{140} have suggested that higher transition temperatures indicate more stable amorphous regions and lower degree of chain branching.

![Fig. 34. DSC thermograms of modified potato flours](image)


Acetylated samples showed reduced gelatinization temperature (GT) and $\Delta H$, compared to native samples (Table 15). This reduction in GT values may be attributed to variation in degree of crystallinity, variation in degree of chain branching. Gelatinization enthalpy of native flour was more as the granular structure is more stable due to greater crystallinity.\textsuperscript{141}

<table>
<thead>
<tr>
<th>Potato flour</th>
<th>$T_0$</th>
<th>$T_p$</th>
<th>$T_c$</th>
<th>$\Delta H$ J / g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>77.0</td>
<td>82.0</td>
<td>92.6</td>
<td>13.7</td>
</tr>
<tr>
<td>Drum dried</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table. 15 DSC characteristics of modified potato flours
DSC data of enzyme modified samples showed that GT has not changed much but the $\Delta H$ increased after enzyme treatment. The DSC curve indicates that the behaviour of conjugate of starch and enzyme is almost same as that of native excepting for a slight difference in peak and conclusion temperatures (Fig. 34). It shows that the crystallinity of granule is comparable with that of native granule even after enzyme modification. The increase in heat energy in enzyme modified flours shows that the granules are bound by protein (enzyme-starch complex) that resulted in stronger association of the molecules.

The gelatinization appeared to be complete in DD and HD samples, due to which changes in the crystallinity of their starches shall be imminent. Therefore starch isolated from DD and HD flour samples of potato was subjected to X-ray diffraction and its structural features were determined by $^{13}$C NMR. The starch fraction resistant to amylolysis (Resistant starch), formed during heat treatment in DD and HD samples, was also determined. The findings are discussed in the subsequent sections.

### 3.11.2 DSC studies of sweet potato flour

The thermal properties of differently treated sweet potato flour samples are given in Table 16. A typical DSC endotherm for gelatinization of native flour was obtained whereas for the processed flour samples (DD and HD), no gelatinization peak was noticed indicating their loss of crystallinity (Fig. 35).
Acetylated samples showed lower gelatinization temperatures, indicating the changes in their structural integrity as a result of substituent groups.

<table>
<thead>
<tr>
<th>Sweet potato flour</th>
<th>$T_0$</th>
<th>$T_p$</th>
<th>$T_c$</th>
<th>$\Delta H$ J / g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>68.0</td>
<td>71.8</td>
<td>78.5</td>
<td>10.6</td>
</tr>
<tr>
<td>Hot air dried</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Drum dried</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acetylated</td>
<td>55.9</td>
<td>63.2</td>
<td>67.3</td>
<td>1.7</td>
</tr>
<tr>
<td>Enzyme modified</td>
<td>73.5</td>
<td>76.9</td>
<td>86.9</td>
<td>11.4</td>
</tr>
</tbody>
</table>

The enthalpy also showed the least value (1.7 Joules / g). Enzyme modified samples showed more stronger internal structure which was reflected in the higher values of their gelatinization temperature range. The onset, peak, endset and the $\Delta H$ values of enzyme modified samples increased (Table 16).
3.12 X-ray diffraction measurements

3.12.1 Potato starch

The crystallinity of the starches isolated from processed samples of potato flour (DD and HD) was determined by X-ray diffraction studies. The X-ray diffractogram tracings of three starches viz. native, DD and HD starches are presented in Fig 36. Except for a few minor differences, all the peaks could be assigned as per literature reports. Native potato starch showed B-type ($2\theta$ 9.9°, 17.2°, 19.5°, 22.3°, 24.0°) whereas DD and HD starches were of V-type ($2\theta$ 17.5°, 20.5°, 22.8°, 23.6°, 26.8° and 15.2°, 17.2°, 22.8°, 30.7°, respectively) diffraction. This indicated that the changes in crystallinity of granules were affected by processing whereby the crystallinity index of DD potato starch was reduced considerably compared to HD and native starches (Table 17).
When amylose and polar lipids are present in native starches, V-structure can result from heating and upon cooling. The development of V-structures has been identified in parboiled rice and in extruded starches containing polar lipids\textsuperscript{142}. A general realignment of polymer chains is viewed as taking place within the non-crystalline regions of granules as well as crystallites.

**3.12.2 X-ray diffraction studies of sweet potato starch**

Although the X-ray diffractograms of these starches (Fig. 36) show a few minor differences, all the peaks could be assigned as per literature reports.
Native sweet potato starch showed Ca type (type C near A-type, with $2\theta$ 9.9°, 10.9°, 15.1°, 17.1°) whereas processed starches showed V-type diffractions ($2\theta$ angles of DD starch 10.6°, 12.2°, 20.4°, 33.2° and HD starch 15.3°, 16.8°, 18.9°, 19.7°, 20.1°), indicating subtle changes in their crystallinity pattern. The $^{13}$C NMR studies of Imberty et al.\textsuperscript{143} indicated that the preferred state for the amorphous phase in granules is a V-type conformation. The crystallinity index of processed sweet potato starch reduces considerably compared to native starch (Table 15).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Potato</td>
</tr>
<tr>
<td>Native</td>
<td>0.52</td>
</tr>
<tr>
<td>Hot air dried</td>
<td>0.28</td>
</tr>
<tr>
<td>Drum dried</td>
<td>0.17</td>
</tr>
</tbody>
</table>

### 3.13 $^{13}$C NMR studies

#### 3.13.1 Potato starch

The isolated starches were subjected to $^{13}$C NMR to determine their structural changes. The $^{13}$C NMR spectra indicate that various carbon signals from starch samples are well resolved and are in broad agreement with those reported in the literature.\textsuperscript{110} Among the $^{13}$C signals observed, those for C-1 and C-6 were resolved between 99-100 and 60-61 ppm, respectively (Fig 37). The spectra showed sharp signals at 71-79 ppm corresponding to C-4, C-2, C-3 and C-5. The anomeric carbon peak of native and HD starches and the peaks for C-3 and C-5 in DD and HD starches showed doublets. The minor peaks observed for C-4 may be attributed to sites of branching (1-6 linkages) and reducing and non-reducing terminal groups. The reduction in the intensity of peaks especially in DD sample indicated molecular degradation of starch components.

#### 3.13.2 Sweet potato starch

The $^{13}$C NMR spectra of native and processed sweet potato starches indicated well resolved carbon signals (Fig. 37), C-1 and C-6 signals were seen between 99-100 and 60-61 ppm, respectively; the anomeric carbon at 99-100 ppm which indicated $\alpha$- configuration and the C-3 and C-5 signals were observed
as a single large peak between 73-74 ppm. Sharp signals at 71-79 ppm resulted due to overlapping clusters of C-4, C-2, C-3 and C-5 signals.

Fig. 37. $^{13}$C NMR spectra of I. Potato and II Sweet potato starches
(A. Native, B. Drum dried, C.Hot air dried)

3.14 Resistant starch

The long held belief that dietary starch, when consumed in the form of processed foods, is completely digested and utilized in the small intestine for energy release has been challenged and debated$^{144}$. In support of this, the dietary fiber (DF) content of processed foods was found to be rather higher than
the corresponding native material before processing, indicating that some man-
made DF is being introduced during processing\(^{145,146}\). It is now recognized that
as much as 30% of the total apparent DF in wheat bread is undigestible starch.\(^ {147,148}\) This fraction of starch, which escapes digestion in the
gastrointestinal (GI) tract but later gets fermented in the colon, is generally
referred to as resistant starch (RS). The beneficial effects of RS fermentation in
the large intestine are so numerous that the present trend in functional foods is to
introduce RS in varying proportions.\(^ {149,150}\) The influence of heat treatment on DF
and starch components of potato has been demonstrated in raw tubers. In the
present study an attempt was made to examine the effect of processing and to
determine the RS and dietary fiber contents of processed flour samples.

The RS levels of processed flour samples increased and it was more in
the case of DD samples. The dietary fiber content of DD samples was also found
to be increased and the values were slightly higher compared to native and HD
flour samples (Table 18).

The significant correlation between IDF (insoluble dietary fiber) and RS
supported the idea that some of the starch in cooked potato had become
indigestible by amylolytic enzymes, and this RS might contribute to the observed
increment in the IDF fraction (Fig.38). Jones at al.\(^ {151}\) found that there was little
RS in raw potato, but that it formed 20 to 50% by weight of the total dietary fiber
of cooked potato.

Retrogradation of amylose has been identified as the main mechanism for
the formation of RS.\(^ {152}\) Retrogradation is due to the association of amylose
molecules. The linear amylose chains are hydrogen bonded; they form
aggregates of low solubility and in high concentrations they form gels\(^ {153}\).

<table>
<thead>
<tr>
<th>Potato</th>
<th>RS (%)</th>
<th>DF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potato</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 18. RS and DF contents of potato and sweet potato flours
<table>
<thead>
<tr>
<th></th>
<th>Soluble</th>
<th>Insoluble</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>0.46±0.02</td>
<td>1.6±0.03</td>
<td>7.1±0.08</td>
</tr>
<tr>
<td>HD</td>
<td>1.1±0.03</td>
<td>1.8±0.03</td>
<td>7.7±0.07</td>
</tr>
<tr>
<td>DD</td>
<td>1.9±0.03</td>
<td>1.6±0.02</td>
<td>8.6±0.1</td>
</tr>
</tbody>
</table>

**Sweet potato**

<table>
<thead>
<tr>
<th></th>
<th>Soluble</th>
<th>Insoluble</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>0.43±0.03</td>
<td>3.5±0.06</td>
<td>13.5±0.5</td>
</tr>
<tr>
<td>HD</td>
<td>1.70±0.03</td>
<td>3.9±0.05</td>
<td>13.8±0.6</td>
</tr>
<tr>
<td>DD</td>
<td>1.95±0.05</td>
<td>3.6±0.04</td>
<td>14.3±0.4</td>
</tr>
</tbody>
</table>

SD±, n=3

The increase in values of IDF indicate the formation of RS which was evident by the presence of higher levels of RS in processed sweet potato samples, compared to native samples (Fig. 39). The formation of RS in processed products could create an incentive for food manufacturers to explore possible ways for raising levels of RS in processed foods as a means of generating extra 'dietary fiber', for beneficial physiological effects.
3.15 Swelling and Solubility Characteristics

3.15.1 Swelling power of Potato flour

The swelling power of modified potato flour samples increased with temperature and among the modified samples, DD flour exhibited higher values at all temperatures studied. It showed an increase in swelling power by 220 % and 430 % at room temperature (30±2°C) and 96°C, respectively compared to native flour (Fig. 40). The effect of temperature on swelling power of differently processed potato flours indicated the differences in the molecular organisation within their starch granules. The swelling power of native flour above 60°C increased rapidly due to improvement in hydration of its starch as a result of gelatinization. The less swelling power of HD flour beyond 70 °C compared to native and DD flour can be attributed to its retrograded starch.
Fig. 40. Swelling power of modified potato flours

When a starch granule is heated in an aqueous medium, the H-bonds holding the structure weaken, allowing the granule to absorb water and swell. Swelling power provides evidence of non-covalent bonding between starch molecules. Factors like amylose - amylopectin ratio, chain length and molecular weight distribution, degree / length of branching and conformation determine the degree of swelling and solubility. The bonding forces within the granules of starch affect swelling power.

The swelling power of acetylated flour samples raised from 60°C onwards. Acetylated samples showed the least swelling power than other treated samples. Though the viscosity values of acetylated samples were reduced, swelling was inhibited due to esterification of substituent groups thereby making the strongly bonded molecules unavailable for water to hydrate and swell. The DSC results corroborated with the view that granular structure is firm. However, stirring during starch paste heating effected granular breakdown, as observed in RVA studies.

High amylose content and presence of stronger or a higher number of intermolecular bonds can reduce swelling. Formation of lipid-starch complex can also offer low swelling volume as also the presence of non-starch carbohydrates and other constituents in the starch. The suppression effect is more due to fibrous material rather than liquid or sugars present in the flour. In DD and HD flours, the effect of fibrous material is not seen as the swelling and solubility have improved due to the depolymerization of degraded starch. The starchy flour extracted from fermented tubers also exhibited the same trend. The low swelling factors indicate the presence of a large number of crystallites.
Crystallite formation would increase granular stability, thereby reducing the extent of granular swelling.\textsuperscript{162}

Enzyme modified samples showed reduced swelling values compared to native sample at all the temperatures studied, though the values increased with temperature (Fig. 40). The bonding forces within the granules of a starch affect its swelling power. Thus, highly associated starch granules with an extensive and strongly bonded micellar structures display relatively great resistance towards swelling\textsuperscript{163}. The presence of protein (enzyme-starch complex), imparts rigidity besides contributing to limiting the leaching of starch in the sample mixture\textsuperscript{164}. Swelling is an essentially a property of the whole amylopectin molecule, rather than parts of it, and amylose alone appears to be diluent, while lipid (as complexes with amylose) strongly inhibit swelling.\textsuperscript{165} The Potato flour with higher water absorption index and lower amylose content resulted in \textit{chapathis} with higher extensibility and lower energy to rupture.\textsuperscript{166}

3.15.2 Solubility

The solubility of native and processed potato flour increases consistently with increasing temperatures (Fig. 41). However, the increase in solubility is highest at 96°C for DD flour followed by HD flour, i.e, 58.5 g/100 g and 21.0 g/100 g, respectively. The increase in swelling and solubility values of the samples, therefore, can be attributed to a greater degree of macromolecular disorganization and also to variations in the degradation of starch during thermal treatments.\textsuperscript{167}
The solubility values of acetylated flour, though slightly increased with temperature, were found to be lower than that of native samples at all temperatures. The substituent groups made the associative bonds stronger in addition to presumably the formation of amyllose-lipid complexes. The solubility characteristics of acetylated starches depended upon degree of substitution and polymerization. The enormous differences among the modified flour samples in their swelling and solubility patterns thus can form the basis of the functional properties that determine their suitability in product development. DD flour with better solubility even at low temperatures becomes an ideal choice for product formulations. The difference in morphological structure of granules may also be responsible for the differences in swelling power and solubility.\textsuperscript{155}

3.15.3 Swelling power and solubility of Sweet potato flour

The DD samples of sweet potato flour showed higher swelling and solubility values whereas the acetylated and enzyme modified samples showed the least values, though all the samples showed increasing values with increase in temperature (Figs. 42 and 43).
The pre-gelatinized starch is expected to exhibit high solubility in cold water than unmodified starch\textsuperscript{168}. The anomalies, if any, are probably due to starch retrogradation and different extents of partial disintegration during milling\textsuperscript{169}. However, swelling power of DD flour is higher than HD flour which in turn is much higher than the native flour up to 70°C (Fig. 42).
3.16 Sediment Volume

Sediment volume of processed starchy products is an index of starch gelatinization. When the test was applied to differently treated potato / sweet potato flour samples, a clear gradation in sediment volume was obtained. The sediment volume showed that processed samples, especially DD samples exhibited higher values than enzyme modified and acetylated samples (Table 19). It is therefore apparent that the degree of gelatinization in DD samples was markedly high, followed by HD samples of potato and sweet potato.

The sedimentation data thus provides a clear and useful distinction between various precooked products. The starch in HD samples is retrograded which is prevented or reduced in DD sample because of quick dehydration. The lower values of sediment volume of acetylated and enzyme modified samples, compared to native samples was the result of modification.

Table 19. Sediment volume of modified potato and sweet potato flours

<table>
<thead>
<tr>
<th>Sample</th>
<th>Potato (ml)</th>
<th>Sweet potato (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>7.0±0.2</td>
<td>10.0±0.1</td>
</tr>
<tr>
<td>DD</td>
<td>28.3±0.3</td>
<td>37.4±0.3</td>
</tr>
<tr>
<td>HD</td>
<td>12.6±0.2</td>
<td>16.6±0.2</td>
</tr>
<tr>
<td>Ac.</td>
<td>5.5±0.2</td>
<td>9.0±0.1</td>
</tr>
<tr>
<td>EM</td>
<td>6.5±0.1</td>
<td>9.0±0.2</td>
</tr>
<tr>
<td>SE</td>
<td>0.08</td>
<td>0.2</td>
</tr>
</tbody>
</table>

DD: Drum dried, HD: Hot air dried, Ac. Acetylated, EM: Enzyme modified flour

3.17 Gel consistency

3.17.1 Potato flour
Gel consistency is a simple, rapid test, complementary to the test for amylose content. It was developed based on the consistency of a cold flour paste in 0.2 N KOH. The consistency values were inversely/negatively correlated with viscoamylograph cold paste viscosity. DD flour sample showed significantly higher gel consistency values than other treated flour samples. HD flour sample also showed higher values compared to enzyme modified and acetylated samples (Table 20). The higher gel consistency values of the former may be attributed to their complete gelatinization.

The values of gel consistency of potato flour samples were correlated with their swelling and solubility patterns. Excepting acetylated flour, all other treated flour samples were also correlated with their cold paste viscosities.

Mobility of rice flour gel increased upon parboiling, and with increasing severity of parboiling. Gel mobility was proportional to the room temperature hydration power of rice as well as to sediment volume of an aqueous flour dispersion, the proportionality among processing conditions being identical in different varieties. Gel mobility appeared to be related to the degree of starch gelatinization, unaffected by starch reassociation, and hence could be a good test for the extent of gelatinization.$^{170}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Potato</th>
<th>Sweet potato</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>25.0±0.5</td>
<td>40.0±0.4</td>
</tr>
<tr>
<td>DD</td>
<td>145.0±1.1</td>
<td>274.0±1.3</td>
</tr>
<tr>
<td>HD</td>
<td>82.6±0.6</td>
<td>156.0±0.5</td>
</tr>
<tr>
<td>Ac.</td>
<td>10.0±0.3</td>
<td>25.0±0.2</td>
</tr>
<tr>
<td>EM</td>
<td>15.0±0.3</td>
<td>20.0±0.2</td>
</tr>
<tr>
<td>SE</td>
<td>0.3</td>
<td>0.84</td>
</tr>
</tbody>
</table>

DD: Drum dried, HD: Hot air dried, Ac. Acetylated, EM: Enzyme modified flour
Though the amylose values among the flour samples did not differ much, the gel consistency values helped in differentiating their texture. It reflected the combined effect of amylose content and the molecular properties of amylose and amyllopectin. The low gel consistency values obtained for acetylated (with lowest cold paste viscosity) and enzyme modified samples (with highest cold paste viscosity) may also be due to the above fact, which may also be responsible for their low swelling power and solubility patterns. Potato flour with high gel consistency value could be useful in the development of products in which higher solid content per unit volume is required, for example, specialty dietetic foods, food formulations, etc.

3.17.2 Sweet potato flour

Gel consistency values of differently modified sweet potato flour showed similar trend as that of potato flour samples (Table 20), although, the values obtained were much higher, especially for the DD and HD samples. The enzyme modified flour with highest cold paste viscosity among the treated flour samples, yielded lowest gel consistency values. Juliano and Perdon\textsuperscript{171} differentiated rice into low, medium and high consistency types for the samples with almost similar amylose contents.

3.18 \textit{In-vitro} Digestibility studies

3.18.1 Potato flour

The gelatinized flour samples incubated with glucoamylase were analysed for released glucose. The results are shown in Fig. 44. Both under \textit{in vitro} and \textit{in vivo} systems, raw starches are usually slowly digested by enzymes, but cooking increases susceptibility of digestion considerably because of the rupture and disintegration of the compact crystalline starch granular structure.
The digestibility of DD flour was significantly higher than other modified flour samples. The processed flours (both DD and HD flour samples) have shown better digestibility than acetylated and enzyme modified flour samples. Potato starch digestibility, which is considered as poorly digestible starch was improved by processing which involved cooking and drying, that led to changes in granule crystallinity. The disrupted state of starch granules of DD and HD samples would have helped in better penetration of enzyme to facilitate digestion. Generally uncooked native starches are less susceptible to amylolysis.\textsuperscript{172,173,174}

The degree of amylolysis is dependent on the chemical nature of starch, physical form, type of processing, possible presence of inhibitors, and physical distribution of starch in relation to other dietary components such as cellulose, hemicelluloses, and lignin.\textsuperscript{175,176} The changes in morphological features have also facilitated better digestibility in enzyme modified flour. Several studies have shown that potato starch digestibility is significantly improved by cooking with either dry or moist heat and fine grinding.\textsuperscript{177,178,179} Hallendorn et al.\textsuperscript{180} compared the \textit{in-vitro} digestibility of starch in processed mashed potato products and
concluded that potato flakes are more digestible than potato granules. Although cooking improved digestibility, a wide variation in digestibility still remained, depending on the cooking conditions.

Leegwater and Luten\textsuperscript{181} employed pancreatin in determining the digestibility and found it increased rapidly in the initial stage of digestion. The effect of degree of substitution (DS) on digestibility was inverse and exponential. The nature of the substituent groups was shown to influence digestibility of modified wheat starches. Hydroxypropyl and acetylated starches sharply reduced the digestibility of gelatinized modified wheat starch by pancreatic amylase\textsuperscript{182}.

Starch susceptibility to enzyme digestion is influenced not only by the plant source of the starch, but also by the processing and storage conditions, particularly in comparison with raw / unprocessed flour. Determination and establishment of differences and changes in starch digestibility in variously treated flours is essential in recommending for suitable utilization of these flours.

Since the break down of large chains was more in DD sample, its digestibility was found to be better. Further, in agreement with this, drum drying led to increase in gel consistency\textsuperscript{183}. The formulation of soup mix, based on processed potato flour samples resulted in acceptable consistency with reduced pasting viscosities\textsuperscript{184}.

\textbf{3.18.2 Sweet potato flour}

The studies on \textit{in vitro} digestibility of sweet potato flour also showed that processed flours which have undergone cooking and drying treatments were more digestible than enzyme modified and acetylated flour samples (Fig. 44). However, unlike in potato samples, HD flour was found to be more digestible than DD flour sample, indicating more break down of starch in the former. The temperature during hot air drying was more conducive for amylolytic hydrolysis of starch by the endogenous amylases present in sweet potato, which also led to
reduction in total amylose and pasting viscosities. The higher digestibility of processed flours may be due to comparatively less branching and low molecular weight of the constituent fractions. Poorly digested flours may also function like dietary fiber and have therapeutic benefits such as, blood glucose control in diabetes, or to aid in weight control. Restricted digestion of starch is critical for infants, senior citizens having reduced digestive capacity and people with physical exhaustion, emotional stress or medical disorders leading to disturbed digestion.

**Final Remarks**

In brief, this study has provided some insights for applicable modes of processing and preparation of potato and sweet potato flours. The structural, rheological and functional properties of modified potato / sweet potato flours were dependent on type of modification. The high stability of drum dried and hot air dried flours during heating and cooling processes, demonstrates their possible use in products requiring sterilization such as baby food. The flours showing low paste viscosities, i.e, physically treated and acetylated flours may be used in formulations requiring high solids per unit volume. Enzyme modified flours with high paste viscosities act as good thickeners. The application of the above modified flours would ensure desirable levels of digestible starch in food products. Furthermore, this information can be used in designing food processing protocols that target consumer requirements, such as for diabetics and obese people who will potentially benefit from lower levels of starch digestibility.
The salient features deduced from this investigation are:

1. The structural, functional and rheological properties of potato and sweet potato flours prepared by physical, chemical and enzymatic modifications differed from each other.

2. Acetylation in the presence of NaHCO$_3$ was found to be most suitable for preparation of acetylated potato / sweet potato flours.

3. The process conditions, viz. incubation time, temperature and enzyme concentration were standardized for preparation of enzyme modified flours.

4. The scanning electron microscopic studies showed that processing resulted in the disappearance of starch granular surface and caused agglomeration of granules that formed into an aggregated mass comprising of several small granules. Acetylated samples showed indentations of the granules, whereby the granules appeared as bunches / clusters. Slight surface erosion was observed in the enzyme treated samples. The penetration of glucoamylase was found to be more in sweet potato starch.

5. GPC on Sepharose CL-2B indicated molecular degradation of starch as a result of modification.

6. Intensity changes in the bands attributed to C-O stretch, C-H, COO group and O-H stretch of IR spectra were observed in the modified samples.

7. The typical native gelatinization endotherm disappeared in processed samples, which clearly indicated no ungelatinized starch or crystalline forms present after processing. DSC revealed a broad endothermic transition temperature for potato and sweet potato flour samples.

8. X-ray diffraction studies showed that native starch samples of potato and sweet potato were A and Ca type, respectively, whereas the processed samples were V-type indicating complete change in their crystallinity. The reduction in intensity of peaks observed in $^{13}$C NMR spectral data, especially in drum dried samples was attributed to loss of crystallinity and debranching of the starch polymer.
9. Reduced pasting viscosities were obtained for processed and acetylated samples. Acetylated potato and sweet potato flours showed least paste viscosities due to the presence of substituent functional groups that weakened the associative forces.

10. Dough rheology of potato and sweet potato flours was influenced by processing conditions, type of modification and moisture content. Drum dried samples were more hard, springy, gummy and chewy, which are indicative of intermolecular forces between the starch granules and swollen granules in the dough.

11. Drum dried flour samples showed higher swelling power followed by hot air dried flour. The poor swelling power of acetylated and enzyme modified samples implies a greater degree of associative forces in the granules.

12. Processed samples showed better solubility, drum dried flour showing the highest values indicating the differences in molecular organization within their starch granules.

13. The higher sediment volume and gel consistency values obtained for drum dried flour followed by hot air dried flour samples indicated the extent of gelatinization in the physically treated samples.

14. The \textit{in vitro} digestibility of physically treated samples was found to be improved due to changes in their granule crystallinity. The changes brought about by enzyme action also facilitated better digestibility of enzyme modified flour. The presence of substituent groups inversely affected the digestibility of acetylated flour.

In brief, it may be concluded that structural, rheological and functional properties of modified potato / sweet potato flour were dependent on type of modification. The high stability of drum dried and hot air dried flours during heating and cooling processes, demonstrates their possible use in products requiring sterilization such as baby food. The flours showing low paste
viscosities, i.e., physically treated and acetylated flours may be used in formulations requiring high solids per unit volume. Enzyme modified flours with high paste viscosities act as good thickeners. The application of the above modified flours would ensure desirable levels of digestible starch in food products. Poorly digested flours may function as a source of dietary fiber or aid in weight control. Thus, the data can be used in designing food processing and preparation protocols that target consumer requirements.


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* Taken from cross references. Originals not seen.